Consecutive 6-*endo trigonal* cyclisations from polyene acyl radical intermediates leading to decalone and perhydrophenanthrone ring constructions

Ligong Chen, G. Bryon Gill, Gerald Pattenden * and Houri Simonian

Department of Chemistry, Nottingham University, Nottingham NG7 2RD, UK

A range of substituted *Se*-phenyl 5,9-dieneselenoates, *viz.* 15a, 25, 26, 27, 42 and 52, have been synthesised and their reactions with Bu_3SnH–AIBN investigated. The diene esters 15a, 42 and 52 are shown to lead to decalone and to perhydrophenanthrone derivatives, *viz.* 19, 43 and 53, respectively, *via* consecutive 6-*endo trig* modes of cyclisations starting from the corresponding 5,9-diene acyl radical intermediates. By contrast, the 5,9-dienoates 25 and 27 lacking alkyl substitution at C-9 instead underwent cyclisation to the indanones 36 and 37, respectively, and the 6-methyl substituted analogue 26 produced only the cyclopentanone 38 on treatment with Bu_3SnH–AIBN.

In the preceding accompanying set of papers we discussed the genesis of our ideas of a complementary approach to the elaboration of polycyclic ring systems, based on cyclisations of polyene based radical systems, where the polyenes were pre-organised to cyclise either *via* a cascade macrocyclisation–transannulation sequence or by several serial *endo*-cyclisations.[1] Furthermore, in the same two publications we showed how the aforementioned radical mediated cascade macrocylisation–transannulation sequence can be used in the synthesis of a range of ring-fused bi- and tri-cyclic carbocycles present in several important natural terpenes, including the taxane ring system.[2] In this paper and the following paper we summarise our complementary studies of the scope for polyolefinic precursors in the elaboration of linear-fused 6-ring carbocycles, including steroid ring systems, by consecutive free radical 6-*endo-trig* cyclisations from (5, 9, 13-) polyolefinic radical precursors (Scheme 1).[3] Thus, in this paper we develop the principles of

Scheme 1

this approach in the synthesis of decalone and perhydrophenanthrone frameworks, and in the following paper we show the scope for this strategy in the elaboration of steroid ring constructions.[4]

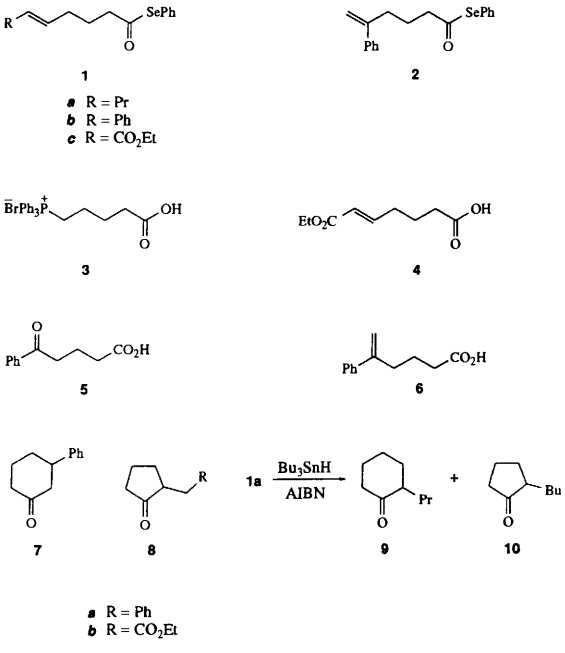
Studies of the sequential cyclisations of polyolefinic compounds in the presence of electrophilic reagents, leading to polycycle constructions, pioneered by W. S. Johnson, have provided organic chemistry with one of its major and enduring methods for steroid ring synthesis.[5] Although these novel electrophilic polyolefin cyclisations mimic closely the biogenetic pathway to steroids from squalene oxide, it is now over 30 years since Breslow *et al.*[6] first entertained the possibility of an alternative, *free radical*, mechanism for the oxidative cyclisation of squalene. Breslow's hypothesis, which was demonstrated for the case of cyclisation of farnesyl acetate to decalin derivatives in the presence of benzoyl peroxide,[7] and later by Julia [8] for the cyclisation of substituted trideca-2,6,10-trienes, has more recently been revisited by Snider [9] and by Zoretic [10] in their independent studies of the *oxidative* free radical cyclisations of polyolefinic β-keto esters with Mn^{III} and Cu^{II} reagents. In addition, Demuth *et al.*[11] have demonstrated some novel photochemically initiated biomimetic terpene cyclisations, leading to decalins and to perhydrophenanthrenes, which proceed *via* radical cation intermediates. The scope for the formation of decalin, perhydrophenathrene and steroid ring systems, by consecutive free radical six-ring forming reactions under *reductive* conditions has not hitherto been evaluated in a systematic manner.

The construction of linear- (and angular- and spiro-) fused polycycles by way of sequential radical mediated cyclistions from *alkyl* centred radicals is well documented.[12] Furthermore, with very few exceptions 5-*exo-trig* cyclisations are generally preferred over 6-*endo trig* closures from hex-5-enyl radical intermediates,[13] and attempts to use consecutive 6-*endo-trig* cyclisations from (5-, 9-, 13-) polyolefinic *alkyl* radical precursors in the formation of linear and angular 6-ring fused constructions have thus far met with failure.[14]

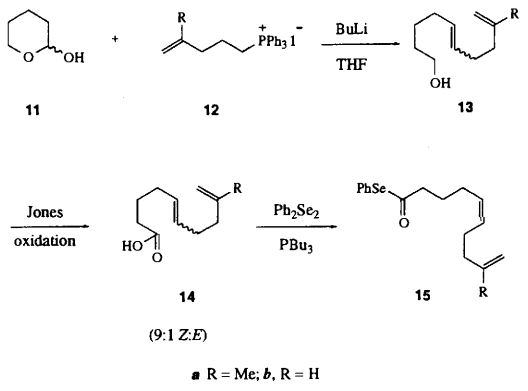
In earlier work, first published in 1987,[15] we described the synthesis of a variety of acylcobalt salphens, and examined their effectiveness as precursors to acyl radical intermediates for use in inter- and intra-molecular carbon-to-carbon bond forming reactions to alkenes.[16] Hitherto, the other sources of acyl radicals had been from treatment of certain aldehydes with peroxides,[17,18] and two early reports of their synthesis from acid chlorides and selenoates by reaction with Bu_3SnH.[19,20] In contemporaneous studies, however, other researchers highlighted the uses of *S*-acyl xanthates,[21] and extended the studies on *Se*-phenyl selenoates [22,23] as precursors to acyl radicals. Even more recently Crich *et al.*[24] have described the uses of acyltellurides in the production of acyl radical intermediates. One of the more remarkable features of the outcome of studies of the cyclisations of substituted hex-5-enylcarbonyl (*i.e.* acyl) radicals, is their unusual propensity for cyclisation *via* the 6-*endo trig* mode leading to six-ring carbocycles, at the expense of five-ring formation. This feature of their reactivity, observed by us and by others,[16,18,19,21–23] and now discussed by Boger *et al.*,[22] is what prompted us to evaluate the consecutive cyclisations of a range of (5, 9, 13-) polyolefinic acyl radical intermediates with a view to the synthesis of linear and angular fused 6-ring systems. We chose *Se*-phenyl selenoates as the most practical and convenient source of the acyl radical intermediates,[22,23] and in this paper we describe the outcome of consecutive bicyclisations of the *Se*-phenyl polyeneselenoates **15**, **25**, **26**, **27**, **42** and **52** with a view to the synthesis of ring systems such as **19**, **36**, **43** and **53**.†

† Both Boger *et al.* and Crich *et al.* have also examined aspects of tandem cyclisations of acyl radicals produced from certain unsaturated selenoates. See under references 22 and 23.

In our earliest studies of the modes of cyclisation of polyene acyl radicals, we first synthesised the simple 5- and 6-substituted *Se*-phenyl hex-5-eneselenoates **1a**, **1b**, **1c** and **2** and examined their reactions with Bu_3SnH in the presence of azoisobutyronitrile (AIBN). The *Se*-phenyl selenoates **1a** and **1b** were smoothly prepared from Wittig reactions between the commercially available salt **3** and the appropriate aldehyde followed by phenylselenylation of the resulting carboxylic acids using diphenyl diselenide and tributylphosphine in dry benzene at room temperature.[21,22] The acid precursor **4** to **1c** was obtained as described previously,[1] and the acid precursor **6** to the selenoate **2** was synthesised from the known keto acid **5** by a Grignard reaction with trimethylsilylmagnesium chloride.[25] Treatment of solutions of the *Se*-phenyl selenoates **1** and **2** in benzene at reflux with Bu_3SnH–AIBN then led to the cycloalkanone products of cyclisation in yields of 70–90%. Thus the *Se*-phenyl selenoate **2** led exclusively to the product **7** of 6-*endo-trig* cyclisation, whereas the hex-5-eneselenoates **1b** and **1c** substituted by activating groups at the 6-position led cleanly to the cyclopentanones **8a** and **8b**, respectively, resulting from 5-*exo-trig* modes of cyclisation. The selenoate **1a** having only alkyl substitution at the 6-position, by contrast, produced a 3:2 mixture of 2-propylcyclohexanone **9** and 2-butylcyclopentanone **10** on treatment with Bu_3SnH–AIBN. These early studies, which complement those of other researchers,[16–22] clearly demonstrated the scope for acyl radical intermediates in 6-ring synthesis and, furthermore, the importance of directing effects of 6- and 5- substituent groups to the regiochemical outcomes of the cyclisations.

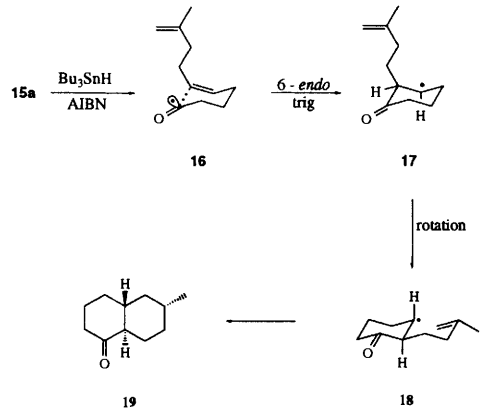


We next investigated the cyclisation of the acyl radical intermediate produced from the *Se*-phenyl 5,9-dieneselenoate **15a**, whose synthesis is shown in Scheme 2. Thus, a Wittig reaction between the cyclic hemi-acetal **11** and the ylide produced from the salt **12a** first led to a 9:1 mixture of *Z*- and *E*-isomers of the dienol **13a** in 62% yield. Oxidation of the alcohol **13a** using Jones reagent next led to the carboxylic acid **14a** which was then converted into the *Se*-phenyl selenoate **15a**. Chromatography separated the pure *Z*-isomer **15a** as a pale yellow oil whose stereochemistry followed conclusively from spectroscopic data and from comparison with model *Z*- and *E*-1,2-disubstituted alkenes. A solution of the *Se*-phenyl selenoate **15a** in benzene when treated with Bu_3SnH–AIBN at reflux for 8 h was found to undergo two consecutive 6-*endo trig* cyclisations leading to a single diastereoisomer of the decalone **19** in 77% yield. The stereochemistry assigned to the decalone **19** followed from detailed inspection of its ^1H NMR and ^{13}C NMR spectroscopic data, and comparison and correlation of these with those of model compounds and literature compounds.‡ The formation of a single diastereoisomer of a single regioisomer of a bicyclic product from cyclisation of **15a** is quite significant.



Scheme 2

The preference for 6-*endo trig* cyclisation of the initially formed acyl radical **16** is consistent with the observed conversion of **1a** into **9**, and with contemporary studies involving related systems.[21,22] We at first felt that the *Z*-geometry of the C-5-double bond in **15a** was important in establishing a favoured transition state for this reaction (see **16**→**17**) (Scheme 3) but investigation of this feature showed



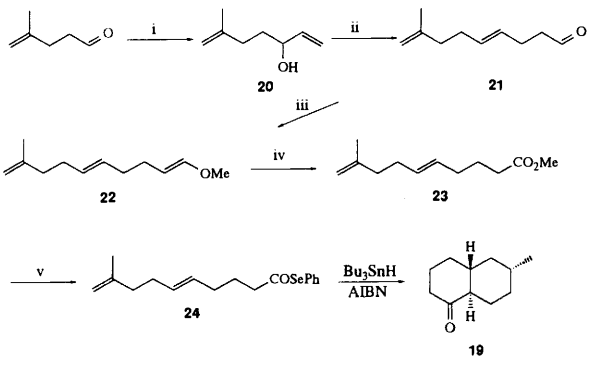
Scheme 3

that the corresponding *E*-**5** isomer **24** of **15a** underwent a similarly facile radical-mediated bicyclisation, and also led to the same diastereoisomer **19** of the decalone, in a comparable yield. The synthesis of the (*E*)-*Se*-phenyl dieneselenoate **24** is shown in Scheme 4.

The formation of the *trans*- fused bicycle **19** from the *Z*- or *E*-isomer of **15a**/**24** could be rationalised on the basis of reversibility in the first ring-forming reaction, *i.e.* **16**→**17**, or more likely, from rapid inversion of the stereochemistry of the β-keto radical intermediate **17**→**18** prior to the second ring-forming reaction. The second, consecutive 6-*endo* cyclisation leading to **19** from **18** reflects a preference for formation of the most stable bicyclic product radical.

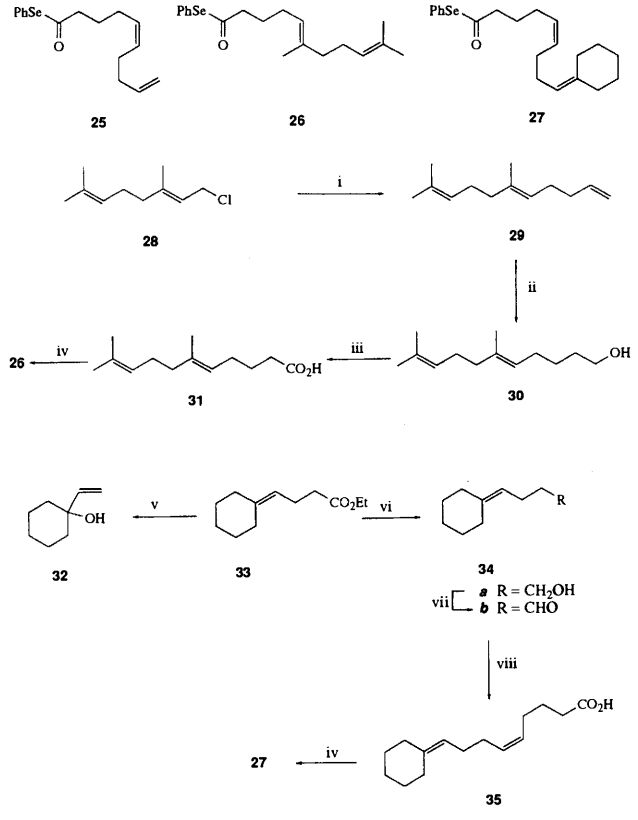
The importance of substitution on the 5- and the 9- double bonds in **15a** in determining the regiochemical outcome of the bicyclisation leading to **19** was next demonstrated by the syntheses of the *Se*-phenyl selenoates **25** (≡ **15b**), **26** and **27** containing additional alkyl group substitution on these double

‡ A detailed discussion of these data and assignments is found in the accompanying paper (ref. 4).

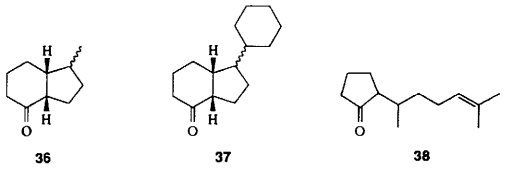


Scheme 4 *Reagents and conditions:* i, CH_2=CHMgCl, THF; ii, EtOCH=CH_2, $Hg(OCOCF_3)_2$; then heat, 120 °C; iii, $MeOCH_2\overset{+}{P}Ph_3\bar{C}l$, BuLi; iv, PCC, CH_2Cl_2; v, K_2CO_3–MeOH; then Ph_2Se_2, BuP_3

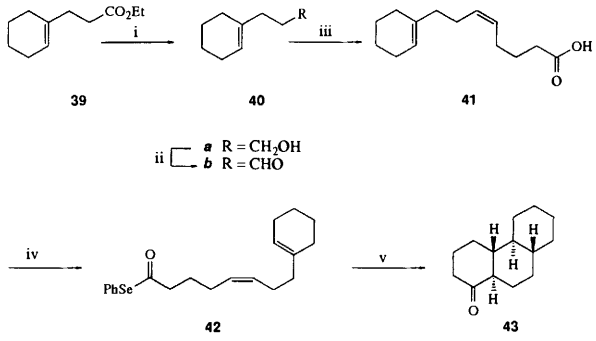
bonds; the esters were prepared as shown in Schemes 2 and 5. Thus, the *Z*-dienoates **25** and **27** when treated with Bu_3SnH–AIBN gave the *cis*-indanones, **36** and **37**, respectively as the sole products, resulting from sequential 6-*endo*, 5-*exo* cyclisations. Furthermore, treatment with Bu_3SnH–AIBN of the diene **26**, containing a methyl group blocking acyl radical cyclisation at the C-6 position gave, as expected, only the product **38** of simple 5-*exo* cyclisation.



Scheme 5 *Reagents and conditions:* i, CH_2=CH·CH_2MgCl, THF–HMPA; ii, $(iAm)_2BH$, H_2O_2–NaOH; iii, PDC, DMF, 25 °C; iv, Ph_2Se_2, Bu_3P; v, $(EtO)_3CMe$, $EtCO_2H$; vi, $LiAlH_4$; vii, PCC; viii, (**3**), NaH–DMSO

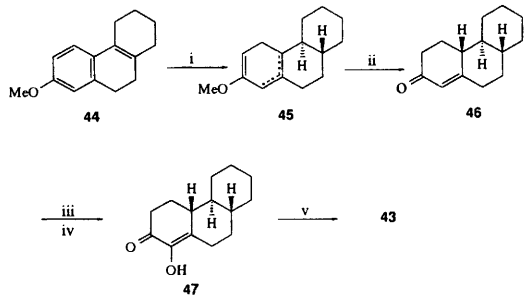


In studies similar to those carried out with **26** and **27** we also examined the cyclisation of the *Z*-dienoate **42**, produced from



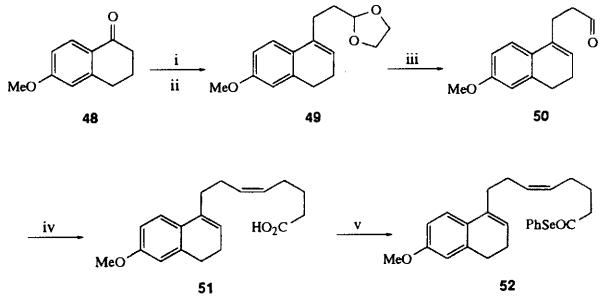
Scheme 6 *Reagents:* i, $LiAlH_4$, Et_2O; ii, PCC; iii, (**3**), NaH–DMSO; iv, Ph_2Se_2, Bu_3P; v, Bu_3SnH, AIBN

the γ-unsaturated ester **39**, Scheme 6. To our pleasure, cyclisation of **42** under the standard conditions led exclusively to the *trans*, *anti*, *trans*-tricycle **43** in 72% yield. The sterechemistry of this tricycle was firmly established by carrying out an independent synthesis, based on literature precedent, as shown in Scheme 7.[26]



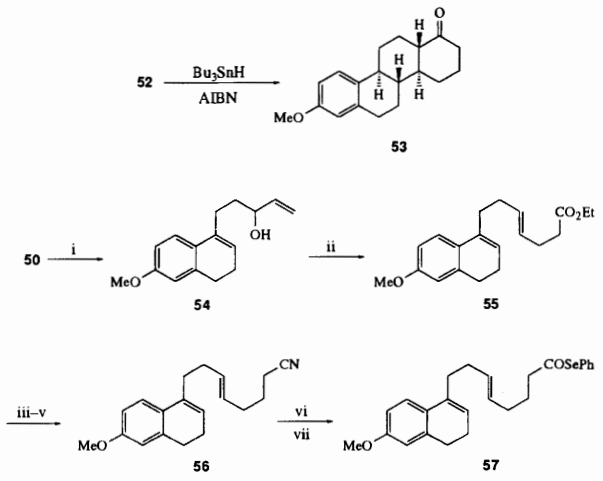
Scheme 7 *Reagents:* i, Li, NH_3, EtOH; ii, HCl–MeOH; iii, NaOH–H_2O_2; iv, $MeCH_2CO_2H$–H_2SO_4; v, HOAc–HI

Finally, and as a prelude to our studies on tri- and tetra-cyclisations, leading to steroid ring constructions, we examined the bicyclisation of the (*Z*)-*Se*-phenyl 5-enselenoate **52** attached to a reduced naphthol ring system. The *Se*-phenyl selenoate **52** was prepared from 6-methoxytetralone **48** according to Scheme 8, using procedures developed in the



Scheme 8 *Reagents and conditions:* i, $\overline{OCH_2CH_2OCH(CH_2)_2MgBr}$, THF, 30 °C; ii, $FeCl_3$–SiO_2–ether or distillation 180 °C/0.1 mmHg; iii, 6 mol dm^{-3} H_2SO_4–THF; iv, **3**, NaH–DMSO; v, Ph_2Se_2, Bu_3P

synthesis of other selenoates described in this paper. Treatment of **52** with Bu_3SnH–AIBN led to a 55:45 mixture of diastereoisomers. Although this mixture registered as a single component on TLC analysis, careful chromatography over silica gel, with combination of the earlier fractions, led to a pure sample of the D-homosteroid with *trans*, *anti*, *trans* geometry **53**, the major product from the reaction. This stereochemical assignment followed from analysis of ^1H NMR and ^{13}C NMR spectroscopic data together with COSY and NOE experiments as well as calculations and correlations of ^{13}C NMR shift data with those of model compounds.‡



Scheme 9 *Reagents and conditions:* i, CH_2=CHMgCl, THF; ii, $(EtO)_3CMe$, $EtCO_2H$, heat; iii, $LiAlH_4$, Et_2O; iv, $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C; v, NaCN, DMSO, 60 °C; vi, KOH–EtOH/H_2O, reflux 36 h; vii, Ph_2Se_2, Bu_3P

The (*E*)-*Se*-phenyl selenoate **57**, which is isomeric with **52**, was prepared from the aldehyde **50** as outlined in Scheme 9. Reductive cyclisation of **57** under the standard conditions gave the same 55:45 mixture of diastereoisomeric ketones as obtained from **52**, but in slightly lower yield. Careful chromatography over silica gel again gave a pure sample of the *trans, anti, trans*-D-homosteroid **53**. The formation of the *same* products, in similar yields, from *Se*-phenyl selenoates of *different* stereochemistry was also noted above for the case **15a**/**24**→**19**. The obvious inferences are that the cyclisations proceed in a stepwise manner, and that there is adequate time for intermediate stereoisomeric radicals to equilibrate.

The studies described here provided the platform for further investigations into the use of polyene acyl radical intermediates in tri- and tetra-cyclic ring constructions, including steroid ring systems, which are described in the accompanying paper.[4]

Experimental

For general experimental details see reference 1.

Preparations of γ-unsaturated aldehydes and esters by Claisen and Claisen–Ireland rearrangements. General procedures

(i) A mixture of the allyl alcohol (5.77 mmol), ethyl vinyl ether (25 g, 346 mmol) and mercuric acetate (0.4 g) was stirred and heated under reflux for 12 h. The mixture was cooled to room temperature and then evaporated to dryness under reduced pressure. Purification of the residue by chromatography over silica gel (light petroleum–ether, 3:1) gave the corresponding vinyl ether (50–80%) as a colourless oil. The allyl vinyl ether was placed in a heavy-walled tube fitted with a Teflon screw valve and a magnetic flea stirrer. The tube was flushed with nitrogen and then sealed. The allyl vinyl ether was then stirred and heated at 120 °C for 20–28 h. The tube was cooled to room temperature and then opened to give the corresponding γ-unsaturated aldehyde (95–98%) which was used without further purification.

(ii) A mixture of the allylic alcohol (22.3 mmol), triethyl orthoacetate (21.7 g, 134 mmol) and a catalytic amount of propionic acid (*ca.* 25 mg) was stirred and heated at 140 °C in a flask equipped with a short Vigreux fractionating column until no more ethanol distilled over. The mixture was cooled to 60 °C and the excess of triethyl orthoacetate and propionic acid were then removed by distillation. Purification by chromatography over silica gel (light petroleum–ether, 5:1) then gave the γ-unsaturated ester (*ca.* 80%) as a colourless oil.

Preparation of *Se*-phenyl selenoates

General procedure. Tributylphosphine (2.0 g, 9.7 mmol) was added dropwise over 10 min to a stirred solution of the carboxylic acid (6.5 mmol) and diphenyl diselenide (3.0 g, 9.7 mmol) in dry benzene (30 cm^3) at room temperature. The mixture was stirred overnight at room temperature, and then diluted with benzene (75 cm^3). The benzene solution was washed with 5% aqueous sodium hydrogen carbonate (50 cm^3), and then dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by chromatography over silica gel (light petroleum or light petroleum–ether, 5:1) to give the selenoate (50–90%) as a pale yellow oil.

Reductive cyclisations of unsaturated *Se*-phenyl selenoates

General procedure. A solution of the *Se*-phenyl selenoate (0.7 mmol) in dry degassed benzene (60 cm^3) containing AIBN (1–2 mg) was stirred and heated at reflux. A solution of tributyltin hydride (1.0 mmol) in dry benzene (6 cm^3) was added dropwise (*via* a syringe pump) over 6 h to the heated mixture, which was then stirred and heated under reflux overnight. The mixture was cooled to room temperature and then evaporated to dryness under reduced pressure. The residue was purified by chromatography over silica gel (light petroleum or light petroleum–ether, 20:1) to give the cyclic products.

***Se*-Phenyl non-5-eneselenoate 1a.** Sodium hydride (60% dispersion in mineral oil; 1.8 g, 44.0 mmol) was washed with several portions of pentane to remove the mineral oil. DMSO (25 cm^3) was introduced into the flask by syringe and the mixture was stirred and heated at 75–80 °C for 1 h, and then cooled with a ice–water bath. A solution of 4-carboxybutyl(triphenyl)phosphonium bromide **3** (10.0 g, 22.0 mmol) in dry DMSO (50 cm^3) was added dropwise over 0.5 h to the stirred mixture, and the mixture was then stirred for a further 10 min. Butanal (1.6 g, 22.0 mmol) was added dropwise over 0.25 h to the mixture which was then stirred for a further 1 h at room temperature. The mixture was quenched by the addition of water (80 cm^3), and then extracted with ether. The aqueous phase was acidified with 2 mol dm^{-3} hydrochloric acid, then re-extracted with ether, and dried over magnesium sulfate. Evaporation of the ether left a residue which was purified by flash chromatography (petroleum–ethyl acetate, 3:1) to give (*Z*)-non-5-enoic acid (1.9 g, 56.4%), containing about 10% of the *E*-acid, as a colourless oil;[27] ν_{max}/cm^{-1} (film) 3500–2500br (CO_2H), 1709, 1456, 1413, 1242 and 938; δ_H 11.15 (br, CO_2H), 5.57–5.38 (2 × dt, *J* 10.9, 7.3 and 7.3, *Z*-CH=CH), 2.46 (*ca.* t, *J* 7.4, CH_2), 2.23–2.05 (m, 2 × CH_2), 1.85–1.74 (m, CH_2), 1.53–1.42 (m, CH_2) and 0.99 (t, *J* 7.4, CH_3); δ_C(*Z*-isomer) 180.4 (CO), 131.1 (=CH), 128.3 (=CH), 33.4 (CH_2), 29.2 (CH_2), 26.4 (CH_2), 24.6 (CH_2), 22.8 (CH_2) and 13.7 (CH_3); δ_C(*E*-isomer) 131.6 (=CH), 128.8 (=CH), 34.6 (CH_2), 33.3 (CH_2), 31.8 (CH_2), 24.4 (CH_2), 22.6 (CH_2) and 13.6 (CH_3) (Found: M^+, 156.1158. $C_9H_{16}O_2$ requires M^+, 156.1150).

Phenylselenylation of the acid, according to the general procedure gave the (*Z*)-*Se*-phenyl selenoate (55%), containing about 10% of the *E*-isomer, as a pale yellow oil, ν_{max}/cm^{-1} (film) 3058, 3003, 2955, 1724, 1579, 1477, 1438, 737 and 689; δ_H 7.54–7.48 (m, 2 × aryl =CH), 7.42–7.35 (m, 3 × aryl =CH), 5.50–5.38 (*ca.* 2 × dt, *Z*-CH=CH), 2.71 (t, *J* 6.8, CH_2), 2.13 (q, *J* 6.8, CH_2), 2.00 (q, *J* 6.8, CH_2), 1.70–1.83 (m, CH_2), 1.33–1.48 (m, CH_2) and 0.90 (t, *J* 6.8, CH_3); δ_C(*Z*-isomer) 200.3 (CO), 135.8 (2 × aryl =CH), 131.3 (=CH), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 128.1 (=CH), 126.5 (quat. C), 46.9 (CH_2), 29.3 (CH_2), 26.2 (CH_2), 25.2 (CH_2), 22.8 (CH_2) and 13.8 (CH_3) (Found: C, 60.5; H, 6.9%; M^+ (^{80}Se), 296.0690. $C_{15}H_{20}OSe$ requires C, 61.0; H, 6.8%; M^+ (^{80}Se), 296.0679).

Reductive cyclisation of the selenoate 1a. Cyclisation of *Se*-phenyl selenoate according to the general procedure led to a 3:2

mixture of 2-propylcyclohexanone **9**[28] and 2-butylcyclopentanone **10** (75%), bp 198–199 °C; δ_C(cyclohexanone) 213.6 (CO), 50.5 (CH), 42.0 (CH_2), 33.8 (CH_2), 31.6 (CH_2), 28.1 (CH_2), 24.8 (CH_2), 20.3 (CH_2) and 14.2 (CH_3); (cyclopentanone)[29] 221.8 (CO), 49.2 (CH), 38.2 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 22.7 (CH_2), 20.8 (CH_2) and 14.0 (CH_3).

***Se*-Phenyl 6-phenylhex-5-eneselenoate 1b.** A Wittig reaction between the salt **3** and benzaldehyde, using the same procedure described for the synthesis of (*Z*)-non-5-enoic acid, first gave a 3:2 mixture of (*E*)- and (*Z*)-6-phenylhex-5-enoic acid (57%) as a colourless oil;[30] ν_{max}/cm^{-1} (film) 3500–2500br (CO_2H), 1705, 1600, 1494, 1453, 1412, 1241, 967, 747 and 700; δ_H 11.80 (br s, CO_2H), 7.50–7.31 (m, 5 × ArH), 6.63–6.52 (2 × d, *J* 12.2 and 17.8, CH=C*H*Ph), 6.38–6.26 (dt, *J* 15.8 and 6.8, C*H*=CHPh), 5.82–5.72 (dt, *J* 11.2 and 7.3, C*H*=CHPh), 2.58–2.37 (m, 2 × CH_2) and 1.99–1.87 (m, CH_2); δ_C(*E*-isomer) 180.2 (CO_2H), 137.3 (quat. C), 131.3 (=CH), 129.9 (=CH), 128.6 (2 × aryl =CH), 128.1 (2 × aryl =CH), 126.6 (aryl =CH), 33.5 (CH_2), 27.7 (CH_2) and 24.7 (CH_2); δ_C(*Z*-isomer) 180.3 (CO_2H), 137.4 (quat. C), 130.9 (=CH), 129.2 (=CH), 128.4 (2 × aryl =CH), 125.9 (2 × aryl =CH), 127.0 (aryl =CH), 33.3 (CH_2), 32.1 (CH_2) and 24.1 (CH_2).

Phenylselenylation of the acid, according to the general procedure, gave the *Se*-phenyl selenoate (53%) as a 3:2 mixture of *E*- and *Z*-isomers as a pale yellow oil; ν_{max}/cm^{-1} (film) 3056, 3023, 2931, 1720, 1596, 1578, 1492, 1476, 1438, 966, 738 and 690; δ_H 7.68–7.38 [m, 2 × (5 × ArH)], 6.68–6.56 (2 × d, *J* 12.2 and 16.8, CH=C*H*Ph), 6.38–6.27 (dt, *J* 16.8 and 7.2, *E*-CH_2C*H*=CHPh), 5.83–5.73 (dt, *J* 12.2 and 7.3, *Z*-CH_2-C*H*=CHPh), 2.95–2.86 (m, CH_2), 2.61–2.39 (m, CH_2) and 2.10–1.96 (m, CH_2); δ_C(*E*-isomer) 200.1 (CO), 137.4 (quat. C), 135.7 (2 × aryl =CH), 131.1 (=CH), 129.3 (2 × aryl =CH), 128.8 (2 × aryl =CH), 128.7 (aryl =CH), 128.1 (aryl =CH), 127.0 (=CH), 126.4 (quat. C), 126.0 (2 × aryl =CH), 46.7 (CH_2), 32.0 (CH_2) and 24.8 (CH_2); δ_C(*Z*-isomer) 200.0 (CO), 137.3 (quat. C), 135.7 (2 × aryl =CH), 130.0 (=CH), 129.3 (2 × aryl =CH), 129.0 (2 × aryl =CH), 128.4 (aryl =CH), 128.1 (aryl =CH), 126.6 (=CH), 126.4 (quat. C), 126.0 (2 × aryl =CH), 46.8 (CH_2), 27.5 (CH_2) and 25.4 (CH_2); *m*/*z* (%) 253 (2) and 173 (100) (Found: C, 65.4; H, 5.5%. $C_{18}H_{18}OSe$ requires C, 65.7; H, 5.5%).

Reductive cyclisation of the *Se*-phenyl selenoate 1b. Cyclisation of the title ester, according to the general procedure, led to 2-benzylcyclopentanone **8a** (86%);[31] ν_{max}/cm^{-1} (film) 3027, 2961, 2876, 1738, 1637, 1602, 1495, 1453, 1404, 1154 and 699; δ_H 7.25–7.07 (m, 5 × aryl =CH), 3.11–3.04 (dd, *J* 13.7 and 4.1, C*H*HPh), 2.50–2.42 (dd, *J* 13.7 and 9.4, CH*H*Ph), 2.31–2.21 (m, CH_2) and 2.09–1.42 (m, CH + 2 × CH_2); δ_C 220.2 (CO), 139.9 (quat. C), 128.8 (2 × aryl =CH), 128.4 (2 × aryl =CH), 126.1 (aryl =CH), 51.0 (CH), 38.2 (CH_2), 35.5 (CH_2), 29.1 (CH_2) and 20.5 (CH_2). This compound was identical with an authentic sample produced *via* benzylation of the pyrrolidine enamine derived from cyclopentanone.

***Se*-Phenyl 5-phenylhex-5-eneselenoate 2.** Anhydrous aluminium chloride (20.0 g, 0.15 mol) was slowly added to a stirred mixture of glutaric anhydride (8.0 g, 0.07 mol) and benzene (35.0 g, 0.45 mol) at room temperature. The reaction mixture was stirred and heated under reflux for 0.5 h, and then cooled to 0 °C, and slowly diluted with water (30 cm^3). The excess of benzene was removed by steam distillation, and the hot residue was at once poured into a beaker. After it had cooled to room temperature, the liquid was decanted from the suspension, and then acidified with concentrated hydrochloric acid and filtered. The residual suspension was boiled for 5 h with water (150 cm^3) containing commercial anhydrous sodium carbonate (36 g) and then filtered and washed with hot water. The filtrate was acidified with concentrated hydrochloric acid and filtered once more. The solids were combined, and then washed with hot water and dried to leave 5-oxo-5-phenylpentanoic acid **5** (2.5 g, 18%), mp 123–124 °C (lit.,[25] 125–126 °C); δ_H 11.2 (br s, CO_2H), 8.0–7.2 (m, 5 × aryl =CH), 3.09 (m, CH_2), 2.49 (m, CH_2) and 2.08 (m, CH_2); δ_C 199.0 (CO), 178.8 (CO_2H), 137.0 (quat. C), 133.2 (aryl =CH), 128.6 (2 × aryl =CH), 128.0 (2 × aryl =CH), 37.3 (CH_2), 33.0 (CH_2) and 19.0 (CH_2).

Chloromethyltrimethylsilane (3.0 g, 24.2 mmol) in dry ether (7 cm^3) was added dropwise over 0.25 h to a suspension of magnesium turnings (0.6 g, 24.2 mmol) in dry ether (15 cm^3), and the mixture was then stirred at room temperature for 10 h.[25] A solution of 5-oxo-5-phenylpentanoic acid (1.9 g, 10.0 mmol) in dry ether (20 cm^3) was slowly added over 0.5 h to the reaction mixture which was then stirred and heated under reflux overnight. Water (30 cm^3) was added to the cooled mixture (ice–water) and the resulting mixture was then extracted with ether. Normal work-up then afforded 5-phenylhex-5-enoic acid **6** (0.8 g, 43%); δ_H 11.5 (br s, CO_2H), 7.26–7.00 (m, 5 × aryl =CH), 5.14 (d, *J* 1, =C*H*H), 4.93 (d, *J* 1, =CH*H*), 2.41 (t, *J* 7.3, $COCH_2$), 2.21 (t, *J* 7.4, =CCH_2) and 1.69–1.56 (m, CH_2); δ_C 179.9 (CO), 147.3 (quat. C), 140.7 (quat. C), 128.3 (2 × aryl =CH), 127.5 (aryl =CH), 126.1 (2 × aryl =CH), 113.1 (=CH_2), 34.4 (CH_2), 33.3 (CH_2) and 23.0 (CH_2).

Phenylselenylation of the carboxylic acid, according to the general procedure, led to the *Se*-phenyl selenoate (31%) as an oil; ν_{max}/cm^{-1} (film) 3056, 2949, 1722, 1626, 1578, 1494, 1479, 1439, 738, 703 and 690; δ_H 7.66–7.29 (m, 10 × aryl =CH), 5.46 (d, *J* 1.3, =C*H*H), 5.23 (d, *J* 1.3, =CH*H*), 2.93–2.80 (t, *J* 7.4, CH_2), 2.75–2.67 (t, *J* 7.4, CH_2) and 2.02–1.94 (pentet, *J* 7.4, $CH_2CH_2CH_2$); δ_C 200.1 (CO), 147.2 (quat. C), 140.6 (quat. C), 135.8 (2 × aryl =CH), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 128.4 (2 × aryl =CH), 128.1 (quat. C), 127.5 (aryl =CH), 126.1 (2 × aryl =CH), 113.3 (=CH_2), 46.7 (CH_2), 34.2 (CH_2) and 23.7 (CH_2); *m*/*z* (%) 173 (−SePh, 87).

Reductive cyclisation of the *Se*-phenyl selenoate 2. Cyclisation of the title ester, according to the general procedure led to 3-phenylcyclohexanone **7** (75%), bp 287–288 °C (lit.,[32] bp 110 °C/0.5 mmHg); ν_{max}/cm^{-1} (film) 3027, 2933, 2864, 1711, 1602, 1496, 1451, 1223, 1030, 910, 756 and 700; δ_H 7.28–7.12 (m, 5 × aryl =CH), 2.97–2.87 (m, CH), 2.55–2.23 (m, 2 × CH_2), 2.11–1.93 (m, CH_2) and 1.85–1.60 (m, CH_2); δ_C 210.9 (CO), 144.3 (quat. C), 128.6 (2 × aryl =CH), 126.6 (aryl =CH), 126.5 (2 × aryl =CH), 48.9 (CH_2), 44.7 (CH), 41.1 (CH_2), 32.7 (CH_2) and 25.5 (CH_2); *m*/*z* 174.1043 (M^+. Calc. for $C_{12}H_{14}O$: M^+, 174.1044).

***Se*-Phenyl 6-ethoxycarbonylhex-5-eneselenoate 1c.** A mixture of ethyl triphenylphosphoranylideneacetate (15.7 g, 45.0 mmol) and 2-hydroxytetrahydropyran (4.6 g, 45.0 mmol) in dry dichloromethane (75 cm^3) was stirred at room temperature for 4 days and then evaporated to dryness. The residue was triturated with light petroleum, and the solvent was then evaporated under reduced pressure. Distillation of the residue afforded ethyl 7-hydroxyhept-2-enoate (5.8 g, 75%), a *ca.* 5:1 mixture of *E*- and *Z*-isomers, as a colourless oil;[30] bp 125–128 °C/20 mmHg; ν_{max}/cm^{-1} (film) 3416br (OH), 2937, 2864, 1719, 1654, 1457, 1417, 1368, 1271, 1191, 1044 and 984; δ_H 6.99 (dt, *J* 15.5 and 6.9, CH_2C*H*=CHCO$_2$Et), 5.85 (*ca.* d, *J* 15.5, CH=C*H*CO$_2$Et), 4.21 (q, *J* 7.3, $CO_2CH_2CH_3$), 3.66 (t, *J* 6.3, CH_2OH), 2.30–2.23 (m, CH_2), 1.70–1.64 (m, 2 × CH_2) and 1.38 (t, *J* 7.5, CH_3); δ_C(*E*-isomer) 166.6 (CO), 148.9 (=CH), 121.3 (=CH), 62.0 (CH_2OH), 60.0 ($CO_2CH_2CH_3$), 31.8 (CH_2), 31.7 (CH_2), 24.1 (CH_2) and 14.1 (CH_3); δ_C(*Z*-isomer) 166.4 (CO), 150.0 (=CH), 119.7 (=CH), 62.1 (CH_2OH), 59.7 ($CO_2CH_2CH_3$), 31.9 (CH_2), 28.3 (CH_2), 24.9 (CH_2) and 14.1 (CH_3) (Found: M^+, 172.1068. $C_9H_{16}O_3$ requires M^+, 172.1099).

A solution of chromium trioxide (3.8 g, 37.7 mmol) in 1.5 mol dm^{-3} sulfuric acid (60 cm^3, 90 mmol) was maintained in the

range 5–10 °C while ethyl 7-hydroxyhept-2-enoate (1.7 g, 10.0 mmol) in acetone (100 cm^3) was added dropwise over 3 h. The mixture was stirred at room temperature for 2 h and then diluted with diethyl ether (75 cm^3). The mixture was extracted with brine, and the organic phase was separated, dried ($MgSO_4$) and evaporated to leave a residue which was purified by flash chromatography (light petroleum–ethyl acetate, 3:1) to give ethyl 6-ethoxycarbonylhex-5-enoic acid **4** (0.9 g, 48%) as a colourless oil,[30] ν_{max}/cm^{-1} (film) 3500–2500br (CO_2H), 1708br, 1651, 1494, 1447, 1414, 1191, 966 and 694; δ_H 10.83 (br s, CO_2H), 6.92–6.81 (dt, *J* 15.5 and 6.9, CH_2CH=$CHCO_2Et$), 5.78 (dt, *J* 15.5 and 1.5, CH=$CHCO_2Et$), 4.11 (q, *J* 7.3, $CO_2CH_2CH_3$), 2.31 (t, *J* 7.4, $COCH_2$), 2.25–2.16 (m, =$CHCH_2$), 1.80–1.71 (m, CH_2) and 1.21 (t, *J* 7.1, CH_3); δ_C 178.5 (CO_2H), 166.5 (CO_2Et), 147.7 (=CH), 122.0 (=CH), 60.2 ($CO_2CH_2CH_3$), 33.3 (CH_2), 31.1 (CH_2), 22.8 (CH_2) and 14.1 (CH_3); *m/z* 168.0787 [$(C_9H_{14}O_4 - H_2O)^+$ requires 168.0786].

Phenylselenylation of the carboxylic acid **4**, according to the general procedure, gave the (*E*)-*Se*-phenyl selenoate (0.8 g, 46%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3058, 2980, 2935, 1715br, 1652, 1579, 1477, 1438, 1367, 1268, 1188, 1152, 1043, 739 and 690; δ_H 7.62–7.46 (m, 5 × ArH), 7.06–6.95 (dt, *J* 15.5 and 6.9, CH_2CH=$CHCO_2Et$), 5.94 (dt, *J* 15.5 and 1.7, CH=$CHCO_2Et$), 4.29 (q, *J* 7.1, $CO_2CH_2CH_3$), 2.83 (t, *J* 7.4, CH_2), 2.42–2.33 (m, CH_2), 1.96 (pentet, *J* 7.4, CH_2) and 1.39 (t, *J* 7.1, CH_3); δ_C 199.8 (CO), 166.3 (CO_2), 147.2 (=CH), 135.7 (2 × aryl =CH), 129.3 (2 × aryl =CH), 128.9 (aryl =CH), 126.2 (quat. C), 122.4 (=CH), 60.2 ($CO_2CH_2CH_3$), 46.4 (CH_2), 31.0 (CH_2), 23.5 (CH_2) and 14.2 (CH_3); *m/z* (%) 312 (4), 253 (5), 169 (100), 157 (26) and 141 (23).

Reductive cyclisation of the *Se*-phenyl selenoate 1c. Cyclisation of the title ester, according to the general procedure, gave ethyl 2-oxocyclopentylacetate **8b** (71%), as an oil;[33] ν_{max}/cm^{-1} (film) 2967, 2877, 1734, 1453, 1406, 1374, 1262, 1183 and 1034; δ_H 4.19 (q, *J* 6.9, OCH_2), 2.83–2.73 (m, CH), 2.53–1.60 (m, 4 × CH_2) and 1.31 (t, *J* 7.3, CH_3); δ_C 219.1 (CO), 172.0 (CO_2), 60.5 (OCH_2), 45.5 (CH), 37.3 (CH_2), 33.9 (CH_2), 29.2 (CH_2), 20.5 (CH_2) and 14.1 (CH_3); *m/z* 170.0926 (M^+. $C_9H_{14}O_3$ requires M^+, 170.0943).

9-Methyldeca-5,9-dien-1-ol 13a. A 2.5 mol dm^{-3} solution of butyllithium (8.0 cm^3, 20 mmol) in hexane was added dropwise over 15 min to a stirred suspension of 4-methylpent-4-enyl(triphenyl)phosphonium iodide (8.5 g, 18.0 mmol) in dry tetrahydrofuran (THF; 40 cm^3) at room temperature. The mixture was stirred at room temperature for 1 h, after which the deep red solution was added *via* a cannula to a stirred suspension of 2-hydroxytetrahydropyran (1.8 g, 18.0 mmol) and sodium hydride (60% dispersion in mineral oil; 0.9 g, 21.5 mmol) in dry THF (30 cm^3) at room temperature. The mixture was stirred over 40 h, and then quenched by cautious addition of saturated aqueous ammonium chloride followed by ether. The mixture was extracted with ether and the extracts were dried and evaporated to leave a residue which was purified by flash chromatography over silica gel (light petroleum–ether, 3:1) to give a 9:1 mixture of *Z*- and *E*-isomers of the decadienol (1.9 g, 62%) as a colourless oil; δ_H 5.57–5.39 (m, CH=CH), 4.80 (d, *J* 1, =C*H*H), 4.77 (d, *J* 1, =CH*H*), 3.71 (t, *J* 6.4, OCH_2), 2.27–2.03 (m, 3 × CH_2), 1.81 (s, CH_3), 1.77–1.59 (m, CH_2) and 1.57–1.45 (m, CH_2); δ_C 145.4 (quat. C), 129.6 (=CH), 129.5 (=CH), 109.9 (=CH_2), 62.6 (OCH_2), 37.6 (CH_2), 32.2 (CH_2), 26.9 (CH_2), 25.8 (CH_2), 25.4 (CH_2) and 22.3 (CH_3).

9-Methyldeca-5,9-dienoic acid 14a. A solution of chromium trioxide (2.6 g, 26.0 mmol) in sulfuric acid (1.5 mol dm^{-3}; 41.4 cm^3, 62.0 mmol) was maintained in the range 5–10 °C while a solution of the dienol **13a** (1.9 g, 6.9 mmol) in acetone (70 cm^3) was added over 3 h. The mixture was stirred for a further 2 h at room temperature and then diluted with ether (52 cm^3). The mixture was extracted with brine, and the organic phase was then dried ($MgSO_4$), evaporated and purified by flash chromatography over silica gel (light petroleum–ethyl acetate, 3:1) to give the acid (a colourless oil) as a *ca.* 9:1 mixture of *Z*- and *E*-isomers (0.45 g, 25%); ν_{max}/cm^{-1} (film) 3500–2500br (CO_2H), 1731, 1649, 1453, 1374, 1174, 1050, 972, 887 and 726; δ_H 10.8 (br s, CO_2H), 5.56–5.39 (*ca.* 2 × dt, *J* 10.9, 6.9 and 6.6, *Z*-CH=CH), 4.82–4.77 (m, =CH_2), 2.46 (t, *J* 7.4, $COCH_2$), 2.30–2.12 (m, 3 × CH_2), 1.82 (s, CH_3) and 1.86–1.76 (m, CH_2), δ_C(*Z*-isomer) 180.01 (CO), 145.3 (quat. C), 130.4 (=CH), 128.4 (=CH), 109.9 (=CH_2), 37.5 (CH_2), 33.3 (CH_2), 26.3 (CH_2), 25.3 (CH_2), 24.4 (CH_2) and 22.3 (CH_3); δ_C(*E*-isomer) 180.13 (CO), 145.3 (quat. C), 131.0 (=CH), 128.9 (=CH), 110.4 (=CH_2), 33.2 (CH_2), 31.6 (CH_2), 30.6 (CH_2), 24.2 (CH_2) and 22.3 (CH_3); *m/z* 182.1305 (M^+. Calc. for $C_{11}H_{18}O_2$: M^+, 182.1306).

(*Z*)-*Se*-Phenyl 9-methyldeca-5,9-dieneselenoate 15a. The ester was prepared according to the general procedure as a pale yellow oil (44%) comprising a *ca.* 9:1 mixture of *Z*- and *E*-isomers; ν_{max}/cm^{-1} (film) 3073, 3005, 2932, 1724, 1648, 1579, 1477, 1438, 887, 738 and 689; δ_H 7.45–7.41 (m, 2 × aryl =CH), 7.32–7.28 (m, 3 × aryl =CH), 5.40–5.20 (2 × dt, *J* 10.9, 6.9 and 6.6, *Z*-CH=CH), 4.65 (s, =C*H*H), 4.61 (s, =CH*H*), 2.64 (t, *J* 7.4, CH_2), 2.11–1.95 (m, 3 × CH_2), 1.74–1.64 (m, CH_2) and 1.65 (s, CH_3); δ_C(*Z*-isomer) 199.7 (CO), 144.9 (quat. C), 135.3 (2 × aryl =CH), 130.2 (=CH), 128.8 (2 × aryl =CH), 128.3 (aryl =CH), 127.8 (=CH), 126.0 (quat. C), 109.6 (=CH_2), 46.4 (CH_2), 37.1 (CH_2), 25.8 (CH_2), 25.0 (CH_2), 24.7 (CH_2) and 21.9 (CH_3); δ_C(*E*-isomer) 130.9 (=CH), 46.2 (CH_2), 31.0 (CH_2), 30.1 (CH_2) and 24.5 (CH_2); *m/z* (%) 165 (16), 157 (11), 147 (34), 119 (20) and 81 (100) (Found: C, 63.5; H, 7.1. $C_{17}H_{22}OSe$ requires C, 63.6; H, 6.9%).

Reductive cyclisation of the (*Z*)-*Se*-phenyl selenoate 15a. Cyclisation of the title ester according to the general procedure gave trans-6-*methyldecahydronaphthalen*-1-*one* **19** (77%) as a colourless oil; ν_{max}/cm^{-1} (film) 2927, 2867, 1706, 1455, 1446, 1377, 1108, 912 and 733; δ_H 2.45–0.85 (m), 0.90 (d, *J* 6.9, CH_3); δ_C 212.8 (CO), 54.6 (CH), 44.6 (CH), 42.9 (CH_2), 41.7 (CH_2), 33.9 (CH_2), 32.9 (CH_2), 31.9 (CH), 26.4 (CH_2), 24.9 (CH_2) and 22.3 (CH_3); *m/z* 166.1354 (M^+. $C_{11}H_{18}O$ requires M^+, 166.1358). For the assignment of the ^{13}C NMR shifts, see the following paper.[4]

(*E*)-8-Methylnona-4,8-dienal 21. A 1.7 mol dm^{-3} solution of vinylmagnesium chloride in THF (81 cm^3, 0.14 mol) was added dropwise over 15 min to a stirred solution of 4-methylpent-4-enal (9 g, 0.09 mol) in dry THF (100 cm^3) at 0 °C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature, and then stirred for a further 3 h. The mixture was poured into saturated aqueous ammonium chloride and then extracted with ether (3 × 70 cm^3). The combined extracts were dried and then evaporated under reduced pressure to leave an oil. Chromatography over silica gel (light petroleum–ethyl acetate, 6:4) gave 6-methylhepta-1,6-diene-3-ol **20** (7.5 g, 65%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3420br (OH), 3075, 2975, 2933, 1648, 1445, 1375, 1340, 1266, 1117, 1057, 993, 922 and 888; δ_H 5.84 (ddd, *J* 17.2, 10.5 and 6.4, C*H*=CH_2), 5.20 (dt, *J* 17.2 and 1.4, CH=C*H*H), 5.08 (dt, *J* 10.5 and 1.3, CH=CH*H*), 4.70 (d, *J* 0.7, =C*H*H), 4.68 (d, *J* 0.7, =CH*H*), 4.12–4.05 (m, C*H*OH), 2.16 (br s, OH), 2.10–2.04 (m, CH_2), 1.71 (s, CH_3) and 1.68–1.62 (m, CH_2); δ_C 145.0 (=*C*Me), 140.9 (=CH), 113.9 (=CH_2), 109.5 (=CH_2), 72.2 (CHOH), 34.5 (CH_2), 33.1 (CH_2) and 22.0 (CH_3); *m/z* 126.1016. (M^+. Calc. for $C_8H_{14}O$: M^+, 126.1045).

The alcohol **20** was treated with ethyl vinyl ether in the presence of mercury(II) trifluoroacetate, according to the general procedure, to give 6-methylhepta-1,6-dienyl vinyl ether as an oil; ν_{max}/cm^{-1} (film) 3076, 3009, 2978, 2934, 1726, 1648, 1614, 1445, 1376, 1320, 1216, 1170, 1096, 1028, 929, 890, 758

and 668; δ_H 6.32 (dd, J 14.1 and 6.5, OC*H*=CH_2), 5.76 (ddd, J 17.3, 10.5 and 6.7, C*H*=CH_2), 5.23 (dt, J 17.4 and 1.3, CH=C*H*H), 5.21 (dt, J 10.5 and 1.3, CH=CH*H*), 4.73 (s, =C*H*H), 4.69 (s, =CH*H*), 4.31 (dd, J 14.1 and 1.5, OCH=C*H*H), 4.17–4.10 (m, CHO), 4.00 (dd, J 6.6 and 1.5, OCH=CH*H*), 2.11–2.05 (m, CH_2), 1.85–1.70 (m, CH_2) and 1.72 (s, CH_3); δ_C 150.4 (OCH=), 144.3 (=*C*Me), 137.7 (=CH), 116.1 (=CH_2), 110.0 (=CH_2), 82.2 (OCH=*C*H_2), 79.6 (CHO), 32.8 (CH_2), 32.7 (CH_2) and 22.1 (CH_3) (Found: C, 78.4; H, 10.5%; M^+, 152.1153. $C_{10}H_{16}O$ requires C, 78.8; H, 10.6%; M^+, 152.1201).

The above vinyl ether was heated at 120 °C for 14 h to give, after work-up and chromatography, the dienal **21** (96%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3074, 2932, 2722, 1727, 1648, 1445, 1374, 1056, 968, 887 and 758; δ_H 9.60 (t, J 1.5, CHO), 5.30–5.27 (m, CH=CH), 4.53 (s, =C*H*H), 4.50 (s, =CH*H*), 2.33 (t, J 6.9, CH_2CHO), 2.20–2.15 (m, CH_2), 1.98–1.89 (m, 2 × CH_2) and 1.54 (s, CH_3); δ_C 201.8 (CO), 145.0 (=*C*Me), 131.2 (=CH), 128.2 (=CH), 110.2 (=CH_2), 43.5 (CH_2), 37.6 (CH_2), 30.6 (CH_2), 25.2 (CH_2) and 22.4 (CH_3).

(*E*)-Methyl 9-methyldeca-5,9-dienoate 23. A Wittig reaction between the dienal **21** and the ylide produced from methoxymethyl(triphenyl)phosphonium chloride (BuLi–THF), according to the general procedure, gave a *ca.* 1:1 mixture of (*E*,*Z*)-1-methoxy-9-methyldeca-1,5(*E*),9-trienes **22** (32%) as an oil; ν_{max}/cm^{-1} (film) 3054, 2929, 1734, 1653, 1435, 1208, 1181, 1108, 968, 887, 743 and 696; δ_H 6.17 and 5.71 (2 × d, J 12.5 and 5.7, *E*- and *Z*-CH=C*H*OMe), 5.32–5.30 (m, CH_2C*H*=C*H*CH_2), 4.72 (s, =C*H*H), 4.70 (s, =CH*H*), 4.73–4.69 (m, *E*- and *Z*-C*H*=CHOMe), 3.38 and 3.32 (2 × s, *E*- and *Z*-CH=CHOCH_3), 2.10–1.98 (m, 2 × CH_2), 1.95–1.88 (m, 2 × CH_2) and 1.60 (s, CH_3); δ_C 147.1 and 146.1 (=*C*HOMe), 145.1 (=*C*Me), 132.7 (=CH), 128.5 (=CH), 109.9 (=CH_2), 106.0 and 102.1 (*C*H=CHOMe), 59.1 and 55.5 (OCH_3), 37.7 (CH_2), 33.8 (CH_2), 32.6 (CH_2), 30.7 (CH_2) and 22.4 (CH_3).

Oxidation of the methyl vinyl ether **22** using PCC in CH_2Cl_2 produced the *dienoate* **23** (30%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3074, 2933, 2847, 1740, 1649, 1438, 1375, 1210, 1171, 1019, 968, 887, 758 and 667; δ_H 5.47–5.31 (m, CH=CH), 4.67 (s, =C*H*H), 4.64 (s, =CH*H*), 3.63 (s, OCH_3), 2.26 (t, J 7.5, CH_2CO), 2.18–2.09 (m, 2 × CH_2), 2.08–1.90 (m, 2 × CH_2) and 1.68 (s, CH_3); δ_C 174.0 (CO_2), 145.2 (=*C*Me), 130.8 (=CH), 129.0 (=CH), 109.9 (=CH_2), 51.2 (OCH_3), 37.6 (CH_2), 33.1 (CH_2), 31.7 (CH_2), 30.6 (CH_2), 24.5 (CH_2) and 22.3 (CH_3); m/z 164.1201 [($C_{12}H_{20}O_2$–CH_3OH)$^+$ requires m/z 164.1201].

(*E*)-*Se*-Phenyl 9-methyldeca-5,9-dieneselenoate 24. Saponification of the dienoate **23** (0.59 g, 3.1 mmol) using potassium carbonate (2.1 g, 15 mmol) in 7% aqueous methanol (40 cm^3) at reflux for 14 h gave the *corresponding acid* (70%) as an oil; ν_{max}/cm^{-1} (film) 3500–2500br (CO_2H), 3074, 2932, 2850, 1709, 1648, 1443, 1420, 968, 887 and 758; δ_H 9.35 (br s, CO_2H), 5.45–5.36 (m, CH=CH), 4.71 (s, =C*H*H), 4.67 (s, =CH*H*), 2.34 (t, J 7.5, CH_2CO), 2.18–2.12 (m, 2 × CH_2), 2.10–2.02 (m, 2 × CH_2) and 1.70 (s, CH_3); δ_C 180.0 (CO_2), 145.4 (=*C*Me), 131.1 (=CH), 129.0 (=CH), 109.9 (=CH_2), 37.6 (CH_2), 33.3 (CH_2), 31.7 (CH_2), 30.6 (CH_2), 24.3 (CH_2) and 22.4 (CH_3) (Found: C, 72.6; H, 10.3%; M^+, 182.1305. $C_{11}H_{18}O_2$ requires C, 72.5; H, 10.0%; M^+, 182.1307).

The *Se*-phenyl selenoate **24** was prepared from the carboxylic acid, according to the general procedure, as a pale yellow oil (46%); ν_{max}/cm^{-1} (film) 3074, 3005, 2933, 1725, 1648, 1580, 1476, 1439, 887, 733 and 688; δ_H 7.43–7.40 (m, 2 × ArH), 7.30–7.28 (m, 3 × ArH), 5.39–5.21 (m, CH=CH), 4.64 (s, =C*H*H), 4.60 (s, =CH*H*), 2.60 (t, J 7.4, CH_2CO), 2.07–1.92 (m, 3 × CH_2), 1.70–1.66 (m, CH_2) and 1.63 (s, CH_3); δ_C 200.0 (CO), 145.2 (=*C*Me), 135.7 (2 × aryl =CH), 131.3 (=CH), 129.2 (2 × aryl =CH), 128.70 (=CH), 128.66 (=CH), 126.4 (quat. =C), 110.0 (=CH_2), 46.6 (CH_2), 37.6 (CH_2), 31.4 (CH_2), 30.6 (CH_2), 24.9 (CH_2) and 22.3 (CH_3).

Reductive cyclisation of the (*E*)-*Se*-phenyl selenoate 24. Cyclisation of the title ester **24** according to the general procedure gave the decalone **19** (55%) which showed spectroscopic data identical with those reported earlier for the product of the reductive cyclisation of **15a**. A proportionally larger amount of 2-(4-methylpent-4-enyl)cyclopentane (~ 14%) was produced concurrently in this reaction–only enriched samples (contaminated with **19**) were obtained; δ_H 4.60 (s, =C*H*H), 4.59 (s, =CH*H*) and 1.63 (s, CH_3); δ_C 221.4 (CO), 145.5 (=*C*Me), 110.0 (=CH_2) and 49.0 (CH).

Deca-5,9-dien-1-ol 13b. The dienol was obtained by a Wittig reaction between 2-hydroxytetrahydropyran and the salt **3** as a *ca.* 7:1 mixture of *Z*- and *E*-isomers (40%), in the same manner as that used in the preparation of the dienol **13a**; δ_H 5.96–5.83 (m, C*H*=CH_2), 5.53–5.41 (m, C*H*=C*H*), 5.15–5.03 (2 × dd, J 17.8 and 10.2, CH=CH_2), 3.75–3.70 (dt, J 6.6 and 1.3, HOCH_2), 2.23–2.10 (m, 3 × CH_2), 1.73–1.61 (m, CH_2) and 1.56–1.47 (m, CH_2); δ_C(*Z*-isomer) 138.4 (=CH), 129.8 (=CH), 129.3 (=CH), 114.6 (=CH_2), 62.8 (OCH_2), 33.8 (CH_2), 32.3 (CH_2), 26.9 (CH_2), 26.6 (CH_2) and 25.8 (CH_2); δ_C(*E*-isomer) 130.4 (=CH), 114.5 (=CH_2), 32.2 (CH_2), 32.1 (CH_2), 31.9 (CH_2) and 25.6 (CH_2); m/z 136.1250 [($C_{10}H_{18}O$ – H_2O)$^+$ requires 136.1252]. The corresponding acetate ester has been synthesised previously.[34]

Deca-5,9-dienoic acid 14b. The acid, which was obtained by oxidation of the alcohol **13b** in the same manner as that described for the preparation of **14a** (30%), showed bp 140 °C (bath temp.)/1.5 mmHg;[35] δ_H 9.90 (br s, CO_2H), 5.97–5.83 (m, C*H*=CH_2), 5.54–5.40 (m, CH=CH), 5.15–5.03 (2 × d, J 18.1 and 10.2, CH=CH_2), 2.45 (t, J 7.6, CH_2), 2.21–2.16 (m, 4 × CH_2) and 1.85–1.74 (m, CH_2); δ_C(*Z*-isomer) 179.9 (CO), 138.1 (=CH), 130.1 (=CH), 128.5 (=CH), 114.5 (=CH_2), 33.6 (CH_2), 33.2 (CH_2), 26.5 (CH_2), 26.3 (CH_2) and 24.4 (CH_2); δ_C(*E*-isomer) 180.1 (CO), 138.1 (=CH), 130.7 (=CH), 129.1 (=CH), 114.4 (=CH_2), 33.1 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 25.6 (CH_2) and 24.2 (CH_2); m/z 168.1152 (M^+. $C_{10}H_{16}O_2$ requires M^+, 168.1150).

***Se*-Phenyl deca-5,9-dieneselenoate 25 ≡ 15b.** The title ester was prepared according to the general procedure, as an oil (55%) comprising a *ca.* 8:1 mixture of *Z*- and *E*-isomers; ν_{max}/cm^{-1} (film) 3074, 3004, 2927, 2858, 1725, 1640, 1579, 1477, 1438, 912, 738 and 689; δ_H 7.45–7.40 (m, 2 × aryl =CH), 7.32–7.27 (m, 3 × aryl =CH), 5.81–5.66 (m, C*H*=CH_2), 5.40–5.21 (m + dt, J 10.9 and 6.9, *Z*-CH=CH), 4.99–4.88 (2 × dd, J 17.8, 10.1 and 1.8, CH=CH_2), 2.63 (t, J 7.4, CH_2), 2.07–1.97 (m, 4 × CH_2) and 1.73–1.62 (*ca.* pentet, J 7.4, $CH_2CH_2CH_2$); δ_C(*Z*-isomer) 200.2 (CO), 138.2 (=CH), 135.7 (2 × aryl =CH), 130.4 (=CH), 129.3 (2 × aryl =CH), 128.8 (=CH), 128.5 (=CH), 126.4 (quat. C), 114.7 (=CH_2), 46.8 (CH_2), 33.7 (CH_2), 26.6 (CH_2), 26.2 (CH_2) and 25.1 (CH_2); δ_C(*E*-isomer) 138.3 (=CH), 131.1 (=CH), 129.0 (=CH), 114.6 (=CH_2), 46.7 (CH_2), 31.9 (CH_2), 31.5 (CH_2) and 24.9 (CH_2); m/z (%) 308 (2), 306 (1), 159 (3), 151 (29) and 133 (41) [Found: C, 63.0; H, 7.0%; M^+ (^{80}Se), 308.064. $C_{16}H_{20}OSe$ requires C, 62.6; H, 6.6%; M^+ (^{80}Se), 308.068].

Reductive cyclisation of the *Se*-phenyl selenoate 25. Cyclisation of the title ester according to the general procedure, gave a 1:1 mixture of the C-6 epimers of cis-1-*methylhexahydroindan*-4-*one* **36** (75%), which was obtained as a colourless oil; ν_{max}/cm^{-1} (film) 2954, 2871, 1706 and 1458; δ_H 2.62–1.07 (series of m) and 0.91 (d, J 6.9, CH_3); δ_C 215.5 (CO), 54.1 (CH), 47.5 (CH), 38.6 (CH), 37.8 (CH_2), 30.4 (CH_2), 27.4 (CH_2), 24.9 (CH_2), 21.4 (CH_2) and 15.1 (CH_3); m/z 152.1207. (M^+. $C_{10}H_{16}O$ requires M^+, 152.1201).

(*E*)-6,10-Dimethylundeca-1,5,9-triene 29. A 2 mol dm^{-3} solution of allylmagnesium chloride (27 cm^3, 54.0 mmol) in

ether was added dropwise over 30 min to a stirred solution of geranyl chloride (1.1 g, 6.4 mmol) in a mixture of THF (23 cm^3) and HMPA (23 cm^3). The resulting mixture was stirred overnight at room temperature, and then treated with saturated aqueous ammonium chloride (20 cm^3). The aqueous layer was separated and extracted with dichloromethane (4 × 25 cm^3), and the combined organic phases were then concentrated under reduced pressure. Ether (50 cm^3) was added to the residue, and the solution was then washed with 2 mol dm^{-3} hydrochloric acid (20 cm^3), water (4 × 25 cm^3), and brine and dried ($MgSO_4$). Distillation gave the *triene* (0.89 g, 78%), as an oil, bp 80–81 °C/10 mmHg;[36,37] ν_{max}/cm^{-1} (film) 3076, 2965, 2923, 1640, 1615, 1446, 1376, 1108, 992 and 910; δ_H 5.98–5.88 (m, C*H*=CH_2), 5.24–5.03 (m, 2 × =CH + =CH_2), 2.20–2.09 (m, 4 × CH_2), 1.79 (s, CH_3) and 1.71 (s, 2 × CH_3); δ_C 138.8 (=CH), 135.4 (quat. C), 131.3 (quat. C), 124.4 (=CH), 123.8 (=CH), 114.4 (=CH_2), 39.7 (CH_2), 34.0 (CH_2), 27.4 (CH_2), 26.7 (CH_2), 25.7 (CH_3), 17.7 (CH_3) and 16.0 (CH_3); *m/z* 178.1737. (M^+. $C_{13}H_{22}$ requires M^+, 178.1722).

6,10-Dimethylundeca-5,9-dien-1-ol 30. A 0.5 mol dm^{-3} solution of bis(3-methylbutan-2-yl)borane (24.7 cm^3, 12.4 mmol) in ether was added dropwise over 10 min to a stirred solution of the triene **24** (2.0 g, 11.2 mmol) in THF (25 cm^3) at 0–5 °C. The mixture was brought to 20–25 °C, and then stirred overnight. 3 mol dm^{-3} Sodium hydroxide (3.5 cm^3) and 30% hydrogen peroxide (3.5 cm^3) were added to the mixture which was then neutralized with saturated aqueous ammonium chloride (10 cm^3) and extracted with ether. The extracts were dried and then evaporated under reduced pressure to leave a residue which was purified by flash chromatography over silica gel (light petroleum–ether, 7:3) to give the alcohol (0.85 g, 38%) as a colourless oil, bp 104–105 °C/0.8 mmHg;[37] ν_{max}/cm^{-1} (film) 3334br (OH), 3077, 2963, 2928, 1641, 1440, 1416, 1376, 1336, 1071, 992 and 910; δ_H 5.15–5.05 (m, 2 × =CH), 3.62 (t, *J* 7.6, OCH_2), 2.10–1.95 (m, 3 × CH_2), 1.65 (s, CH_3), 1.60 (s, 2 × CH_3), 1.62–1.50 (m, CH_2) and 1.44–1.34 (m, CH_2); δ_C 135.1 (quat. C), 131.2 (quat. C), 124.3 (=CH), 124.2 (=CH), 62.7 (OCH_2), 39.6 (CH_2), 32.2 (CH_2), 27.5 (CH_2), 26.6 (CH_2), 25.9 (CH_2), 25.6 (CH_3), 17.6 (CH_3) and 15.9 (CH_3).

6,10-Dimethylundeca-5,9-dienoic acid 31. Pyridinium dichromate (PDC) (3.5 g, 8.9 mmol) was added to a solution of the alcohol **30** (0.5 g, 2.6 mmol) in *N*,*N*-dimethylformamide (DMF) (15 cm^3) at room temperature and the reaction mixture was stirred for 20 h. It was then poured onto water (80 cm^3) and extracted with ether (3 × 60 cm^3). The extracts were dried (Na_2SO_4) and purified by flash chromatography to give the title acid (0.17 g, 33%) as a colourless oil, bp 139–144 °C/0.5 mmHg, which showed spectroscopic data identical with literature values.[37]

***Se*-Phenyl 6,10-dimethylundeca-6,10-dieneselenoate 26.** The ester was prepared from the acid **31** according to the general procedure (87%) as an oil; ν_{max}/cm^{-1} (film) 3058, 2924, 2855, 1724, 1579, 1477, 1438, 1376, 737 and 689; δ_H 7.51–7.30 (m, 5 × aryl =CH), 5.15–5.05 (m, 2 × =CH), 2.70 (t, *J* 8.0, CH_2), 2.12–2.01 (m, 3 × CH_2), 1.81–1.74 (m, CH_2), 1.73 (s, CH_3), 1.67 (s, CH_3) and 1.65 (s, CH_3); δ_C 200.4 (CO), 136.5 (quat. C), 135.8 (2 × aryl =CH), 131.4 (quat. C), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 126.5 (quat. C), 124.2 (=CH), 122.9 (=CH), 46.9 (CH_2), 39.7 (CH_2), 26.9 (CH_2), 26.6 (CH_2), 25.7 (CH_3), 25.3 (CH_2), 17.7 (CH_3) and 16.0 (CH_3) (Found: C, 65.2; H, 7.7. $C_{19}H_{26}OSe$ requires C, 65.3; H, 7.5%).

Reductive cyclisation of the *Se*-phenyl selenoate 26. Cyclisation of the title ester according to the general procedure led to a *ca.* 1:1 mixture of diastereoisomers of 2-(1,5-dimethylhex-4-enyl)cyclopentanone **38** (85%); ν_{max}/cm^{-1} (film) 2961, 2925, 2875, 1737, 1703sh, 1453, 1378 and 1154; δ_H 5.06–4.97 (m, =CH), 2.28–1.78 (m), 1.61 (s, CH_3), 1.52 (s, CH_3), 0.90 (d, *J* 6.9) and 0.79 (d, *J* 6.6, CH_3); δ_C 221.4 (CO), 131.5 and 131.3 (quat. C), 124.4 and 124.2 (=CH), 54.8 and 53.5 (CH), 39.3 (CH_2), 35.5 and 33.3 (CH_2), 32.2 and 31.4 (CH), 26.0 and 25.8 (CH_2), 25.6 and 25.3 (CH_3), 25.3 and 23.6 (CH_2), 20.6 (CH_2), 17.8 and 17.6 (CH_3) and 15.4 (CH_3) (Found: C, 79.7; H, 11.6%; M^+, 194.1713. $C_{13}H_{22}O$ requires C, 80.3; H, 11.4%; M^+, 194.1671).

Ethyl 4-cyclohexylidenebutanoate 33. The title ester was prepared from 1-vinylcyclohexanol **32**, according to the general procedure (70%);[38] ν_{max}/cm^{-1} (film) 2930, 2854, 1736, 1447, 1371, 1186, 916 and 733; δ_H 5.20–5.09 (m, =CH), 4.20 (q, *J* 7.1, OCH_2), 2.40–2.37 (m, 2 × CH_2), 2.25–2.15 (m, CH_2), 2.14–2.10 (m, CH_2), 1.60–1.56 (m, 3 × CH_2) and 1.33 (t, *J* 7.1, CH_3); δ_C 173.4 (CO), 141.1 (quat. C), 119.0 (=CH), 60.1 (OCH_2), 37.0 (CH_2), 34.9 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 27.8 (CH_2), 26.8 (CH_2), 22.7 (CH_2) and 14.2 (CH_3); *m/z* 194.1306. [($C_{12}H_{20}O_2$ − H_2)$^+$ requires 194.1307].

10-Cyclohexyldeca-5,9-dienoic acid 35. Reduction of ethyl 4-cyclohexylidenebutanoate **33**, using lithium aluminium hydride in ether, first gave 4-cyclohexylidenebutan-1-ol **34a** (75%) as a colourless oil, bp 180 °C/20 mmHg;[39] δ_H 5.10–5.01 (*ca.* t, *J* 6.5, =CH), 3.62 (t, *J* 7.0, CH_2), 2.20–2.08 (m, 3 × CH_2), 1.61–1.48 (m, 4 × CH_2) and 1.25 (br s, OH); δ_C 139.8 (quat. C), 120.4 (=CH), 62.6 (OCH_2), 37.1 (CH_2), 33.0 (CH_2), 28.6 (2 × CH_2), 27.8 (CH_2), 26.8 (CH_2) and 23.4 (CH_2).

Oxidation of the alcohol with pyridinium chlorochromate (PCC) in CH_2Cl_2 next led to 4-cyclohexylidenebutanal **34b** (90%); ν_{max}/cm^{-1} (film) 2928, 2854, 1725, 1673, 1447, 1054, 913 and 733; δ_H 9.69 (t, *J* 1.6, CHO), 4.97 (t, *J* 6.4, =CH), 2.42–2.30 (m, CH_2), 2.29–2.20 (m, CH_2), 2.08–1.92 (m, 2 × CH_2) and 1.58–1.35 (m, 3 × CH_2); δ_C 202.7 (CO), 141.3 (quat. C), 118.7 (=CH), 44.2 (CH_2), 37.0 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 27.7 (CH_2), 26.8 (CH_2) and 20.0 (CH_2).

A Wittig reaction between the aldehyde **34b** and the ylide from the phosphonium salt **3**, according to the procedure used to prepare **15**, then produced the title acid **35** (36%) as a *ca.* 8:1 mixture of *Z*- and *E*-isomers; ν_{max}(film)/cm^{-1} 3500–2500br (CO_2H), 1708, 1446, 1412, 1240 and 935; δ_H 9.6 (br s, CO_2H), 5.50–5.28 (m + dt, *J* 10.8, 7.1, *Z*-CH=CH), 5.06 (t, *J* 5.9, =CH), 2.35 (t, *J* 7.5, CH_2), 2.15–1.95 (m, 5 × CH_2), 1.73–1.65 (m, CH_2) and 1.60–1.40 (m, 3 × CH_2); δ_C(*Z*-isomer) 180.0 (CO), 140.0 (quat. C), 130.7 (=CH), 128.4 (=CH); 120.5 (=CH), 37.1 (CH_2), 33.4 (CH_2), 28.65 (CH_2), 28.61 (CH_2), 27.8 (2 × CH_2), 27.1 (CH_2), 26.9 (CH_2), 26.4 (CH_2) and 24.5 (CH_2); δ_C(*E*-isomer) 180.1 (CO), 139.8 (quat. C), 131.3 (=CH) and 128.9 (=CH); *m/z* 236.1776 (M^+. Calc. for $C_{15}H_{24}O_2$: M^+, 236.1770).

***Se*-Phenyl 10-cyclohexyldeca-5,9-dieneselenoate 27.** The title ester was prepared according to the general procedure as a pale yellow oil (53%) comprising a *ca.* 9:1 mixture of *Z*- and *E*-isomers; ν_{max}/cm^{-1} (film) 3058, 3003, 2924, 2851, 1724, 1580, 1477, 1438, 1404, 737 and 689; δ_H 7.64–7.54 (m, 2 × aryl =CH), 7.51–7.46 (m, 3 × aryl =CH), 5.64–5.38 (m + dt, *J* 10.9 and 6.9, *Z*-CH=CH), 5.20–5.15 (t, *J* 6.1, =CH), 2.79 (t, *J* 7.5, CH_2), 2.25–2.14 (m, 5 × CH_2), 1.92–1.81 (m, CH_2) and 1.65–1.60 (m, 3 × CH_2); δ_C(*Z*-isomer) 200.2 (CO), 140.1 (quat. C), 135.7 (2 × aryl =CH), 131.0 (=CH), 129.3 (2 × aryl =CH), 128.8 (aryl =CH), 128.2 (=CH), 126.5 (quat. C), 120.5 (=CH), 46.85 (CH_2), 37.1 (CH_2), 28.7 (CH_2), 28.6 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 27.1 (CH_2), 26.9 (CH_2), 26.3 (CH_2) and 25.2 (CH_2); δ_C(*E*-isomer) 131.5 (=CH), 128.6 (=CH), 46.80 (CH_2), 31.8 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 27.7 (CH_2), 26.8 (CH_2) and 25.1 (CH_2); *m/z* (%) 202 (4), 201 (22), 191 (6), 173 (8), 165 (6), 158 (5.5), 157 (9), 137 (6.5) and 135 (47) (Found: C, 67.1; H, 7.7. $C_{21}H_{28}OSe$ requires C, 67.2; H, 7.5%).

Reductive cyclisation of the *Se*-phenyl selenoate 27. Cyclisation of the title ester according to the general procedure, gave the *indanone* **37** (66%), as a *ca.* 1:1 mixture of diastereoisomers; ν_{max}/cm^{-1} (film) 2923, 2850, 1706, 1448, 1234 and 1133; δ_C 214.7 (CO), 53.2 (CH), 50.3 (CH), 44.4 (CH), 41.2 (CH), 39.7 (CH_2), 32.1 (CH_2), 29.6 (CH_2), 28.6 (CH_2), 28.1 (CH_2), 27.1 (CH_2), 26.62 (CH_2), 26.56 (CH_2), 26.4 (CH_2) and 23.6 (CH_2) (Found: C, 81.5; H, 11.4%; M^+, 220.1818. $C_{15}H_{24}O$ requires C, 81.8; H, 11.0%; M^+, 220.1827).

Ethyl 3-cyclohex-1-enylpropanoate 39. The title ester was prepared from 2-methylenecyclohexanol according to the general procedure (88%), and showed bp 178 °C/20 mm Hg;[40] ν_{max}/cm^{-1} (film) 2931, 1735, 1445, 1370, 1178, 916 and 733; δ_H 5.55–5.51 (m, =CH), 4.24 (q, *J* 7.1, OCH_2), 2.55–2.49 (m, CH_2), 2.41–2.34 (m, CH_2), 2.11–2.02 (m, 2 × CH_2), 1.78–1.61 (m, 2 × CH_2) and 1.37 (t, *J* 7.1, CH_3); δ_C 173.5 (CO), 136.0 (quat. C), 121.4 (=CH), 60.1 (OCH_2), 33.0 (CH_2), 32.8 (CH_2), 28.1 (CH_2), 25.1 (CH_2), 22.8 (CH_2), 22.3 (CH_2) and 14.2 (CH_3); *m/z* 182.1309 (M^+. Calc. for $C_{11}H_{18}O_2$: M^+, 182.1306).

9-Cyclohex-1-enylnon-5-enoic acid 41. Reduction of the ester **39** using lithium aluminium hydride first gave 3-cyclohex-1-enylpropanol **40a** (93%) as an oil, bp 165 °C/20 mmHg; ν_{max}/cm^{-1} (film) 3356br (OH), 2931, 1661, 1439, 1059 and 919; δ_H 5.45–5.35 (m, =CH), 3.62 (t, *J* 7.3, OCH_2), 2.20–1.93 (m, 3 × CH_2) and 1.70–1.54 (m, 3 × CH_2); δ_C 137.3 (quat. C), 121.1 (=CH), 62.7 (CH_2O), 34.2 (CH_2), 30.4 (CH_2), 28.1 (CH_2), 25.1 (CH_2), 22.9 (CH_2) and 22.4 (CH_2); *m/z* 140.1208 (M^+. Calc. for $C_9H_{16}O$: M^+, 140.1201).

Oxidation of the alcohol **40a** with PCC next led to 3-cyclohex-1-enylpropanal **40b** (78%), bp 160 °C/20 mmHg;[41] δ_H 9.75 (t, *J* 1.4, CHO), 5.50–5.43 (m, =CH), 2.55–2.45 (m, CH_2), 2.30–2.21 (m, CH_2), 2.08–1.90 (m, 2 × CH_2) and 1.60–1.48 (m, 2 × CH_2); δ_C 202.3 (CO), 135.2 (quat. C), 121.3 (=CH), 41.3 (CH_2), 29.6 (CH_2), 27.9 (CH_2), 24.6 (CH_2), 22.3 (CH_2) and 21.8 (CH_2).

A Wittig reaction between the aldehyde **40b** and the ylide formed from the salt **3**, according to the general procedure used to prepare **15a**, then produced the acid **41** (30%) as a *ca.* 8:1 mixture of *Z*- and *E*-isomers; δ_H 11.10 (br s, CO_2H), 5.55–5.36 (m, 3 × =CH), 2.48–2.43 (m, CH_2), 2.25–2.14 (m, CH_2), 2.12–2.01 (m, 3 × CH_2) and 1.84–1.61 (m, 4 × CH_2); δ_C(*Z*-isomer) 180.3 (CO), 137.3 (quat. C), 130.9 (=CH), 128.2 (=CH), 121.0 (=CH), 37.9 (CH_2), 33.4 (CH_2), 28.3 (CH_2), 26.4 (CH_2), 25.6 (CH_2), 25.2 (CH_2), 24.5 (CH_2), 23.0 (CH_2) and 22.5 (CH_2); *m/z* 222.1565 (M^+. Calc. for $C_{14}H_{22}O_2$: M^+, 222.1619).

***Se*-Phenyl 9-cyclohex-1-enylnon-5-eneselenoate 42.** The title ester was prepared (51%) according to the general procedure as a *ca.* 8:1 mixture of *Z*- and *E*-isomers; ν_{max}/cm^{-1} (film) 3058, 3002, 2924, 2855, 1724, 1579, 1477, 1438, 737 and 689; δ_H 7.64–7.59 (m, 2 × aryl =CH), 7.58–7.36 (m, 3 × aryl =CH), 5.56–5.40 (m + dt, *J* 10.9 and 7.3, =CH + *Z*-CH=CH), 2.82 (t, *J* 7.4, CH_2) and 2.24–1.66 (m, 8 × CH_2); δ_C(*Z*-isomer) 200.2 (CO), 137.2 (quat. C), 135.7 (2 × aryl =CH), 131.1 (=CH), 129.3 (2 × aryl=CH), 128.8 (aryl=CH), 128.0 (=CH), 126.4 (quat. C), 121.0 (=CH), 46.8 (CH_2), 37.8 (CH_2), 28.3 (CH_2), 26.2 (CH_2), 25.6 (CH_2), 25.2 (2 × CH_2), 22.9 (CH_2) and 22.5 (CH_2); δ_C(*E*-isomer) 129.6 (=CH), 128.5 (=CH), 122.3 (=CH), 46.7 (CH_2), 33.2 (CH_2), 31.5 (CH_2), 28.2 (CH_2), 25.0 (CH_2), 22.8 (2 × CH_2), 22.4 (CH_2) and 22.3 (CH_2); *m/z* (%) 205 (7) and 187 (18).

Reductive cyclisation of the *Se*-phenyl selenoate 42. Cyclisation of the title ester according to the general procedure gave *trans*, *anti*, *trans*-perhydrophenanthren-1-one **43** (72%) as colourless crystals from hexane at −10 °C, mp 71–72 °C (lit.,[26] 71–72 °C); ν_{max}/cm^{-1} (CCl_4) 2916, 2852, 1700, 1450, 1366, 1347, 1313, 1138, 1121 and 956; δ_C 213.1 (CO), 54.9 (CH), 49.4 (CH), 48.6 (CH), 42.1 (CH), 41.6 (CH_2), 34.2 (CH_2), 32.7 (CH_2), 30.2 (CH_2), 28.9 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 26.1 (CH_2) and 24.9 (CH_2) (Found: C, 81.5; H, 11.1%; M^+, 206.1639. Calc. for $C_{14}H_{22}O$: C, 81.5; H, 10.8%; M^+, 206.1671).

7-Methoxy-1,2,3,4,9,10-hexahydrophenanthrene 44. According to the published procedure,[26] treatment of 7-methoxy-1,9,10,10a-tetrahydrophenanthren-3(2*H*)-one hydrazone with potassium *tert*-butoxide in boiling dry toluene gave the title compound **44**, instead of the stated isomer 1,2,3,9,10,10a-hexahydro-7-methoxyphenanthrene, as a pale yellow viscous oil (81%); δ_H 7.08 (d, *J* 8.3, aryl =CH), 6.68 (dd, *J* 8.3 and 2.7, aryl =CH), 6.67 (d, *J* 2.7, aryl =CH), 3.77 (s, OCH_3), 2.71 (t, *J* 7.9, CH_2), 2.35–2.30 (m, CH_2), 2.14–2.10 (m, 2 × CH_2), 1.79–1.73 (m, CH_2) and 1.69–1.63 (m, CH_2); δ_C 157.7 (quat. C), 137.0 (quat. C), 131.7 (quat. C), 129.9 (quat. C), 126.3 (quat. C), 122.3 (=CH), 113.4 (=CH), 110.7 (=CH), 55.2 (OCH_3), 30.8 (CH_2), 29.1 (CH_2), 28.7 (CH_2), 25.4 (CH_2), 23.2 (CH_2) and 23.0 (CH_2).

***trans*-7-Methoxy-1,2,3,4,4a,4b,5,9,10,10a-decahydrophenanthrene and *trans*-7-methoxy-1,2,3,4,4a,5,8,9,10,10a-decahydrophenanthrene 45.** A solution of the substituted anisole **44** (4.7 g, 21.8 mmol) in dry THF (209 cm^3) was added dropwise to a solution of lithium (6.1 g, 0.88 mol) in liquid ammonia (965 cm^3) with vigorous stirring. Following the addition, stirring was continued for 2 h, after which sufficient ethanol was carefully added to the reaction mixture so that it assumed a milky appearance. The ammonia was evaporated, and the residue was then diluted with water and extracted with ether. The combined etheral extracts were washed several times with water and then dried ($MgSO_4$) and evaporated under reduced pressure to leave the product which solidified on addition of methanol. The title compounds, with the conjugated diene predominating (*ca.* 4:1) (4.4 g, 93%) were thus obtained, mp 62–64 °C (lit.,[26] mp 62–65 °C); ν_{max}/cm^{-1} (KBr) 2918, 2850, 2830, 1697, 1664, 1447, 1223 and 784; δ_H 5.31 (br s, =CH), 5.22 (s, =CH), 3.57 (OCH_3) and 2.20–0.88 (17 H, complex series of m); δ_C(major isomer) 157.4 (=C–O), 135.8 (quat. C), 118.4 (=CH), 99.4 (=CH), 54.4 (OCH_3), 43.4 (CH), 41.6 (CH), 38.3 (CH), 34.3 (CH_2), 33.7 (CH_2), 31.2 (CH_2), 28.8 (CH_2), 26.8 (CH_2), 26.6 (CH_2) and 26.3 (CH_2).

4,4aα,4bβ,5,6,7,8,8aα,9,10-Decahydrophenanthren-2(3*H*)-one 46. 2 mol dm^{-3} Hydrochloric acid (17.9 cm^3, 35.7 mmol) was added to a solution of the enol ether **45** (4.4 g, 20.2 mmol) in methanol (143 cm^3) and the mixture was heated under reflux for 2 h. It was then evaporated to dryness under reduced pressure. The residue was diluted with water, and then extracted with ether. The dried ether extracts were evaporated under reduced pressure to leave a residue which was purified by flash chromatography over silica gel (benzene–ether, 9:1) to afford the title compound, mp 70–71 °C (lit.,[26] mp 71–72 °C); ν_{max}/cm^{-1} (KBr) 2926, 2851, 1671, 1616, 1447, 1260 and 912; δ_H 5.82 (s, =CH), 2.47–2.37 (2 H, m), 2.37–2.20 (3 H, m), 2.01–1.97 (2 H, m), 1.82–1.63 (4 H, m), 1.60–1.51 (1 H, m), 1.32–1.13 (4 H, m) and 1.01–0.84 (3 H, m); δ_C 200.1 (CO), 167.2 (quat. C), 124.4 (=CH), 48.9 (CH), 42.9 (CH), 42.0 (CH), 36.5 (CH_2), 35.7 (CH_2), 34.0 (CH_2), 33.7 (CH_2), 30.6 (CH_2), 26.3 (CH_2) and 26.0 (2 × CH_2).

1-Hydroxy-4,4aα,4bβ,5,6,7,8,8aα,9,10-decahydrophenanthren-2(3*H*)-one 47. 4 mol dm^{-3} Sodium hydroxide (2.7 cm^3, 10.1 mmol) was added dropwise to a stirred and cooled (−5 °C) solution of the enone **46** (0.8 g, 4.0 mmol) in methanol (76 cm^3). Hydrogen peroxide (30%; 10.1 cm^3, 8.9 mmol) was added to the mixture which was then stirred for a further 1 h below 0 °C before being poured into aqueous saturated sodium chloride (338 cm^3). The mixture was extracted with ether and the extract evaporated to leave *trans*-*trans*-1,10a-epoxyperhydrophenanthren-2-one (0.68 g, 78%)

as a colourless viscous oil which was used without further purification.

A solution of 98% sulfuric acid (0.6 cm^3) in propanoic acid (1.4 cm^3) was added dropwise to a stirred solution of the above epoxy ketone (0.68 g, 3.1 mmol) in propanoic acid (6.8 cm^3). The resulting dark solution was kept at room temperature for 18 h, and then diluted with water at 0 °C and extracted with ether. The dried ether extracts were evaporated under reduced pressure to leave a residue which was purified by flash chromatography over silica gel (light petroleum–ether, 4:1) to give the title compound (0.26 g, 38%) as an oil, which solidified. Recrystallisation from methanol gave material of mp 123–125 °C (lit.,[26] mp 124–125 °C); δ_H 6.09 (br s, OH), 3.09 (dd, *J* 17.5 and 3.3, CH), 2.55 (dt, *J* 17.0 and 4.2, CH), 2.37–2.20 (2 H, m), 2.08–1.65 (6 H, m), 1.53–1.43 (1 H, m), 1.31–1.10 (4 H, m), 1.07–0.82 (4 H, m); δ_C 194.3 (CO), 142.0 (quat. C), 135.9 (quat. C), 48.9 (CH), 41.9 (CH), 41.6 (CH), 34.5 (CH_2), 33.9 (CH_2), 32.9 (CH_2), 30.5 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 26.1 (CH_2) and 25.6 (CH_2).

***trans,anti,trans*-Perhydrophenanthren-1-one 43.** A mixture of the enol **47** (0.25 g, 1.14 mmol), acetic acid (5.8 cm^3) and aqueous hydrogen iodide (57%; 1.2 cm^3) was heated under reflux under an atmosphere of nitrogen for 90 min, and then poured into a cold (0 °C) solution of sodium hydroxide (4.8 g) and sodium hydrogen sulfite (1.4 g) in water (28.9 cm^3). The mixture was extracted with ether, and the ether extracts were dried and then evaporated under reduced pressure to leave a residue. Flash chromatography of this over silica gel (light petroleum–ether, 8:1) gave the tricyclic ketone (164 mg, 70%) which crystallised from pentane at −5 °C as colourless needles, mp 71–72 °C (lit.,[26] 71–72 °C); ν_{max}/cm^{-1} (CCl_4) 2925, 2854, 1700, 1448, 1367, 1312, 1120 and 956; δ_H 2.31–2.17 (2 H, m), 2.10–1.74 (5 H, m), 1.73–1.40 (5 H, m), 1.39–1.01 (5 H, m) and 1.00–0.67 (5 H, m); δ_C 213.1 (CO), 54.9 (CH), 49.4 (CH), 48.6 (CH), 42.1 (CH), 41.6 (CH_2), 34.2 (CH_2), 32.7 (CH_2), 30.2 (CH_2), 28.9 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 26.1 (CH_2) and 24.9 (CH_2). See the following paper for the assignment of the ^{13}C NMR shifts.[4]

2-[1-(6-Methoxy-3,4-dihydro-1-naphthyl)ethyl]-1,3-dioxolane 49. A solution of 2-(2-bromoethyl)-1,3-dioxolane (12.3 g, 67.5 mmol) in dry THF (50 cm^3) was added dropwise over 1.0 h to a stirred suspension of magnesium (1.6 g, 65.0 mmol) in dry THF at 30–35 °C. The mixture was stirred at 30 °C for 1 h, after which a solution of 6-methoxy-1-tetralone (8.9 g, 50.0 mmol) in dry benzene (20 cm^3) was added dropwise over 0.5 h at 30 °C. After the mixture had been stored overnight at room temperature, it was poured into ice-cold aqueous ammonium chloride. The resulting mixture was extracted with ether and the extract was washed with water, dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (light petroleum–ether, 3:1) to give the corresponding dioxolanol (85%) as an oil; ν_{max}/cm^{-1} (film) 3462br (OH), 3053, 2937, 2877, 2837, 1607, 1574, 1498, 1454, 1255, 1142, 1038 and 736; δ_H 7.42 (d, *J* 8.7, aryl =CH), 6.73 (dd, *J* 8.7 and 2.6, aryl =CH), 6.55 (d, *J* 2.6, aryl =CH), 4.84 (t, *J* 4.5, O_2CH), 3.91–3.77 (m, OCH_2CH_2O), 3.74 (s, OCH_3), 2.76–2.68 (m, CH_2), 2.46 (br s, OH), 1.96–1.85 (m, 2 × CH_2) and 1.83–1.72 (m, 2 × CH_2); δ_C 158.2 (=CO), 138.1 (quat. C), 134.6 (quat. C), 127.6 (=CH), 112.9 (=CH), 112.4 (=CH), 104.5 (O_2CH), 71.4 (COH), 64.8 (OCH_2CH_2O), 55.0 (OCH_3), 36.2 (CH_2), 36.0 (CH_2), 30.1 (CH_2), 28.6 (CH_2) and 19.7 (CH_2); *m/z* 260.1436 [($C_{16}H_{22}O_4 - H_2O$)$^+$ requires 260.1412].

A mixture of the above dioxolanol (12.0 g) and $FeCl_3$–SiO_2 (200 g)[42] in dry ether (50 cm^3) was stirred at room temperature for 1 h after which the mixture was filtered and the residue was washed with ether. Evaporation of the filtrate left a residue consisting largely of the desired title compound **49** (10.5 g, 87%). Distillation of the dioxolanol at *ca.* 180 °C/0.1 mmHg also effected the desired dehydration (95%); ν_{max}/cm^{-1} (film) 2932, 2880, 2832, 1606, 1568, 1497, 1455, 1428, 1303, 1251, 1141, 1078, 1037 and 824; δ_H 7.19 (d, *J* 8.7, aryl =CH), 6.80–6.60 (m, 2 × aryl =CH), 5.75 (t, *J* 4.5, =CH), 4.94 (t, *J* 4.7, CHO_2), 4.01–3.85 (2 × m, OCH_2CH_2O), 3.79 (s, OCH_3), 2.70 (t, *J* 8, CH_2), 2.61–2.51 (m, CH_2), 2.24–2.19 (m, CH_2) and 1.91–1.86 (m, CH_2); δ_C 158.3 (=CO), 138.6 (quat. C), 135.4 (quat. C), 127.9 (quat. C), 123.8 (=CH), 122.4 (=CH), 113.8 (=CH), 110.9 (=CH), 104.4 (OCH_2), 65.0 ($O_2CH_2CH_2O$), 55.2 (OCH_3), 32.8 (CH_2), 28.9 (CH_2), 27.0 (CH_2) and 23.1 (CH_2); *m/z* 260.1406 (M^+. $C_{16}H_{20}O_3$ requires M^+, 260.1412).

3-(6-Methoxy-3,4-dihydro-1-naphthyl)propanal 50. A mixture of the acetal **49** (10.0 g) and THF–1.5 mol dm^3 H_2SO_4 (1:1; 400 cm^3) was stirred at room temperature for 1 h, and then extracted with ether. The combined organic phases were washed with saturated aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated to dryness. The residue was purified by flash chromatography over silica gel (light petroleum–ether, 3:1), to give the *aldehyde* **50** (6.5 g, 79%) as an oil; ν_{max}/cm^{-1} (film) 2933, 2831, 2720, 1722, 1606, 1568, 1498, 1303, 1251, 1141, 1079, 1038 and 822; δ_H 9.92 (s, CHO), 7.26 (d, *J* 9.2, aryl =CH), 6.86–6.83 (m, 2 × aryl =CH), 5.87–5.84 (t, *J* 4.5, =CH), 3.91 (s, OCH_3), 2.87–2.77 (m, 3 × CH_2), and 2.39–2.31 (m, CH_2); δ_C 201.4 (CO), 158.1 (quat. C), 138.1 (quat. C), 134.0 (quat. C), 126.9 (quat. C), 123.1 (=CH), 122.3 (=CH), 113.6 (=CH), 110.4 (=CH), 54.5 (OCH_3), 42.0 (CH_2), 28.3 (CH_2), 24.5 (CH_2) and 22.6 (CH_2); *m/z* 216.1149 (M^+. $C_{14}H_{16}O_2$ requires M^+, 216.1150); *m/z* 216 (54%), 187 (34), 174 (100), 169 (65) and 115 (33).

(*Z*)-8-(6-Methoxy-3,4-dihydro-1-naphthyl)oct-5-enoic acid 51. A Wittig reaction between the aldehyde **50** and the ylide formed from the salt **3**, according to the general procedure used to prepare **15**, produced a mixture of the *Z*- and *E*-isomers (*ca.* 3:1) of the carboxylic acid **51** (98%) as an oil; ν_{max}/cm^{-1} (film) 3500–2500br (CO_2H), 1706, 1606, 1568, 1497, 1428, 1250, 1140, 1032, 824 and 738; δ_H 10.6 (br s, CO_2H), 7.26 (d, *J* 9.2, aryl =CH), 6.83–6.80 (m, 2 × aryl =CH), 5.83–5.80 (*ca.* t, *J* 4.3, =CH), 5.56–5.46 (2 × dt, *J* 10.8, 7.3 and 7.3, *Z*-CH=CH), 3.888 and 3.885 (2 × s, OCH_3), 2.80 (t, *J* 7.9, CH_2), 2.57–2.51 (m, CH_2), 2.42–2.30 (m, 3 × CH_2), 2.18–2.10 (m, CH_2) and 1.80–1.72 (m, CH_2); δ_C(*Z*-isomer) 180.2 (CO), 158.2 (quat. C), 138.5 (quat. C), 135.43 (quat. C), 130.6 (=CH), 128.5 (=CH), 127.9 (quat. C), 123.6 (=CH), 122.53 (=CH), 113.8 (=CH), 110.7 (=CH), 55.1 (OCH_3), 33.4 (CH_2), 32.7 (CH_2), 28.9 (CH_2), 26.4 (CH_2), 26.2 (CH_2), 24.5 (CH_2) and 23.0 (CH_2); δ_C(*E*-isomer) 180.1 (CO), 135.40 (quat. C), 131.2 (=CH), 129.0 (=CH), 128.0 (quat. C), 123.7 (=CH), 122.46 (=CH), 31.8 (CH_2), 31.5 (CH_2) and 24.3 (CH_2) (Found: C, 75.8; H, 8.1%; M^+, 300.1735. $C_{19}H_{24}O_3$ requires C, 75.9; H, 8.1%; M^+, 300.1725).

(*Z*)-*Se*-Phenyl 8-(6-methoxy-3,4-dihydro-1-naphthyl)oct-5-eneselenoate 52. The ester was prepared (58%) according to the general procedure as a yellow oil comprising a *ca.* 5:1 mixture of *Z*- and *E*-isomers; ν_{max}/cm^{-1} (film) 3001, 2931, 2831, 1723, 1607, 1568, 1497, 1438, 1303, 1251, 1140, 824, 739 and 690; δ_H 7.53–7.50 (m, 2 × aryl =CH), 7.39–7.35 (m, 3 × aryl =CH), 7.20 (d, *J* 9.2, aryl =CH), 6.77–6.74 (m, 2 × aryl =CH), 5.76 (t, *J* 4.3, =CH), 5.55–5.33 (*ca.* 2 × dt, *J* 10.8, 7.2 and 7.2, *Z*-CH=CH), 3.81 (s, OCH_3), 2.74 (t, *J* 7.9, $ArCH_2$), 2.67 (t, *J* 7.5, $COCH_2$), 2.49 (t, *J* 7.5, $=CCH_2$), 2.31–2.23 (m, 2 × CH_2), 2.12–2.07 (m, CH_2) and 1.78–1.72 (m, CH_2). Irradiation at δ 2.31–2.23 caused the signal at δ 2.49 to collapse to a singlet, and the signal at δ 5.51 to simplify to a doublet (*J* 10.8), thereby confirming the *Z*-stereochemistry. This conclusion was verified by NOE experiments; δ_C 200.1 (CO), 158.2 (quat. C), 138.5 (quat. C), 135.7 (2 × aryl =CH), 135.4 (quat. C), 130.7 (=CH), 129.2 (2 × aryl =CH), 128.7 (=CH), 128.3 (=CH), 127.8 (quat. C), 126.4 (quat. C), 123.6 (=CH), 122.5 (=CH), 113.8 (=CH),

110.7 (=CH), 55.1 (OCH_3), 46.8 (CH_2), 32.7 (CH_2), 28.9 (CH_2), 26.2 (2 × CH_2), 25.1 (CH_2) and 23.0 (CH_2) [Found: C, 67.8; H, 6.4%; M^+(^{80}Se), 440.1246. $C_{25}H_{28}O_2Se$ requires C, 68.3; H, 6.4%; M^+(^{80}Se), 440.1255].

Reductive cyclisation of the *Se*-phenyl selenoate 52. Cyclisation of the title ester **52** according to the general procedure, led to a 55:45 mixture (^{13}C NMR analysis) of two diastereoisomeric tetracyclic ketones in 78% yield. The oily mixture of diastereoisomers set to a waxy solid with time, mp 90–97 °C and 135–145 °C. The mixture behaved as a single component on TLC analysis under a variety of conditions. However, careful chromatography over silica gel (light petroleum–ether, 50:1), gave: the *trans,anti,trans*-isomer of the tetracyclic ketone **53**, the major component, mp 146–150 °C; δ_H(steroid numbering) 7.23 (d, *J* 8.6, 1-H), 6.73 (dd, *J* 8.6 and 2.8, 2-H), 6.64 (d, *J* 2.8, 4-H), 3.79 (s, OCH_3), 2.87–2.83 (dd, *J* 8.4 and 4.3, 2 × 6-H), 2.55–2.50 (1 H, ddd, *J* 13.0, 6.8 and 3.3), 2.42–2.33 (2 H, m), 2.32–2.22 (2 H, m), 2.21–2.05 (4 H, m), 1.73–1.61 (2 H, m), 1.60–1.47 (1 H, m, *ca.* ddd), 1.40–1.31 (2 H, m) and 1.30–1.16 (2 H, m); δ_C 212.6 (CO), 157.5 (quat. C), 137.8 (quat. C), 132.3 (quat. C), 126.6 (=CH), 113.4 (=CH), 111.6 (=CH), 55.2 (OCH_3), 54.5 (CH), 49.1 (CH), 46.4 (CH), 42.1 (CH), 41.5 (CH_2), 30.2 (CH_2), 29.8 (CH_2), 29.1 (CH_2), 26.4 (CH_2), 26.3 (CH_2) and 25.0 (CH_2) (Found: C, 80.7; H, 8.8%; M^+, 284.1774. $C_{19}H_{24}O_2$ requires C, 80.3; H, 8.5%; M^+, 284.1776). The connectivity and partial assignment of the stereochemistry of the tetracycle **53** was confirmed by COSY and NOE experiments. For the calculated ^{13}C NMR shifts, see the following paper.[4] Combination of the later chromatography fractions gave a mixture of the diastereoisomers, with enrichment in the minor component; δ_C 212.4 (CO), 157.2 (quat. C), 138.0 (quat. C), 129.8 (quat. C), 127.2 (=CH), 113.8 (=CH), 112.0 (=CH), 55.2 (OCH_3), 54.8 (CH), 41.5 (CH), 41.0 (CH), 37.2 (CH), 29.7 (CH_2), 29.1 (CH_2), 27.5 (CH_2), 25.64 (CH_2), 25.59 (CH_2), 20.1 (CH_2) and *either* 41.5 *or* 26.3 (CH_2).

(*E*)-Ethyl 7-(6-Methoxy-3,4-dihydro-1-naphthyl)hept-5-enoate 55. A solution of vinylmagnesium chloride (1.7 mol dm^{-3}) in ether (12.3 cm^3, 20.8 mmol) was added dropwise over 20 min to a stirred solution of the aldehyde **50** (3.0 g, 13.9 mmol) in dry THF (40 cm^3) at 0 °C, under an atmosphere of nitrogen. The mixture was allowed to warm to room temperature, and stirred at this temperature for 2 h. Saturated aqueous ammonium chloride (20 cm^3) was added cautiously to the mixture which was then extracted with ether (2 × 30 cm^3). The extracts were dried, and evaporated under reduced pressure to leave a residue which was purified by chromatography over silica gel (light petroleum–ethyl acetate, 3:2) to give 5-(6-*methoxy*-3,4-*dihydro*-1-*naphthyl*)*pent*-1-*en*-3-*ol* **54** (1.9 g, 56%) as a pale orange oil; ν_{max}/cm $^{-1}$ (film) 3416br, 2934, 2832, 1616, 1568, 1497, 1463, 1426, 1372, 1302, 1250, 1142, 1038, 924, 824, 737 and 657; δ_H 7.22 (d, *J* 9.2, aryl-H), 6.76–6.74 (m, 2 × aryl-H), 6.00–5.86 (ddd, *J* 17.1, 10.5 and 6.3, C*H*=CH_2), 5.79 (t, *J* 4.3, =CH), 5.28 (d, *J* 17.1, =C*H*H), 5.15 (d, *J* 10.5, =CH*H*), 4.24–4.16 (m, C*H*OH), 3.82 (s, OCH_3), 2.74 (t, *J* 7.9, aryl-CH_2), 2.65–2.43 (m, CH_2), 2.29–2.21 (m, CH_2), 1.99 (br s, OH) and 1.82–1.73 (m, CH_2); δ_C 158.0 (=*C*OMe), 141.0 (*C*H=CH_2), 138.3 (quat. C), 135.4 (quat. C), 127.6 (quat. C), 123.5 (=CH), 122.2 (=CH), 114.2 (=CH_2), 113.5 (=CH), 110.5 (=CH), 72.4 (CHOH), 54.8 (OCH_3), 35.5 (CH_2), 28.6 (CH_2), 28.3 (CH_2) and 22.8 (CH_2).

(*E*)-Ethyl 7-(6-methoxy-3,4-dihydro-1-naphthyl)hept-5-enoate 55. The title compound, prepared from the vinyl alcohol **54**, according to the general procedure, was purified by chromatography over silica gel (light petroleum–ethyl acetate, 7:3) to give a colourless oil (69%); ν_{max}/cm^{-1} (film) 2933, 2834, 1731, 1606, 1568, 1498, 1250, 1038 and 822; δ_H 7.17 (d, *J* 9.2, aryl-H), 6.75–6.73 (m, 2 × aryl-H), 5.73 (t, *J* 4.5, =CH), 5.59–5.41 (2 × dt, *J* 15.3, 6.5 and 6.0, *E*-CH=CH), 4.15 (q, *J* 7.2, OCH_2), 3.82 (s, OCH_3), 2.72 (t, *J* 8.0, CH_2CO), 2.46 (t, *J* 7.7, aryl-CH_2), 2.39–2.32 (m, 2 × CH_2), 2.26–2.19 (m, 2 × CH_2) and 1.27 (t, *J* 7.2, CH_3); δ_C 173.0 (CO_2), 158.1 (=*C*OMe), 138.4 (quat. C), 135.4 (quat. C), 131.0 (=CH), 128.2 (=CH), 127.8 (quat. C), 123.5 (=CH), 122.2 (=CH), 113.6 (=CH), 110.6 (=CH), 60.0 (CH_2O), 55.0 (OCH_3), 34.2 (CH_2), 32.6 (CH_2), 31.3 (CH_2), 28.8 (CH_2), 27.8 (CH_2), 22.9 (CH_2) and 14.1 (CH_3); *m*/*z* 314.1881 (M^+. $C_{20}H_{26}O_3$ requires M^+, 314.1882).

(*E*)-8-(6-Methoxy-3,4-dihydro-1-naphthyl)oct-5-enenitrile 56. Reduction of the ester **55** using lithium aluminium hydride, according to the general procedure, first gave (*E*)-7-(6-methoxy-3,4-dihydro-1-naphthyl)hept-4-en-1-ol (86%) as a colourless oil; ν_{max}/cm^{-1} (film) 3405br, 3003, 2934, 2836, 1606, 1568, 1498, 1250, 1038, 969, 823 and 756; δ_H 7.18 (d, *J* 9.1, aryl-H), 6.75–6.72 (m, 2 × aryl-H), 5.73 (t, *J* 4.5, =CH), 5.57–5.41 (2 × dt, *J* 15.3, 6.4 and 6.2, *E*-CH=CH), 3.82 (s, OCH_3), 3.66 (t, *J* 6.5, CH_2OH), 2.72 (t, *J* 8.0, aryl-CH_2), 2.47 (t, *J* 7.4, CH_2), 2.26–2.17 (m, 2 × CH_2), 2.13–2.06 (m, CH_2), 1.68–1.61 (m, CH_2) and 1.41 (br s, OH); δ_C 158.0 (=*C*OMe), 138.5 (quat. C), 135.4 (quat. C), 130.4 (=CH), 129.7 (=CH), 127.9 (quat. C), 123.6 (=CH), 122.3 (=CH), 113.6 (=CH), 110.7 (=CH), 62.3 (CH_2OH), 55.1 (OCH_3), 32.7 (CH_2), 32.3 (CH_2), 31.4 (CH_2), 28.82 (CH_2), 28.79 (CH_2) and 22.9 (CH_2); *m*/*z* 272.1770 (M^+. $C_{18}H_{24}O_2$ requires M^+, 272.1776).

Triethylamine (1.88 cm^3, 135 mmol) followed by methanesulfonyl chloride (1.05 cm^3, 13.5 mmol) were added to a stirred solution of the above heptenol (3.33 g, 12 mmol) in dry CH_2Cl_2 (55 cm^3) at 0 °C, under an atmosphere of nitrogen. The mixture was stirred at 0 °C for 1 h after which it was evaporated under reduced pressure. Sodium cyanide (1.8 g, 0.037 mol) was added to the crude mesyl ester (4.1 g, 12 mmol) in dimethyl sulfoxide (80 cm^3), under an atmosphere of nitrogen after which the mixture was stirred and heated at 60 °C for 15 h. After it had been allowed to cool it was poured into ether (300 cm^3). The ethereal solution was extracted with water (4 × 200 cm^3) and saturated aqueous sodium chloride (100 cm^3), dried (Na_2SO_4), filtered and evaporated under reduced pressure. The residue was purified by chromatography over silica gel (light petroleum–ethyl acetate, 4:1) to give the *nitrile* (3.2 g, 95%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3001, 1933, 2834, 2245, 1606, 1568, 1497, 1250, 1140, 1039, 970, 825 and 756; δ_H 7.18 (d, *J* 9.2, aryl =CH), 6.76–6.71 (m, 2 × aryl =CH), 5.74 (t, *J* 4.5, =CH), 5.60–5.31 (2 × dt, *J* 15.3, 6.8 and 6.7, *E*-CH=CH), 3.82 (s, OCH_3), 2.73 (t, *J* 7.9, CH_2), 2.51–2.47 (m, CH_2), 2.33–2.06 (m, 4 × CH_2) and 1.75–1.65 (m, CH_2); δ_C 158.1 (=*C*OMe), 138.4 (quat. C), 135.3 (quat. C), 132.3 (=CH), 127.7 (quat. C), 127.5 (=CH), 123.5 (=CH), 122.4 (=CH), 119.6 (≡CN), 113.6 (=CH), 110.7 (=CH), 55.0 (OCH_3), 32.5 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 28.8 (CH_2), 24.9 (CH_2), 22.9 (CH_2) and 16.0 (CH_2); *m*/*z* 281.1770 (M^+. $C_{19}H_{23}NO$ requires M^+, 281.1780).

(*E*)-*Se*-Phenyl 8-(6-methoxy-3,4-dihydro-1-naphthyl)oct-5-eneselenoate 57. A mixture of the nitrile **56** (2.81 g, 10 mmol), potassium hydroxide (2.81 g, 50 mmol), water (160 cm^3), and ethanol (80 cm^3) was boiled under reflux for 12 h. A further portion of potassium hydroxide (2.81 g, 50 mmol) and water (25 cm^3) were added to the mixture which was then boiled under reflux for a further 24 h. The mixture was cooled, and the ethanol was removed under reduced pressure. The aqueous alkaline residue was extracted with ether (40 cm^3) and then acidified with concentrated hydrochloric acid. The aqueous acidic solution was extracted with ether (4 × 40 cm^3) and the extracts were dried and evaporated under reduced pressure. The residue was purified by chromatography over silica gel (light petroleum–ethyl acetate, 1:1) to give recovered nitrile (0.8 g, 28.5%), and (E)-8-(6-*methoxy*-3,4-*dihydro*-1-*naphthyl*)*oct*-5-*enoic acid* (1.0 g, 33%) as a colourless oil; ν_{max}/cm^{-1} (film) 3500–2500 (br, CO_2H), 1712, 1607, 1568, 1497, 1249, 1141, 1042, 968, 824 and 757; δ_H 9.25–9.05 (br s, CO_2H), 7.21 (d, *J* 8.9, aryl-H),

6.78–6.76 (m, 2 × aryl-H), 5.77 (br s, =CH), 5.59–5.34 (2 × dt, *J* 15.3, 6.5 and 6.2, *E*-CH=CH), 3.84 (s, OCH_3), 2.75 (t, *J* 7.8, CH_2CO), 2.51 (t, *J* 7.6, aryl-CH_2), 2.42–2.34 (m, CH_2), 2.30–2.25 (m, 2 × CH_2), 2.13–2.08 (m, CH_2) and 1.79–1.72 (m, CH_2); δ_C 180.3 (CO_2H), 158.1 (=*C*OMe), 138.5 (quat. C), 135.5 (quat. C), 131.2 (=CH), 129.0 (=CH), 127.9 (quat. C), 123.6 (=CH), 122.4 (=CH), 113.7 (=CH), 110.7 (=CH), 55.1 (OCH_3), 33.2 (CH_2), 32.7 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 28.9 (CH_2), 24.3 (CH_2) and 23.0 (CH_2); *m/z* 300.1728 (M^+, $C_{19}H_{24}O_3$ requires M^+, 300.1725).

The (E)-Se-*phenyl selenoate* **57** was prepared according to the general procedure as a yellow oil (82%); ν_{max}/cm^{-1} (film) 3001, 2931, 2833, 1723, *1606*, *1568*, 1497, 1438, 1302, 1250, 1140, 1044, 969, 824, 755 and 690; δ_H 7.61–7.54 (m, 2 × aryl =CH), 7.45–7.40 (m, 3 × aryl =CH), 7.23 (d, *J* 9.2, aryl =CH), 6.81–6.76 (m, 2 × aryl =CH), 5.78 (t, *J* 4.5, =CH), 5.55–5.33 (m, CH=CH), 3.85 (s, OCH_3), 2.80–2.71 (m, Ar-CH_2 + $COCH_2$), 2.55 (t, *J* 7.5, =CCH_2), 2.33–2.23 (m, 2 × CH_2), 2.17–2.08 (m, CH_2) and 1.88–1.75 (m, CH_2); δ_C 200.1 (CO), 158.1 (quat. C), 138.5 (quat. C), 135.7 (2 × aryl =CH), 135.4 (quat. C), 131.4 (=CH), 129.2 (2 × aryl =CH), 128.8 (=CH), 128.7 (=CH), 127.9 (quat. C), 126.5 (quat. C), 123.6 (=CH), 122.4 (=CH), 113.7 (=CH), 110.7 (=CH), 55.1 (OCH_3), 46.7 (CH_2), 32.7 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 28.9 (CH_2), 24.9 (CH_2) and 23.0 (CH_2); *m/z* 440.1255 (M^+. $C_{25}H_{28}O_2{}^{80}Se$ requires M^+, 440.1255).

Reductive cyclisation of the (*E*)-*Se*-phenyl selenoate 57. Cyclisation of the title ester **57** according to the general procedure, led to a 55:45 mixture of two diastereoisomeric tetracyclic ketones (53%). Careful chromatography over silica gel (light petroleum–ether, 50:1), as for the products from the cyclisation of **52**, again gave: (a) the *trans,anti,trans*-isomer of the tetracyclic ketone **53**, as an oil which crystallised with time, mp 146–150 °C, and: (b) mixed fractions enriched in the minor diastereoisomer. The spectroscopic data for both the diastereoisomeric mixtures, and for the two samples of **53** formed separately from the *Z*- and *E*-esters, **52** and **57** respectively, were identical in all respects.

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