Acyl Radical Cyclizations in Synthesis. Part 5.[1] Further Tandem Processes: Formation of an α-Methylenecyclohexanone by a Cyclization–Fragmentation Hydrogen-abstraction Sequence

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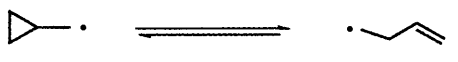
Two *Se*-phenyl 7-cyclopropyl(selenohept-6-enoate) esters were prepared and their reactions with tributylstannane and a free-radical initiator were studied. In both cases the initial acyl radical cyclization proceeded smoothly to give cyclopropylmethyl radicals which then suffered clean ring opening to homoallylic radicals. In the case of the initial substrate carrying a phenyl group at the 7-position a further radical rearrangement involving δ-hydrogen abstraction occurred to give, after chain transfer with the stannane, an α-alkylidenecyclohexanone.

In previous papers in this series we have described our development of acyl radical cyclizations as a means of entry into highly functionalized cyclohexanones and cycloheptanones.[1] We set out below the results of our investigation into the application of these acyl radical cyclizations into a multiple radical cyclization, fragmentation and, inadvertently, δ-hydrogen-abstraction sequence initiated with a view towards the preparation of medium-size rings.

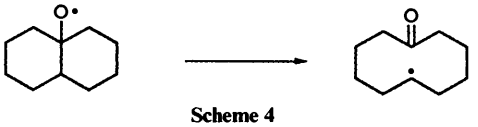
The concept underlying the present study was that the four known radical processes outlined in Schemes 1–4 could be

Scheme 1



Scheme 2

Scheme 3



Scheme 4

coupled in a cascade to provide an entry to cyclodecanones, from an acyclic precursor, by a multiple radical cyclization–fragmentation–cyclization–fragmentation sequence as summarized in Scheme 5. Each of the individual steps is well precedented. Hence we have demonstrated that 3,3-ethylenedioxyhept-6-enoyl radicals cyclize efficiently in the 6-*exo*-mode,[2] and the cyclopropylmethyl-to-but-3-enyl transposition is a prototypical radical rearrangement having first-order rate constants of $\sim 10^8$ and 10^4 s^{-1} for the forward and reverse reactions at 25 °C, respectively.[3,4] The kinetically favoured

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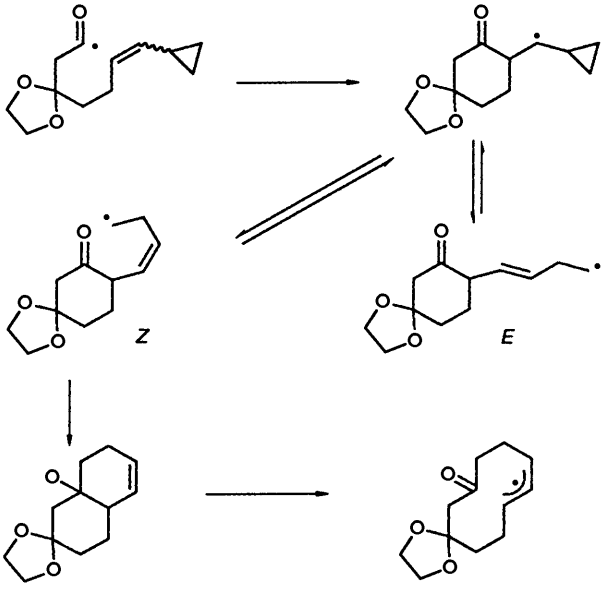
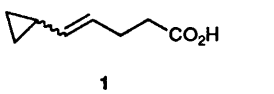


Scheme 5

cyclization of alkyl radicals onto aldehydes (Scheme 3, X = H) has been described and exploited by Fraser-Reid[5] and quantified by Beckwith.[6] Cyclization of alkyl radicals onto the carbonyl carbon of germyl esters (Scheme 3, X = $GePh_3$) and acyl silanes (Scheme 3, X = $SiMe_3$) has been established by Curran[7] and Tsai,[8] respectively, and the cyclization of alkyl radicals onto ketones (Scheme 3, X = alkyl) is a fundamental step in a number of radical ring expansions reported by several groups.[9] The fragmentation of decalin-9-oxyl radicals has been studied by Beckwith and others and shown to be both fast and reversible under appropriate conditions.[10,11]

We began our study with the preparation of the simple cyclopropyl-substituted selenoheptenoate **5**. Wittig olefination of cyclopropanecarbaldehyde with sodium 4-(triphenylphosphoranylidene)butanoate[12] gave compound **1** essentially quantitatively as a 3:1 *Z*:*E* mixture. Homologation of this mixture of geometric isomers to the β-keto ester **2** was achieved by the Masamune protocol, involving sequential reaction with carbonyl diimidazolide (CDI) and magnesium monoethylmalonate, in 91% yield. Ketalization with ethylene glycol and catalytic camphor-10-sulfonic acid in toluene with azeotropic removal of water gave compound **3** but only in 18% after 22 h. Considerable degradation was observed in the course of this reaction, presumably reflecting the instability of the

vinylcyclopropane moiety under these acidic conditions. We therefore turned to the Noyori protocol[13] of stirring the keto ester **2** with *O,O'*-bistrimethylsilyl ethylene glycol and a catalytic quantity of trimethylsilyl triflate in dichloromethane and were rewarded by a yield of 79% of the desired ketal **3**. Saponification gave the acid **4** and reaction with benzeneselenenyl chloride and tributylphosphine under our standard conditions[14] gave the cyclization precursor **5** in good overall yield. Dropwise addition of tributyltin hydride and a catalytic quantity of azoisobutyronitrile (AIBN) during 30 min to a solution of selenoester **5** in benzene at reflux resulted in the clean formation of the *E*-butenylcyclohexanone **6** in 95% isolated yield with no indication of the expected cyclodecenone. The vinyl group in compound **6** was assigned the pure *E*-configuration in the light of subsequent results (*vide infra*). Evidently, ring opening of the intermediate cyclopropylmethyl radical was occurring to give the *E*-homoallylic radical exclusively,* so blocking further evolution of the desired sequence.



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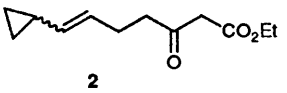

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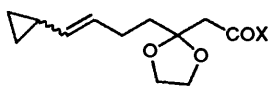
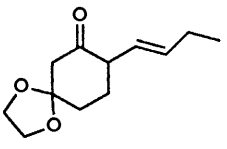
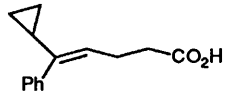


3 X = OEt
4 X = OH
5 X = SePh



6

We reasoned[15] that introduction of a bulky substituent at the 7-position of selenoester **5**, as in compound **11**, would direct opening of the intermediate cyclopropylmethyl radical towards the *Z* isomer of the homoallylic radical. The 7-cyclopropyl-7-phenyl selenoheptenoate **11** was prepared from cyclopropyl phenyl ketone in a manner exactly analogous to that described above for the formation of compound **5**, *via* the intermediates **7**–**10**. Interestingly, the trisubstituted alkene **7** was isolated as a 20:1 *Z*:*E* mixture with the configurational assignments based on the chemical shifts of the olefinic hydrogens. Reaction of compound **11** with tributyltin hydride under conditions identical with those described for compound **5** resulted in the formation of the two major products **12** and **13** in 56 and 30% yield, respectively, but once again no cyclodecenone was formed. The tetrasubstituted alkene **12** was a single geometric isomer but in the absence of conclusive nuclear Overhauser enhancement (NOE) data we are unable to assign the configuration conclusively. The stereochemistry of the triply substituted double bond in compound **13** was assigned on the basis of the chemical shift of the olefinic proton (δ 5.47).† This ensemble of products is best interpreted in terms of an approximate 2:1 partitioning of the homoallylic radical formed on cyclopropylmethyl ring opening between the *Z*- and *E*-isomers with the *Z* isomer evolving by intramolecular δ-hydrogen abstraction from C-2 to give a highly stabilized, delocalized radical which is ultimately quenched with high selectivity at its exocyclic terminus (Scheme 6).[17] In experiments in which tributyltin deuteride replaced the tin hydride the label was found in the δ-position of the side chain of compound **12**, in full support of this rationalization. These experiments with the selenoester **11** not only clearly define the flaw in our original plan, *viz* δ-hydrogen abstraction, but also set limits on what may be achieved by the type of ring expansion described by Baldwin, Beckwith and Dowd. Therefore, whilst the process outlined in Scheme 7 is a generally favourable one for four-



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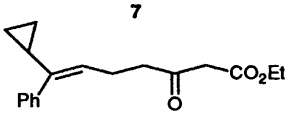

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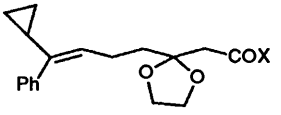
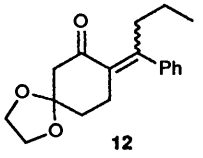


9 X = OEt
10 X = OH
11 X = SePh



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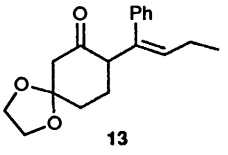

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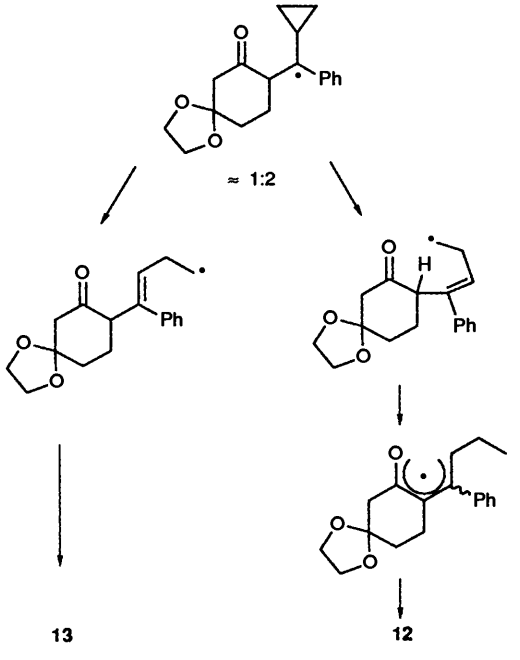
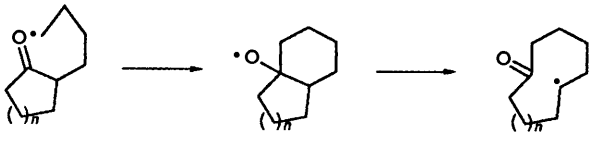
carbon-ring expansion,‡ any attempt to include unsaturation β,γ to the ketone as in Schemes 8 and 9 will lead to failure due to efficient δ-hydrogen abstraction.



Scheme 6



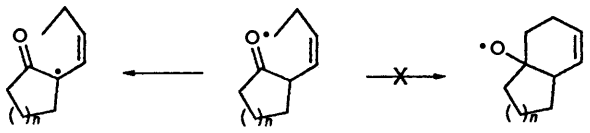
Scheme 7

In conclusion, although we have not achieved our primary aim of a multiple cyclization fragmentation sequence resulting in the formation of 10-membered rings we have very clearly

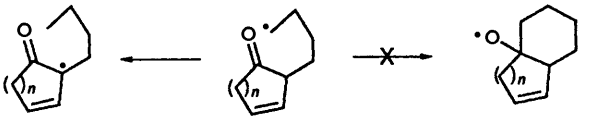
* To avoid possible confusion arising from changing of priorities on introduction of substituents we will refer, in the discussion, to ring-opened cyclopropylmethyl radicals as being *Z* or *E* where *Z* is that configuration required for cyclization onto the cyclohexanone carbonyl as indicated in Scheme 5.

† The calculated value for this substitution pattern is δ 5.47 and that for the geometric isomer δ 5.78.

‡ Very recently, Baldwin has noted δ-hydrogen abstraction as a minor competing pathway in this type of reaction.



Scheme 8



Scheme 9

identified the limitations in the four-carbon-radical ring-expansion process. We feel that these guidelines may prove useful to others planning tandem radical processes.

Experimental

General.—The general experimental conditions are as in Part 4.[1]

5-Cyclopropylpent-4-enoic Acid **1**.—Sodium hydride (80%; 600 mg, 20 mmol) was stirred in dimethyl sulfoxide (DMSO) (40 cm^3) under nitrogen for 40 min at 70 °C. After cooling of the mixture to room temperature, 3-carboxypropyl(triphenyl)-phosphonium bromide (4.29 g, 10 mmol) was added portion-wise and the mixture was stirred for 45 min at room temperature before a solution of cyclopropanecarbaldehyde (280 mg, 4 mmol) in DMSO (5 cm^3) was added. After being stirred for a further 2 h the reaction mixture was poured into a mixture of ether (200 cm^3) and water (200 cm^3) and was then acidified with dil. hydrochloric acid. The aqueous phase was further extracted with ether (2 × 50 cm^3) and the combined ether layers were washed successively with water (50 cm^3) and brine (50 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure. Purification of the resulting oil by chromatography on silica gel [eluent light petroleum–ether (1:1)] gave the title acid as an oil (555 mg, 99%) as an approximately 3:1 *Z*:*E* mixture with ν_{max}(film)/cm^{-1} 3083 and 1709; *m*/*z* 140 (M^+). Diagnostic features for the *Z*-isomer: δ_H(200 MHz) 0.35 (2 H, m), 0.70 (2 H, m), 1.55 (1 H, m), 2.45 (4 H, m), 4.81 (1 H, dd, $J_{4,5}$ 10.6, $J_{5,6}$ 9.8, 5-H) and 5.30 (1 H, dt, $J_{4,5}$ 10.6, $J_{3,4}$ 6.2, 4-H); δ_C(50 MHz) 6.82, 9.48, 22.97, 34.27, 125.42, 135.67 and 179.53. The *E*-isomer had δ_H(200 MHz) 5.05 (1 H, dd, $J_{4,5}$ 15.2, $J_{5,6}$ 8.2, 5-H) and 5.49 (1 H, dt, $J_{4,5}$ 15.2, $J_{3,4}$ 6.4, 4-H); δ_C(50 MHz) 6.36, 13.34, 27.44, 34.22, 125.42, 135.43 and 179.53.

Ethyl 7-Cyclopropyl-3-oxohept-6-enoate **2**.—To a stirred solution of the acid **1** (500 mg, 3.6 mmol) in dry tetrahydrofuran (THF) (40 cm^3) at room temperature under nitrogen was added carbonyl-1,1′-diimidazolide (723 mg, 4.5 mmol), and after the mixture had been stirred for 6 h the magnesium salt of ethyl hydrogen malonate (1.29 g, 4.5 mmol) was added. The reaction mixture was then stirred for a further 18 h at room temperature before the solvent was removed under reduced pressure. The residue was dissolved in ether (100 cm^3) and acidified with dil. hydrochloric acid (0.5 mol dm^{-3}; 50 cm^3), and the aqueous phase was extracted with ether (2 × 50 cm^3). The combined ether layers were washed with saturated aq. sodium hydrogen carbonate (60 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure to give an oil which, after chromatography on silica gel [eluent light petroleum–ether (5:1)], yielded the *title ester* as an oil (682 mg, 91%) as a 3:1 *Z*:*E* mixture with ν_{max}(film)/cm^{-1} 1745, 1716 and 1652 (Found: C, 67.9; H, 8.8. $C_{12}H_{18}O_3$ requires C, 68.55; H, 8.63%). The *Z*-isomer had δ_H(200 MHz) 0.35 (2 H, m), 0.70 (2 H, m), 1.28 (3 H, t), 1.55 (1 H, m, 8-H), 2.45 (2 H, m), 2.65 (2 H, m), 3.45 (2 H, s), 4.19 (2 H, q), 4.77 (1 H, dd, $J_{6,7}$ = $J_{7,8}$ = 10.1, 7-H) and 5.24 (1 H, m, 6-H). The distinguishing features of the *E*-isomer were δ_H(200 MHz) 1.65 (1 H, m, 8-H), 2.30 (2 H, m), 2.64 (2 H, m), 3.42 (2 H, s), 4.99 (1 H, dd, $J_{6,7}$ 15.2, $J_{7,8}$ 7.3, 7-H) and 5.46 (1 H, m).

Ethyl 7-Cyclopropyl-3,3-ethylenedioxyhept-6-enoate **3**.—To a stirred solution of trimethylsilyl triflate (1 mg, 0.05 mmol) in dichloromethane (1 cm^3) at −78 °C under nitrogen was added *O*,*O*′-bis(trimethylsilyl)ethyleneglycol[19] (196 mg, 0.95 mmol). After 2 min the β-keto ester **2** (100 mg, 0.48 mmol) was added and the reaction mixture was stirred for 2.5 h before gradually warming to room temperature, and was then stirred at that temperature for 18 h. Pyridine (0.1 cm^3) was then added and the reaction mixture was poured into saturated aq. sodium hydrogen (15 cm^3) and then extracted with ether (3 × 20 cm^3). The extracts were dried ($MgSO_4$) and, after removal of solvent under reduced pressure and chromatography on silica gel [eluent light petroleum–ether (3:1)], gave the *title ester* as an oil (95 mg, 79%) again as a 3:1 *Z*:*E* mixture, with ν_{max}(film)/cm^{-1} 1738 and 1653; *m*/*z* 254 (M^+) (Found: C, 65.9; H, 8.7. $C_{14}H_{22}O_4$ requires C, 66.12; H, 8.72%). The *Z*-isomer had δ_H(200 MHz) 0.28 (2 H, m), 0.64 (2 H, m), 1.24 (3 H, t), 1.51 (1 H, m), 1.85 (2 H, m), 1.91 (2 H, m), 2.65 (2 H, s), 3.99 (4 H, m), 4.14 (2 H, q), 4.72 (1 H, dd, $J_{6,7}$ = $J_{7,8}$ = 9.8, 7-H) and 5.28 (1 H, m, 6-H). The *E*-isomer was distinguished by δ_H(200 MHz) 2.62 (2 H, s), 4.97 (1 H, dd, $J_{6,7}$ 15.2, $J_{7,8}$ 8.4, 7-H) and 5.47 (1 H, dt, $J_{6,7}$ 15.2, $J_{5,6}$ 8.6, 6-H).

Se-Phenyl 7-Cyclopropyl-3,3-(ethylenedioxy)selenohept-6-enoate **5**.—The ester **3** (280 mg, 1.1 mmol) was stirred in methanol (25 cm^3) and treated with a solution of potassium hydroxide (310 mg) in water (5 cm^3). After being stirred for 18 h the reaction mixture was poured into a mixture of ether (150 cm^3) and water (150 cm^3) and was then acidified with hydrochloric acid (2 mol dm^{-3}; 5 cm^3). The aqueous layer was further extracted with ether (2 × 50 cm^3) and the combined ether layers were washed with brine (50 cm^3), dried ($MgSO_4$), evaporated, and filtered on silica gel [eluent light petroleum–ether (2:3)] to give the corresponding acid **4** (159 mg, 65%) as a 2:1 mixture of the *Z*:*E*-isomers with ν_{max}(film)/cm^{-1} 3082, 1722 and 1655; *m*/*z* 226.1194 (M^+, $C_{12}H_{18}O_4$ requires *M*, 226.1205). The *Z*-isomer was characterised by δ_H(200 MHz) 0.35 (2 H, m), 0.70 (2 H, m), 1.55 (1 H, m), 1.95 (2 H, m), 2.2 (2 H, m), 2.70 (2 H, s), 4.00 (4 H, m), 4.75 (1 H, dd, $J_{7,8}$ = $J_{6,7}$ = 10.1, 7-H) and 5.26 (1 H, m, 6-H). The distinguishing features of the *E*-isomer were δ_H(200 MHz) 0.65 (2 H, m), 1.35 (1 H, m), 2.65 (2 H, s), 4.97 (1 H, dd, $J_{7,8}$ 8.5, $J_{6,7}$ 15.3, 7-H) and 5.47 (1 H, dt, $J_{6,7}$ 15.3, $J_{5,6}$ 8.9, 6-H).

This acid (150 mg, 0.66 mmol) was stirred at room temperature in dichloromethane (10 cm^3) and treated with triethylamine (67 mg, 0.66 mmol). The solution was evaporated to dryness and the residue was taken up in THF (3 cm^3) and added to a stirred solution of benzeneselenyl chloride (190 mg, 1.0 mmol) and tributylphosphine (210 mg, 1.0 mmol) in THF (15 cm^3) under nitrogen at room temperature. After being stirred at room temperature for 2 h the reaction mixture was poured into a mixture of ether (100 cm^3) and water (50 cm^3) and the aqueous layer was separated and further extracted with ether (2 × 25 cm^3). The combined organic phases were washed successively with water (25 cm^3) and brine (25 cm^3), dried ($MgSO_4$), evaporated under reduced pressure, and the residue was purified by chromatography on silica gel [eluent light petroleum–ether (5:1)] to yield the *title selenoester* as an oil (162 mg, 67%) in the form of a 1.3:1 *Z*:*E* mixture of isomers with ν_{max}($CHCl_3$)/cm^{-1} 1711 (Found: C, 59.6; H, 5.8. $C_{18}H_{22}O_3Se$ requires C, 59.18; H, 6.07%). The *Z*-isomer had δ_H(200 MHz) 0.29 (2 H, m), 0.72 (2 H, m), 1.50 (1 H, m), 1.80 (2 H, m), 2.28 (2 H, m), 3.05 (2 H, s), 4.0 (4 H, m), 4.74 (1 H, dd,

$J_{6,7} = J_{7,8}$ = 10, 7-H), 5.28 (1 H, dt, $J_{5,6}$ 7.4, $J_{6,7}$ 10, 6-H), 7.37 (3 H, m) and 7.49 (2 H, m). The *E*-isomer had the following distinguishing features: δ_H(200 MHz) 0.30 (2 H, m), 0.65 (2 H, m), 1.30 (1 H, m), 1.80 (2 H, m), 2.1 (2 H, m), 3.02 (2 H, s), 4.98 (1 H, dd, $J_{6,7}$ 15.2, $J_{7,8}$ 8.4, 7-H) and 5.47 (1 H, dt, $J_{6,7}$ 15.2, $J_{5,6}$ 8.7, 6-H).

Reaction of Selenoester **5** *with Tributyltin Hydride: Formation of the Cyclohexanone* **6**.—To a solution of the selenoester **5** (75 mg, 0.21 mmol) at reflux in benzene (4.0 cm^3) under nitrogen was added a solution of tributyltin hydride (66 mg, 0.23 mmol) and AIBN (3 mg) in benzene (1.0 cm^3) during 30 min. The reaction mixture was maintained at reflux for a further 90 min, then was cooled to room temperature, and concentrated under reduced pressure, and the residue was purified by chromatography on silica gel [eluent light petroleum–ether (2:1)] to yield 2-[(*E*)-*but*-1-*enyl*]-5,5-*ethylenedioxycyclohexanone* **6** as an oil (41 mg, 95%) with δ_H(400 MHz) 0.96 (3 H, t, *J* 7.4, CH_2Me), 1.75 (1 H, m), 2.00 (5 H, m), 2.60 (2 H, m, 6-H_2), 2.95 (1 H, m, 2-H), 3.95 (4 H, m, OCH_2CH_2O) and 5.55 (2 H, m, CH=CH); δ_C(100 MHz) 13.55, 25.69, 27.40, 33.53, 33.65, 50.92, 52.30, 64.64, 64.74, 110.19, 125.42, 135.01 and 195.17; ν_{max}(film)/cm^{-1} 1717 and 1631; *m/z* 210.1269 (M^+, $C_{12}H_{18}O_3$ requires *M*, 210.1256).

5-*Cyclopropyl*-5-*phenylbut*-4-*enoic Acid* **7**.—The title acid was prepared in the same manner as acid **1** but cyclopropyl phenyl ketone was used instead of cyclopropanecarbaldehyde. *Compound* **7** was isolated in 97% yield as a crystalline solid in the form of a 20:1 *Z*:*E* mixture of isomers with m.p. 54 °C; ν_{max}($CHCl_3$)/cm^{-1} 3081 and 1710 (Found: C, 77.8; H, 7.5. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%). The *Z*-isomer had δ_H(400 MHz) 0.39 (2 H, m), 0.54 (2 H, m), 1.54 (1 H, m), 2.15 (2 H, dt, $J_{2,3} = J_{3,4}$ = 7.5, 3-H_2), 2.31 (2 H, t, $J_{2,3}$ 7.5, 2-H_2), 5.40 (1 H, t, $J_{3,4}$ 7.5, 4-H), 7.10 (2 H, m), 7.25 (1 H, m) and 7.27 (2 H, m); δ_C(50 MHz) 5.16, 18.39, 24.14, 34.21, 122.78, 126.73, 127.99 and 128.67. In the ^1H NMR spectrum the *E*-isomer was distinguished by δ_H(400 MHz) 2.50 (t, 2-H_2), 2.70 (dt, 3-H_2) and 5.65 (t, 4-H).

Ethyl 7-*Cyclopropyl*-3-*oxo*-7-*phenylhept*-6-*enoate* **8**.—Homologation of acid **7** (400 mg, 1.8 mmol) as described for the formation of ester **2** above gave the β-keto ester **8** as an oil (412 mg, 78%) as a 20:1 *Z*:*E* mixture of isomers with ν_{max}(film)/cm^{-1} 1745 and 1722. The *Z*-isomer had δ_H(200 MHz) 0.35 (2 H, m), 0.60 (2 H, m), 1.25 (3 H, t), 1.55 (1 H, m), 2.16 (2 H, dt, 5-H_2), 2.51 (2 H, t, 4-H_2), 3.33 (2 H, s, 2-H_2), 4.16 (2 H, q), 5.38 (1 H, t, *J* 6.7, 6-H), 7.1 (2 H, m) and 7.25 (3 H, m); δ_C(50 MHz) 5.19, 14.07, 18.43, 23.18, 41.72, 43.24, 49.25, 61.41, 123.06, 126.79, 128.06, 128.72, 143.79, 166.54 and 210.64. The *E*-isomer had its olefinic-proton resonance at δ_H(200 MHz) 5.55.

Ethyl 7-*Cyclopropyl*-3,3-*ethylenedioxy*-7-*phenylhept*-6-*enoate* **9**.—Repetition of the ketalization method for the formation of ketal **3** on the ketone **8** (100 mg, 0.35 mmol) gave the *title ketal* as an oil (58 mg, 51%) and recovered substrate (33 mg, 33%). The *ketal* **9** was an approximately 4:1 *Z*:*E* mixture of isomers with ν_{max}(film)/cm^{-1} 1736 and 1645 (Found: C, 72.7; H, 8.0. $C_{20}H_{26}O_4$ requires C, 72.70; H, 7.93%). The *Z*-isomer had δ_H 0.35 (2 H, m), 0.55 (2 H, m), 1.24 (3 H, t), 1.50 (1 H, m), 1.80 (2 H, m), 2.00 (2 H, m), 2.52 (2 H, s, 2-H_2), 3.85 (4 H, m), 4.12 (2 H, q), 5.40 (1 H, t, *J* 7.9, 6-H), 7.10 (2 H, m) and 7.25 (3 H, m). The *E*-isomer was distinguished by δ_H(200 MHz) 2.69 (s, 2-H_2) and 5.66 (t, *J* 6.7, 6-H).

Se-*Phenyl* 7-*Cyclopropyl*-3,3-*ethylenedioxy*-7-*phenyl*(*selenohept*-6-*enoate*) **11**.—The ketal **9** (210 mg, 0.63 mmol) was saponified as described for the formation of acid **4** from ester **3** to give the corresponding acid **10** as an oily (149 mg, 78%) 4:1 *Z*:*E* mixture with ν_{max}/cm^{-1} 3081 and 1711. The *Z*-isomer had δ_H(200 MHz) 0.40 (2 H, m), 0.60 (2 H, m), 1.55 (1 H, m), 1.75 (2 H, m, 5-H_2), 1.95 (2 H, m, 4-H_2), 2.52 (2 H, s, 2-H_2), 3.85 (4 H, m), 5.34 (1 H, t, *J* 6.7, 6-H) and 7.2 (5 H, m). The *E*-isomer had δ_H(200 MHz) 2.62 (s, 2-H_2) and 5.61 (t, *J* 7, 6-H).

This acid was converted into the selenoester **11** in 61% yield essentially as for the formation of compound **5** above. Compound **11** was an oily 4:1 *Z*:*E* mixture with ν_{max}($CHCl_3$)/cm^{-1} 1712; *m/z* 314 [M^+(^{80}Se) − $COCH_2C(OCH_2CH_2O)CH_2$]. The *Z*-isomer had δ_H(200 MHz) 0.39 (2 H, m), 0.59 (2 H, m), 1.50 (1 H, m), 1.75 (2 H, m, 5-H_2), 1.95 (2 H, m, 4-H_2), 2.90 (2 H, s, 2-H_2), 3.90 (4 H, m), 5.38 (1 H, t, *J* 6.7, 6-H) and 7.06–7.57 (10 H, m). The *E*-isomer was distinguished by δ_H 3.07 (s, 2-H_2) and 5.63 (t, *J* 6.8, 6-H).

Reaction of Selenoester **11** *with Tributyltin Hydride: Formation of Cyclohexanones* **12** *and* **13**.—To a stirred solution of the selenoester **11** (66 mg, 0.15 mmol) in benzene (2.9 cm^3) under nitrogen at reflux was added a solution of tributyltin hydride (66 mg, 0.23 mmol) and AIBN (2 mg) in benzene (0.7 cm^3). Reflux was continued for a further 2 h before the reaction mixture was allowed to cool to room temperature and was then evaporated to dryness under reduced pressure. Chromatography on silica gel then gave the α-*alkylidenecyclohexanone* **12** as an oil (24 mg, 56%) with δ_H(200 MHz) 0.85 (3 H, t, *J* 7.2, Me), 1.30 (2 H, m, CH_2Me), 1.82 (2 H, t, $J_{3,4}$ 6.5, 4-H_2), 2.35 (2 H, t, $J_{3,4}$ 6.5, 3-H_2), 2.52 (2 H, dd, $J_{8,9}$ 7.9 and 5.7, 8-H_2), 2.75 (2 H, s, 6-H_2), 3.95 (4 H, m, OCH_2CH_2O), 7.10 (2 H, m) and 7.3 (3 H, m); δ_C(50 MHz) 13.94, 21.76, 26.57, 34.81, 37.50, 53.13, 64.70, 127.24, 127.86 and 128.34; ν_{max}($CHCl_3$)/cm^{-1} 1723 and 1687; *m/z* 286.1573 (M^+, $C_{18}H_{22}O_3$ requires *M*, 286.1569). Further elution with the same solvent gave 5,5-*ethylenedioxy*-2-(1-*phenylbut*-1-*enyl*)*cyclohexanone* **13**, also as an oil (13 mg, 30%), with δ_H(200 MHz) 0.92 (3 H, t, *J* 7.5, Me), 1.95 (6 H, m, 3- and 4-H_2 and CH_2Me), 2.60 (1 H, d, J_{gem} 14, 6-H), 2.65 (1 H, d, J_{gem} 14, 6-H), 3.25 (1 H, t, $J_{2,3}$ 7.2, 2-H), 3.95 (4 H, m), 5.47 (1 H, t, *J* 6.2, =C*H*CH_2) and 7.12–7.36 (5 H, m); δ_C(100 MHz) 14.35, 22.44, 25.90, 33.85, 51.45, 57.52, 64.63, 64.72, 110.14, 126.62, 127.98, 128.96, 132.80, 137.11, 140.33 and 206.55; ν_{max}($CHCl_3$)/cm^{-1} 1714 and 1640; *m/z* 286.1584 (M^+). This major component contained approximately 10% of its geometrical isomer which was distinguished by δ_H(200 MHz) 5.75 (t, *J* 6.5).

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