Sulfur-mediated Intramolecular Double Michael-Type Reaction: Synthesis of *trans*-Hydroindanes and Mechanism

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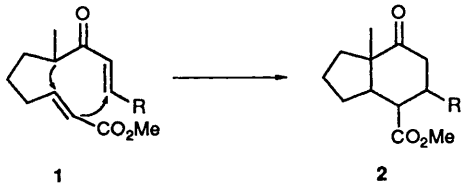
A sulfur-mediated intramolecular double Michael-type reaction stereoselectively producing *trans*-hydroindanes was developed. ε-Caprolactone **3** was transformed into four [(*E*,*E*), (*E*,*Z*), (*Z*,*E*) and (*Z*,*Z*)] isomers of methyl 7-methyl-8-oxo-10-(phenylthio)deca-2,9-dienoate (**14**, **16**, **18** and **19**). Treatment of these four isomers, **14**, **16**, **18** and **19**, respectively, with *tert*-butyldimethylsilyl trifluoromethanesulfonate in the presence of triethylamine gave the *trans*-hydroindane **20** as the main product together, with a small amount of the *cis*-isomer **22**. The annulation was accelerated by the presence of an electron-donating group on the phenylthio group. Substrates **8**, **34**, **36** and **37**, having hydrogen, isopropyl, trimethylsilyl and phenylsulfinyl instead of the sulfenyl group at the 10-position, provided no cyclised product under the same reaction conditions.

Since the *trans*-hydroindane moiety possessing a methyl group at an angular position is a part of the framework of steroids and various terpenoids, several new methods for its synthesis have recently appeared. The focal point of these investigations has been to generate the crucial *trans* relationship of the vicinal bridgehead carbons by utilizing different approaches such as intramolecular Diels–Alder reaction,[1] intramolecular Michael reaction,[2] conjugate addition-trapping sequence,[3] and intramolecular ene reaction.[4] Although the intramolecular Diels–Alder reaction[5] is one of the most effective methods, the preferred formation of *cis*-hydroindanes has been frequently observed with this approach.[6] We now report that the sulfur-mediated intramolecular double Michael-type reaction provides an effective method for the construction of *trans*-hydroindanes.[7]

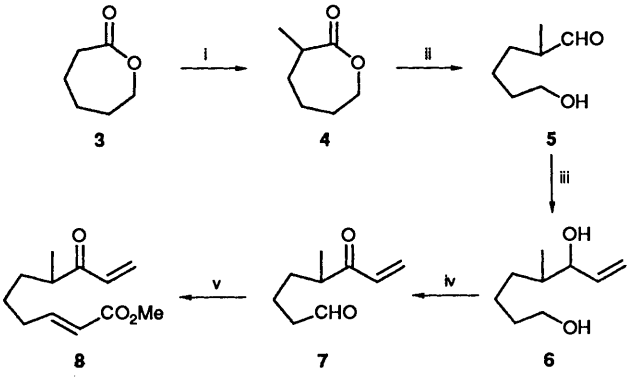
As an extension of our recent studies using the intramolecular double Michael reaction,[8] the assembly of hydroindanones **2** by the sequential conjugate addition of the α,β-unsaturated ketones **1** (Scheme 1) was investigated. First, we examined



1 **2**

Scheme 1

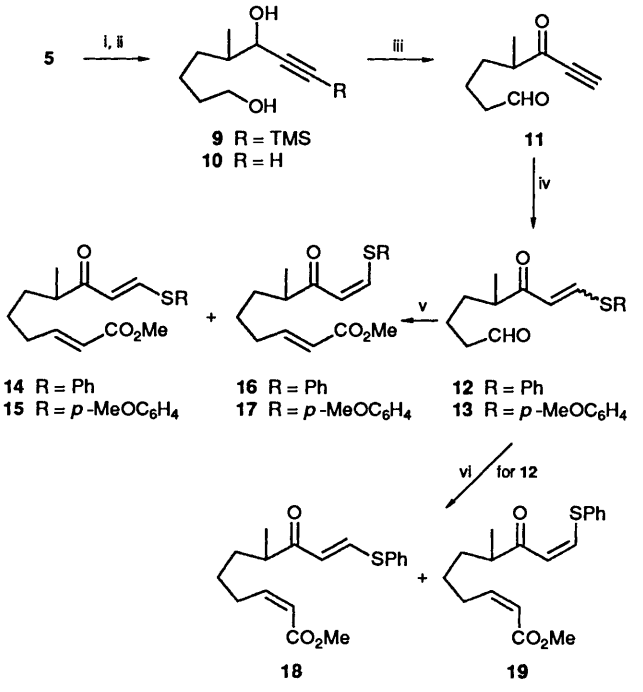
the intramolecular double Michael reaction of the enone ester **8** having no substituent at the β-position of the enone part. The substrate **8** of the key step was prepared starting from ε-caprolactone **3** (Scheme 2). Methylation of compound **3** was carried out under the conditions reported by Murai and co-workers.[9] Thus, reaction of caprolactone **3** with methyl iodide in the presence of lithium hexamethyldisilazide (LHMDS)† and hexamethylphosphoric triamide (HMPA) in tetrahydrofuran (THF) at −78 °C gave the methylated compound **4** in 55% yield. Reduction of compound **4** with diisobutylaluminium hydride (DIBAH) in a mixture of methylene dichloride and 1,2-dimethoxyethane (DME) at −78 °C provided the aldehyde **5**, which was treated with vinylmagnesium bromide in THF at 0 °C. Acidic work-up of the product afforded the allylic alcohols **6** as a mixture of two diastereoisomers in 69% overall yield from lactone **4**. Oxidation of diol **6** was successfully carried out using the Dess–Martin triacetoxyperiodinane (TAPI)[10] in methylene dichloride. Wittig reaction of the crude keto aldehyde **7** with the stable ylide methyl triphenylphosphoranylideneacetate provided exclusively the (*E*)-α,β-unsaturated ester **8** in 21% overall yield from diol **6**. Double Michael reaction of compound **8** was attempted under two different conditions, heating with trimethylsilyl chloride (TMSCl), zinc chloride and triethylamine at 160 °C[11] or treatment with *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) in the presence of triethylamine,[12] but no hydroindanone derivative was formed. Treatment of compound **8** with a lithium amide such as LHMDS[13] was not examined, since the conjugate addition of the amide to the vinyl ketone group was a possible side-reaction.[14] It had thus been made clear that the vinyl ketone function was too labile under the reaction conditions.



Scheme 2 *Reagents:* i, LHMDS, HMPA, MeI; ii, DIBAH; iii, CH_2=CHMgBr; iv, TAPI; v, Ph_3P=$CHCO_2Me$

† The following abbreviations have been used throughout for reagents and solvents: lithium hexamethyldisilazide (LHMDS), hexamethylphosphoric triamide (HMPA), tetrahydrofuran (THF), diisobutylaluminium hydride (DIBAH), 1,2-dimethoxyethane (DME), triacetoxyperiodinane (TAPI), trimethylsilyl chloride (TMSCl), *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), tetrabutylammonium fluoride (TBAF), potassium hexamethyldisilazide (KHMDS), lithium diisopropylamide (LDA) and trimethylsilyl trifluoromethanesulfonate (TMSOTf).

It was expected that the introduction of a sulfenyl group at the β-position of the vinyl ketone would increase the stability and assist the functional group interconversion of the cyclised product. The transformation of enone **8** into the β-phenylthio enones **14** and **16** *via* the Michael addition of thiophenol, followed by Pummerer-type reaction, failed. Therefore, the above lactone **4** was first converted into the acetylenic ketone **11** (Scheme 3) as follows. The aldehyde **5**, derived from **4**, was



Scheme 3 *Reagents:* i, ≡–TMS, BuLi, TMEDA; ii, TBAF; iii, TAPI; iv, PhSH or *p*-$MeOC_6H_4SH$, Et_3N; v, $Ph_3P{=}CHCO_2Me$; vi, $(CF_3CH_2O)_2P(O)CH_2CO_2Me$, KHMDS, 18-crown-6

treated with trimethylsilylacetylene in the presence of butyllithium and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) at −78 °C to afford a mixture of epimeric alcohols **9** in 88% yield. Removal of the trimethylsilyl group of compounds **9** using tetrabutylammonium fluoride (TBAF), followed by oxidation of diol **10**, obtained in 95% yield, with TAPI[10] provided the keto aldehyde **11**, which was treated with thiophenol in the presence of a catalytic amount of triethylamine at ambient temperature. The 1:2 mixture of (*E*)- and (*Z*)-olefin **12** formed was further treated with the stable ylide to provide a 1:2 mixture of the (*E,E*)- and (*E,Z*)-ester **14** and **16** in 41% overall yield from diols **10**. When the mixture of esters **14** and **16** was treated with iodine at ambient temperature for 43 h in carbon tetrachloride, the ratio of isomers **14**:**16** changed to 2:1. Two isomers **14** and **16** were separable using high-performance liquid chromatography (HPLC).

The corresponding (*Z*)-α,β-unsaturated esters **18** and **19** were preferentially produced by Still's procedure.[15] Thus, reaction of the aldehyde **12** with methyl bis-(2,2,2-trifluoroethoxy)phosphonylacetate in the presence of potassium hexamethyldisilazide (KHMDS) and 18-crown-6 afforded, in 68% overall yield from diol **10**, a 1:2:12:24 mixture of isomers **14**, **16**, **18** and **19**, which was separable by HPLC.

Neither treatment of the 1:2 mixture of phenylthio esters **14** and **16** with lithium diisopropylamide (LDA) or LHMDS,[13] nor heating with TMSCl, zinc chloride and triethylamine[12] provided the desired hydroindane derivative. When the 1:2 mixture of isomers **14** and **16** was treated with TBDMSOTf in the presence of triethylamine in methylene dichloride for 45 min at ambient temperature, the *trans*-hydroinane **20**, m.p. 78–80 °C, was obtained in 48% yield after recrystallisation from hexane (Scheme 4). Treatment of each of the four isomers **14**, **16**, **18** and **19** under the same reaction conditions produced the same product **20** in 56, 62, 62 and 47% yield, respectively. The 500 MHz ^{1}H NMR spectra of the products prior to the purification by recrystallisation revealed the concomitant formation of the *cis*-isomer **22** as a minor product. It was determined on the basis of 500 MHz ^{1}H NMR spectroscopy that the ratio of the two isomers **20** and **22**, formed by the reactions of isomers **14**, **16**, **18** and **19**, was uniformly ~5:1. The stereostructure of the major product was assigned as the *trans*-hydroindane **20** possessing an equatorially oriented methoxycarbonyl group and an axially oriented sulfenyl group on the basis of ^{1}H NMR analysis. Thus, a 13.7% nuclear Overhauser effect (NOE) was observed between the angular methyl group and the hydrogen at the 4-position. Furthermore, the hydrogen at the 4-position, resonating at δ 2.96, was coupled with the hydrogens at the 3a- and 5-position with coupling constants *J* 11.8 and 5.0 Hz, respectively.

Treatment of the 5:1 mixture of indanes **20** and **22** with 10% perchloric acid in THF gave the *trans*-isomer **24** in 76% yield and the *cis* one **26** in 17% yield after purification utilizing flash chromatography. The stereostructure of the *trans*-isomer **24**, m.p. 79.5–80 °C was confirmed by X-ray crystallography (see Fig. 1 and Tables 1 and 2). The sulfenyl group of both

Table 1 Crystal data for compound **24**

Formula	$C_{18}H_{22}O_3S$
M	318.43
Crystal system	monoclonic
Space group	$P2_1/c$
Unit-cell parameters	
a	8.376(2) Å
b	18.205(3) Å
c	11.134(1) Å
β	92.78(1)°
V	1695.8(5) Å^3
Z	4
D_c	1.247 g cm^{-3}
μ(Mo-Kα)	1.909 cm^{-1}
Total unique reflections	4033
Used reflections	2643 ($>3\sigma\|F_0\|$)
R	0.088
R_w	0.131

Table 2 Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for compound **24**

	x/a	*y/b*	*z/c*
S	6237(3)	1616(1)	5164(2)
O(1)	9890(8)	2674(4)	4039(6)
O(2)	3943(7)	2974(4)	6646(6)
O(3)	5006(7)	2118(4)	7902(5)
C(1)	8569(13)	4106(5)	4553(8)
C(2)	7231(14)	4588(5)	5002(10)
C(3)	6359(12)	4136(5)	5928(9)
C(4)	6985(10)	3352(4)	5779(7)
C(5)	6804(9)	2769(4)	6750(7)
C(6)	7557(10)	2033(4)	6351(7)
C(7)	9264(10)	2129(5)	5913(8)
C(8)	9386(9)	2762(5)	5036(7)
C(9)	8760(10)	3491(4)	5470(7)
C(10)	9808(11)	3757(5)	6552(8)
C(11)	5068(10)	2648(5)	7069(7)
C(12)	6837(10)	678(4)	5348(7)
C(13)	6409(11)	283(5)	6332(8)
C(14)	6850(12)	−443(5)	6447(7)
C(15)	7682(13)	−758(5)	5564(11)
C(16)	8112(13)	−379(5)	4568(9)
C(17)	7691(11)	345(5)	4466(8)
C(18)	3422(13)	1924(7)	8291(10)

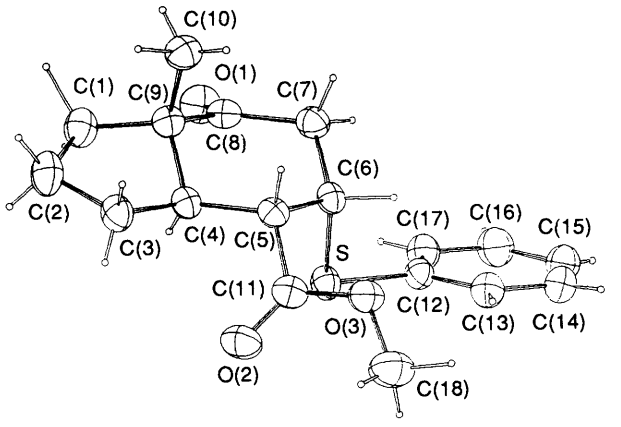
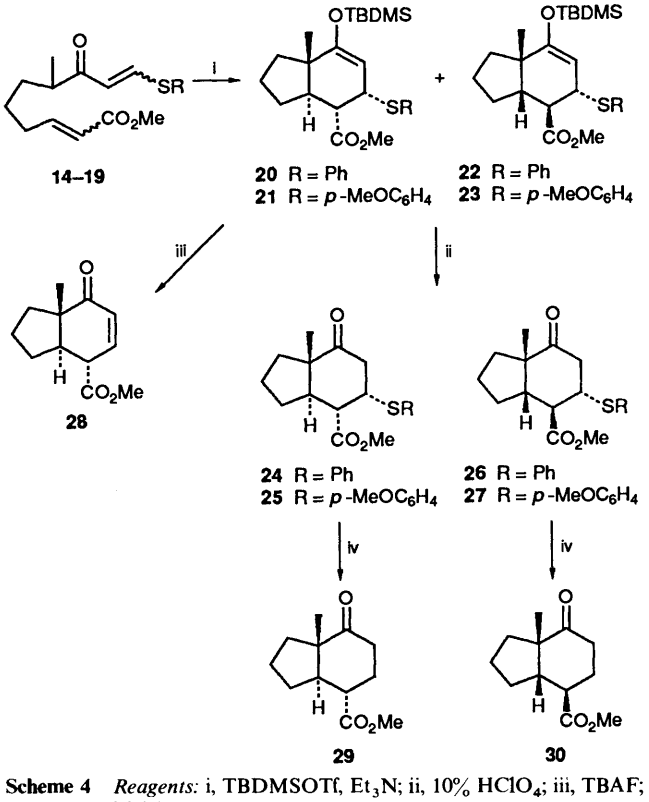


Fig. 1 X-Ray molecular structure for compound **24**

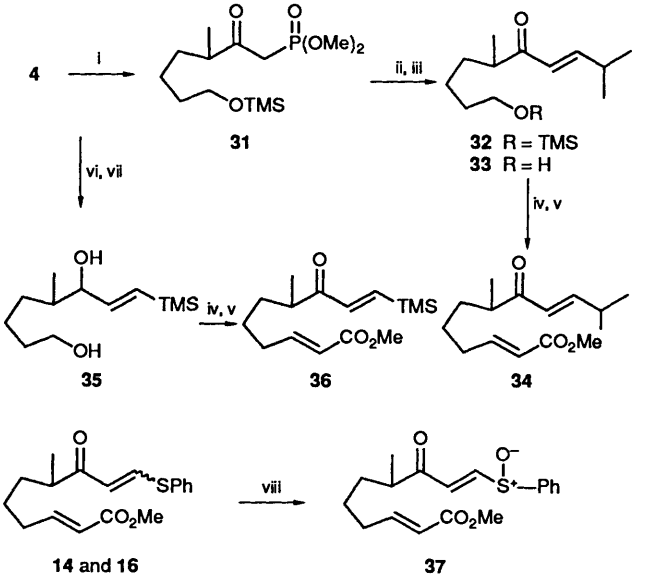


Scheme 4 *Reagents*: i, TBDMSOTf, Et_3N; ii, 10% $HClO_4$; iii, TBAF; iv, Raney Ni(W-2)

compounds **24** and **26** was removed by treatment with Raney nickel (W-2) to give different keto esters **29** and **30** in 63 and 95% yield. The *cis* ring juncture of compound **30** was determined by the 7.2% NOE between the angular methyl group and the angular hydrogen. The relative configuration of the four contiguous stereogenic centres of the *cis*-isomer was deduced on the basis of ^1H NMR analysis of its progenitor **26**. It is interesting that the reaction of the 1:2 mixture of esters **14** and **16** with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in the presence of triethylamine in methylene dichloride at ambient temperature for 15 min, followed by treatment of the crude product with 10% perchloric acid, produced a 52:35 mixture of the *trans* and *cis* isomers **24** and **26** in 87% yield although the reason for the difference in proportions due to the reagents is obscure at present.

Direct formation of the enone **28** was attained in 46% yield by treatment of the *trans*-isomer **20** with TBAF. Thus a novel approach to polyfunctionalised *trans*-hydroindanes was developed. The formation of the same products **20** and **22** in the same ratio from the four isomers **14**, **16**, **18** and **19** indicates a stepwise process for the annulation. In order to test the effect of the sulfenyl group, introduction of an electron-donating group into the phenylsulfenyl group was next investigated. Michael addition of 4-methoxy(thiophenol) to the acetylenic ketone **11**, followed by Wittig reaction of the intermediate **13** with the stable ylide methyl triphenylphosphoranylideneacetate provided a 2:3 mixture of the (*E*,*E*)- and the (*E*,*Z*)-unsaturated esters **15** and **17**, separable by HPLC. We observed a faster formation of the cyclised products **21** and **23** compared with the annulation without the electron-donating group. Hence, treatment of compound **15** with TBDMSOTf in the presence of triethylamine at ambient temperature for 35 min furnished a 5:1 mixture of hydroindanes **21** and **23** in 79% yield, while the same treatment of compound **17** gave the same mixture of products **21** and **23** in 81% yield. The reaction proceeded even at −10 °C in a more stereoselective manner. Namely, a 7:1 mixture of the *trans* and *cis* isomers **21** and **23** was obtained in 75% yield by the reaction of the 2:3 mixture of enones **15** and **17** with the same reagents at −10 °C for 2 h. Removal of the *tert*-butyldimethylsilyl group from the products **21** and **23** by using 10% perchloric acid provided the readily separable ketones **25** and **27** in good yield. ^1H NMR spectra of both products **25** and **27** were similar to those of the previous compounds **24** and **27**, respectively. Desulfenylation of this compound **25** with Raney nickel (W-2) gave the *trans*-ketone **29** in 71% yield, whereas compound **27** was converted into *cis* compound **30** in 99% yield. The products **29** and **30** were identical with the above specimens obtained from substrates **24** and **26**. It was thus clear that the annulation was accelerated by the resonance effect of the methoxy group on the phenylsulfenyl substituent.

The importance of the sulfenyl group in the annulation reaction was further demonstrated by the failure of attempted cyclisation of several substrates which did not possess a sulfenyl group. The enone **34**, having an isopropyl group at the β-position, was prepared from the above lactone **4** (Scheme 5).



Scheme 5 *Reagents*: i, $MeP(O)(OMe)_2$, BuLi; then LDA, TMSCl; ii, NaH; Pr^iCHO; iii, TBAF; iv, TAPI; v, $Ph_3P{=}CHCO_2Me$; vi, DIBAH; vii, (*E*)-TMSCH=CHSnBu_3, BuLi; viii, $NaIO_4$

Reaction of compound **4** with dimethyl methylphosphonate in the presence of butyllithium, followed by treatment *in situ* with TMSCl in the presence of LDA,[16] afforded the phosphonate **31** in 75% yield. The phosphonate **31** was condensed with isobutyraldehyde in the presence of sodium hydride to form the enone **32** in 82% yield. The trimethylsilyl group of compound **32** was quantitatively removed by the action of TBAF. Oxidation of

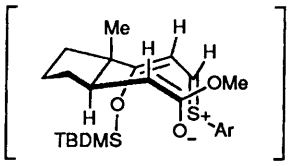


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Fig. 2

the resulting alcohol **33** with TAPI,[10] followed by Wittig reaction using the stable ylide (Ph_3P=$CHCO_2Me$) provided the (*E*,*E*)-α,β-unsaturated ester **34** in 79% overall yield from compound **33**.

The enone **36**, possessing a trimethylsilyl group at the β-position, was also synthesized from the lactone **4**. After reduction of compound **4** to the aldehyde **5**, reaction of the latter with the stannylethene $TMSCH$=$CHSnBu_3$[17] in the presence of butyllithium afforded an epimeric mixture of diols **35** in 47% yield. Transformation of compound **35** into the (*E*,*E*)-unsaturated ester **36** was carried out in 82% overall yield in two steps, oxidation using TAPI[10] followed by Wittig reaction.

Oxidation of the 1:2 mixture of compounds **14** and **16** with sodium periodate in aq. methanol produced only the (*E*,*E*)-sulfoxides **37** as a mixture of two diastereoisomers in 30% yield. Treatment of the three different enone esters **34**, **36** and **37** with TBDMSOTf in the presence of triethylamine provided no cyclised product. Thus the association of the sulfenyl group with the annulation has been established. It was assumed that the *trans*-substituted cyclopentane derivative was preferentially formed under kinetic control[2] or thermodynamic control by the first intramolecular Michael addition. The second cyclisation would proceed *via* the zwitterionic intermediate **38** (Fig. 2), in which the oppositely charged groups are close enough to each other to produce the *trans*-hydroindanes **20** and **21** as the major products. It is clear that the sulfur-mediated intramolecular double Michael-type reaction is a useful route to angularly methylated *trans*-hydroindanes.

Experimental

General Methods.—M.p.s were determined on a Yanako micromelting point apparatus and are uncorrected. IR spectra were recorded on a JASCO-IR-Report-100 spectrophotometer, with the sample prepared as a neat film or in chloroform solution. The assignable absorptions are reported. ^1H NMR spectra were recorded on the following instruments: JEOL JNP-PMX-60 (60 MHz), Hitachi R-1200 (60 MHz), JEOL JNM-FX-90A (90 MHz) and JEOL GX-500 (500 MHz). Chemical shifts are measured relative to tetramethylsilane (δ 0), using either $SiMe_4$ or the solvent as internal reference. All *J*-values are given in Hz and only characteristic signals are recorded. The ratio of products was determined by integrations in the 500 MHz NMR spectra. Mass spectra were recorded on either a JEOL-DX-300 or a JEOL-DX-303 instrument. Ordinary chromatography was performed on Merck Kieselgel 60 Art 7734, while flash chromatography was carried out using Merck Kieselgel 60 Art 9385. HPLC was carried out with a Gilson HPLC system Model 302/303 and monitored by UV absorption and refractive-index measurements. All reactions except hydrogenation were carried out under N_2 or Ar atmosphere. Solvents were freshly distilled prior to use: THF, Et_2O, DME, benzene, and HMPA were distilled from sodium–benzophenone, CH_2Cl_2 was distilled from P_2O_5. All extracts were dried over $MgSO_4$ unless otherwise stated, and solvents were removed on a rotary evaporator at 30–40 °C. Oily NaH was washed with dry hexane three times prior to use. All new compounds described in this Experimental section were homogeneous on TLC and HPLC.

2-*Methylhexan*-6-*olide* **4**.—To a stirred solution of LHMDS in THF (1 mol dm^{-3}; 10.5 cm^3, 10.5 mmol) in dry THF (5.0 cm^3) at −78 °C was slowly added a solution of ε-caprolactone **3** (1.00 g, 8.77 mmol) in dry THF (3.0 cm^3) and the mixture was stirred for 50 min at the same temperature. After addition of HMPA (1.6 cm^3, 9.2 mmol), the mixture was stirred for 10 min at the same temperature, and to the resulting mixture was slowly added a solution of MeI (0.7 cm^3, 11.2 mmol) in dry THF (2.0 cm^3). After being stirred for 20 min at the same temperature, the reaction mixture was poured into 10% aq. $KHSO_4$ and thoroughly extracted with Et_2O. The extract was washed successively with 2% aq. $Na_2S_2O_3$ and brine, dried and evaporated under reduced pressure. The residue was purified by silica gel chromatography with hexane–AcOEt (7:3 v/v) as the eluent to afford the methyl compound **4** (622 mg, 55%) as an oil; ν_{max}(neat)/cm^{-1} 1729 (C=O); δ_H(500 MHz; $CDCl_3$) 1.21 (3 H, d, *J* 6.5, 2-Me), 2.72 (1 H, ddq, *J* 18.0, 6.5 and 1.5, 2-H), and 4.19–4.32 (2 H, m, 6-H_2); *m*/*z* 128 (M^+).

Methyl (E)-7-*Methyl*-8-*oxodeca*-2,9-*dienoate* **8**.—To a stirred solution of the lactone **4** (1.47 g, 11.5 mmol) in a mixture of CH_2Cl_2 (15.0 cm^3) and DME (15.0 cm^3) at −78 °C was slowly added a mixture of DIBAH in hexane (1 mol dm^{-3}; 12.6 cm^3, 12.6 mmol), and the mixture was stirred for 10 min at the same temperature. After addition of Et_2O (20.0 cm^3) and water (12.0 cm^3) at 0 °C, the resulting mixture was stirred for 30 min at room temperature and then filtered through Celite. The filtrate was dried, and evaporated under reduced pressure to give the aldehyde **5** as a pale yellowish oil; ν_{max}(neat)/cm^{-1} 3410 (OH) and 1724 (C=O); δ_H(60 MHz; $CDCl_3$) 1.18 (3 H, d, *J* 8.0, Me) and 9.60 (1 H, d, *J* 2.0, CHO), which was used in the following reaction without purification.

To a stirred solution of the crude aldehyde **5** in dry THF (30.0 cm^3) at 0 °C was slowly added a solution of vinylmagnesium bromide in THF (1 mol dm^{-3}; 35.0 cm^3, 35.0 mmol), and the mixture was stirred for 2.5 h at room temperature. The mixture was poured into cold, saturated aq. NH_4Cl and thoroughly extracted with $CHCl_3$. The extract was washed with brine, dried and evaporated to dryness under reduced pressure. Chromatography on silica gel with benzene–acetone (4:1 v/v) as the eluent yielded an epimeric mixture of diols **6** (1.26 g, 69%) as an oil; ν_{max}(neat)/cm^{-1} 3380 (OH) and 1642 (C=C); δ_H(90 MHz; $CDCl_3$) 0.90 (3 H, d, *J* 6.3, Me), 2.08 (2 H, br s, 2 × OH), 3.26–3.73 (2 H, m, CH_2OH), 3.83–4.21 (1 H, m, CHOH), 5.02–5.33 (2 H, m, CH=CH_2) and 5.87 (1 H, ddd, *J* 17.1, 9.0 and 5.9, C*H*=CH_2).

To a stirred solution of TAPI[10] (7.02 g, 16.6 mmol) in dry CH_2Cl_2 (50.0 cm^3) at room temperature was added a solution of the diols **6** (688 mg, 4.36 mmol) in dry CH_2Cl_2 (20.0 cm^3), and the mixture was stirred for 30 min at the same temperature. After addition of pentane–Et_2O (1:1 v/v), the resulting mixture was poured into a (1:7 v/v) mixture of saturated aq. $NaHCO_3$ and 2% aq. $Na_2S_2O_3$, and thoroughly extracted with Et_2O. The extract was washed successively with saturated aq. $NaHCO_3$ and brine, dried and evaporated under reduced pressure to afford the keto aldehyde **7** as an oil; ν_{max}(neat)/cm^{-1} 1721 (CH=O), 1695 and 1674 (C=O) and 1609 (C=C); δ_H(60 MHz; $CDCl_3$) 1.05 (3 H, d, *J* 5.8, Me), 3.17–3.77 (2 H, m, CH_2CHO), 3.93–4.15 (1 H, m, C*H*Me) and 9.70 (1 H, m, CHO), which was used in the next reaction without purification.

A mixture of the crude aldehyde **7** and methyl triphenylphosphoranylideneacetate (1.23 g, 3.69 mmol) in dry CH_2Cl_2 (25.0 cm^3) was stirred for 11 h at room temperature. Evaporation of the solvent under reduced pressure gave a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (17:3 v/v) afforded the *enone* **8** (196 mg, 21% overall yield from the diol **6**) as an oil; ν_{max}(neat)/cm^{-1} 1721 (C=O), 1696, 1674 and 1655 (C=O and C=C) and 1610

(C=C); δ_H(500 MHz; $CDCl_3$) 1.11 (3 H, d, *J* 6.2, 7-Me), 2.14–2.26 (2 H, m, 4-H_2), 2.81 (1 H, tq, *J* 6.3 and 6.2, 7-H), 3.72 (3 H, s, OMe), 5.78 (1 H, dd, *J* 10.4 and 1.6, 10-H), 5.82 (1 H, dt, *J* 2.0 and 15.6, 2-H), 6.27 (1 H, dd, *J* 17.6 and 1.6, 10-H), 6.43 (1 H, dd, *J* 17.6 and 10.4, 9-H) and 6.93 (1 H, dt, *J* 7.5 and 15.6, 3-H); *m/z* 210 (M^+) (Found: M^+, 210.1256. $C_{12}H_{18}O_3$ requires *M*, 210.1255).

5-*Methyl*-8-(*trimethylsilyl*)*oct*-7-*yne*-1,6-*diols* **9**.—The lactone **4** (401 mg, 3.12 mmol) was reduced with DIBAH in hexane (0.99 mol dm^{-3}; 3.16 cm^3, 3.13 mmol) as above to the aldehyde **5**. To a stirred solution of trimethylsilylacetylene (1.10 cm^3, 7.78 mmol) and TMEDA (0.94 cm^3, 6.23 mmol) in dry THF (6.0 cm^3) at −78 °C was added BuLi in hexane (1.56 mol dm^{-3}; 4.00 cm^3, 6.24 mmol), and the mixture was stirred for 30 min at the same temperature. To the resulting solution was slowly added a solution of the above aldehyde **5** in dry THF (2.0 cm^3), and the mixture was stirred for 30 min at −78 °C and then for 30 min at room temperature. The resulting mixture was poured into cold, 10% aq. $KHSO_4$ and thoroughly extracted with Et_2O. The extract was washed with brine, dried and evaporated under reduced pressure. Chromatography on silica gel with hexane–AcOEt (3:2 v/v) as the eluent gave an epimeric mixture of the *diols* **9** (631 mg, 88%) as an oil (Found: C, 63.25; H, 10.5. $C_{12}H_{24}O_2Si$ requires C, 63.1; H, 10.6%); ν_{max}(neat)/cm^{-1} 3370 (OH), 2170 (C≡C) and 1250 (C–Si); δ_H(500 MHz; $CDCl_3$) 0.16 (9 H, s, $SiMe_3$), 0.98 and 0.99 [3 H (1:1), each d, each *J* 6.3, 5-Me], 3.66 (2 H, t, *J* 5.1, 1-H_2) and 4.23 and 4.24 [1 H (1:1), each d, *J* 5.4, 6-H]; *m/z* 195 ($M^+ - H_2O$ – Me).

5-*Methyloct*-7-*yne*-1,6-*diols* **10**.—To a stirred solution of the diols **9** (218 mg, 0.954 mmol) in dry THF (4.0 cm^3) at 0 °C was added TBAF in THF (1 mol dm^{-3}; 1.43 cm^3, 1.43 mmol), and the mixture was stirred for 20 min at the same temperature. The reaction mixture was poured into 10% aq. $KHSO_4$ and thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried and evaporated under reduced pressure to afford a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (1:4 v/v) gave the *alcohols* **10** (141 mg, 95%) as an oil (Found: C, 69.05; H, 10.4. $C_9H_{16}O_2$ requires C, 69.2; H, 10.3%); ν_{max}(neat)/cm^{-1} 3400–3550 (OH and ≡C–H), 3295 (OH) and 2108 (C≡C); δ_H(500 MHz; $CDCl_3$) 1.01 and 1.02 [3 H (1:1), each d, each *J* 5.4, 5-Me], 2.46 (0.5 H, d, *J* 2.0, 8-H), 2.47 (0.5 H, d, *J* 2.0, 8-H), 3.67 (2 H, t, *J* 6.4, 1-H_2) and 4.24–4.34 (1 H, m, 6-H).

Methyl (2E,9E)- **14** *and* (2E,9Z)-7-*Methyl*-8-*oxo*-10-(*phenylthio*)*deca*-2,9-*dienoate* **16**.—The epimeric mixture of alcohols **10** (151 mg, 0.965 mmol) was oxidised using TAPI[10] (1.56 g, 3.67 mmol) as above to afford the keto aldehyde **11** as an oil; ν_{max}(neat)/cm^{-1} 3250 (≡C–H), 2092 (C≡C) and 1721 and 1678 (C=O); δ_H(90 MHz; $CDCl_3$) 1.19 (3 H, d, *J* 8.2, Me), 3.25 (1 H, s, ≡CH) and 9.73 (1 H, t, *J* 0.9, CHO), which was subjected to the next reaction without purification.

A mixture of a catalytic amount of Et_3N and thiophenol (0.109 cm^3, 1.06 mmol) in dry benzene (5.5 cm^3) was stirred for 15 min at room temperature, before the slow addition of a solution of the above keto aldehyde **11** in dry benzene (2.5 cm^3) at 5 °C. The resulting mixture was stirred for 2 h at the same temperature. After dilution with benzene, the mixture was washed successively with saturated aq. $NaHCO_3$ and brine, dried and evaporated under reduced pressure to provide a 1:2 mixture of the crude sulfides **12** as an oil; ν_{max}(neat)/cm^{-1} 1720 and 1658 (C=O) and 1531 (C=C); δ_H(90 MHz; $CDCl_3$) 0.98 and 1.08 [3 H (1:2), each d, each *J* 9.0, Me], 6.04 (0.33 H, d, *J* 15.2, 1-H), 6.32 (0.67 H, d, *J* 9.5, 1-H), 6.99–7.52 (5.67 H, m, 5 × ArH and 1-H), 7.33 (0.33 H, d, *J* 15.2, 1-H) and 9.63 (1 H, m, CHO), which was used in the next reaction without purification.

The above products **12** were treated for 15 h with methyl triphenylphosphoranylideneacetate (312 mg, 0.933 mmol) in dry CH_2Cl_2 (10.0 cm^3) as above and the product was purified by flash chromatography on silica gel. Elution with hexane–Et_2O (4:1 v/v) gave a 1:2 mixture of the α,β-unsaturated esters **14** and **16** (125 mg, 41% from **10**) as an oil. Separation of two isomers was carried out by HPLC on Si 80-199-C5 (10 × 250 mm) with hexane–AcOEt (17:3 v/v; 4.0 cm^3 min^{-1}) as the eluent to give the (E,E)-*enone* **14** as an oil; ν_{max}(neat)/cm^{-1} 1716 (C=O) and 1671 and 1650 (C=O and C=C); δ_H(90 MHz; $CDCl_3$) 1.06 (3 H, d, *J* 7.3, 7-Me), 2.02–2.31 (2 H, m, 4-H_2), 2.43–2.71 (1 H, m, 7-H), 3.72 (3 H, s, OMe), 5.81 (1 H, dt, *J* 14.4 and 1.1, 2-H), 6.13 (1 H, d, *J* 16.0, 9-H), 6.93 (1 H, dt, *J* 14.4 and 7.6, 3-H), 7.35–7.52 (5 H, m, 5 × ArH) and 7.80 (1 H, d, *J* 16.0, 10-H); *m/z* 318 (M^+) (Found: M^+, 318.1286. $C_{18}H_{22}O_3S$ requires *M*, 318.1288).

The second eluate afforded the (E,Z)-*enone* **16** as an oil; ν_{max}(neat)/cm^{-1} 1716 (C=O) and 1653 (C=O and C=C); δ_H 1.15 (3 H, d, *J* 7.3, 7-Me), 2.05–2.35 (2 H, m, 4-H_2), 2.41–2.73 (1 H, m, 7-H), 3.72 (3 H, s, OMe), 5.81 (1 H, dt, *J* 14.4 and 1.1, 2-H), 6.40 (1 H, d, *J* 9.8, 9-H), 6.93 (1 H, dt, *J* 14.4 and 7.6, 3-H), 7.31 (1 H, d, *J* 9.8, 10-H) and 7.34–7.51 (5 H, m, 5 × ArH); *m/z* 318 (M^+) (Found: M^+, 318.1286).

Isomerisation of the (E)- *and* (Z)-*Isomer* **14** *and* **16**.—The 1:2 mixture of the (*E*)- and (*Z*)-isomer **14** and **16** (88 mg) and a catalytic amount of I_2 in CCl_4 (5.0 cm^3) was set aside for 43 h at room temperature under protection from light. After dilution with CH_2Cl_2, the mixture was washed successively with 2% $Na_2S_2O_3$ and brine, dried and evaporated to dryness under reduced pressure. Purification by flash chromatography on silica gel with hexane–Et_2O (4:1 v/v) as the eluent gave a 2:1 mixture of compounds **14** and **16** (69 mg, 79%) as an oil.

Methyl (2Z,9E)- **18** *and* (2Z,9Z)-7-*Methyl*-8-*oxo*-10-(*phenylthio*)*deca*-2,9-*dienoate* **19**.—Oxidation of the diols **10** (91 mg, 0.58 mmol) with TAPI[10] (864 mg, 2.03 mmol), followed by treatment of the keto aldehyde **11** with thiophenol (0.06 cm^3, 0.58 mmol) in the presence of a catalytic amount of Et_3N as above, gave the sulfides **12**, which were used in the following reaction without purification.

To a stirred solution of methyl bis-(2,2,2-trifluoroethoxy)-phosphonylacetate (0.136 cm^3, 0.643 mmol) and 18-crown-6 (655 mg, 2.48 mmol) in dry THF (7.0 cm^3) at −78 °C was added a mixture of KHMDS in toluene (0.5 mol dm^{-3}; 1.09 cm^3, 0.545 mmol), and the reaction mixture was stirred for 30 min at the same temperature. After slow addition of the solution of the crude sulfides in dry THF (3.0 cm^3) at the same temperature, the mixture was stirred for 30 min. The mixture was poured into cold, saturated aq. NH_4Cl and thoroughly extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to give a residue, which was purified by flash chromatography on silica gel. Elution with hexane–AcOEt (9:1 v/v) yielded a (1:2:12:24) mixture of four isomers **14**, **16**, **18** and **19** (125 mg, 68% from **10**) as an oil.

Separation of isomers was carried out by HPLC on Si 80-199-C5 (10 × 250 mm) with hexane–AcOEt (9:1 v/v; 4.0 cm^3 min^{-1}) as the eluent to give the (Z,E)-*enone* **18** as an oil; ν_{max}(neat)/cm^{-1} 1719 (C=O) and 1677 and 1650 (C=O, C=C); δ_H(500 MHz; $CDCl_3$) 1.06 (3 H, d, *J* 6.7, 7-Me), 3.70 (3 H, s, OMe), 5.78 (1 H, dt, *J* 11.6 and 1.8, 2-H), 6.14 (1 H, d, *J* 14.7, 9-H), 6.18 (1 H, dt, *J* 11.6 and 8.0, 3-H), 7.39–7.44 (3 H, m, 3 × ArH), 7.47–7.50 (2 H, m, 2 × ArH) and 7.80 (1 H, d, *J* 14.7, 10-H); *m/z* 318 (M^+) (Found: M^+, 318.1255. $C_{18}H_{22}O_3S$ requires *M*, 318.1288).

The second eluate provided the (Z,Z)-*enone* **19** as an oil;

ν_{max}(neat)/cm^{-1} 1719 (C=O) and 1611 (C=C); δ_H(500 MHz; $CDCl_3$) 1.16 (3 H, d, *J* 7.0, 7-Me), 3.71 (3 H, s, OMe), 5.79 (1 H, dt, *J* 11.7 and 1.9, 2-H), 6.22 (1 H, dt, *J* 11.7 and 7.2, 3-H), 6.42 (1 H, d, *J* 9.8, 9-H), 7.30 (1 H, d, *J* 9.8, 10-H), 7.33–7.42 (3 H, m, 3 × ArH) and 7.47–7.52 (2 H, m, 2 × ArH); *m/z* 318 (M^+) (Found: M^+, 318.1290).

The third and fourth eluates afforded the (*E,E*)- **14** and the (*E,Z*)-enone **16**.

Methyl (±)-(3aR*,4S*,5S*,7aS*)-7-(tert-*Butyldimethylsilyoxy*)-3a,4,5,7a-*tetrahydro*-7a-*methyl*-5-*phenylthioindane*-4-*carboxylate* **20**.—*Method A*. To a stirred solution of the 1:2 mixture of (*E,E*)- **14** and (*Z,E*)-enone **16** (35 mg, 0.11 mmol) and Et_3N (0.125 cm^3, 0.897 mmol) in dry CH_2Cl_2 (3.0 cm^3) at room temperature was added TBDMSOTf (0.125 cm^3, 0.544 mmol), and the mixture was stirred for 45 min at the same temperature. After dilution with CH_2Cl_2, the resulting mixture was washed successively with saturated aq. $NaHCO_3$ and brine, and dried. Evaporation of the solvent under reduced pressure gave a residue, which was subjected to flash chromatography on silica gel. Elution with hexane–AcOEt (99:1 v/v) yielded a 5:1 mixture of silyl enol ethers **20** and **22** as a solid, recrystallisation of which from hexane provided the trans-*isomer* **20** (23 mg, 48%) as needles, m.p. 78–80 °C (Found: C, 66.65; H, 8.6; S, 7.3%; M^+, 432.2155. $C_{24}H_{36}O_3SSi$ requires C, 66.65; H, 8.4; S, 7.4%; *M*, 432.2152); ν_{max}($CHCl_3$)/cm^{-1} 1747 (C=O) and 1639 (C=C); δ_H(500 MHz; $CDCl_3$) 0.14 and 0.16 (6 H, each s, $SiMe_2$), 0.90 (3 H, s, 7a-Me), 0.92 (9 H, s, SiBu^t), 2.96 (1 H, dd, *J* 11.8 and 5.0, 4-H), 3.18 (3 H, s, OMe), 4.37 (1 H, dd, *J* 5.0 and 5.0, 5-H), 4.68 (1 H, d, *J* 5.0, 6-H), 7.17–7.20 (1 H, m, ArH), 7.24–7.28 (2 H, m, 2 × ArH) and 7.40–7.44 (2 H, m, 2 × ArH); *m/z* 432 (M^+).

Method B. The (*E,E*)-enone **14** (8.0 mg, 0.087 mmol) was transformed, using Et_3N (0.03 cm^3, 0.22 mmol) and TBDMSOTf (0.03 cm^3, 0.13 mmol) as above, into the indane **20** (6.4 mg, 56%), which was identical with the above sample in all respects.

Method C. The (*Z,E*)-enone **16** (17.6 mg, 0.0553 mmol) was transformed, using Et_3N (0.06 cm^3, 0.44 mmol) and TBDMSOTf (0.06 cm^3, 0.26 mmol) as above, into compound **20** (14.9 mg, 62%), which was identical with the above sample in all respects.

Method D. The (*E,Z*)-enone **18** (21.4 mg, 0.0673 mmol) was transformed, using Et_3N (0.08 cm^3, 0.57 mmol) and TBDMSOTf (0.08 cm^3, 0.35 mmol) as above, into compound **20** (18.0 mg, 62%), which was identical with the above specimen in all respects.

Method E. The (*Z,Z*)-enone **19** (11.2 mg, 0.035 mmol) was converted, using Et_3N (0.04 cm^3, 0.29 mmol) and TBDMSOTf (0.04 cm^3, 0.18 mmol) as above, into compound **20** (7.2 mg, 47%), which was identical with the above specimen in all respects.

Methyl (±)-(3aR*,4S*,5S*,7aS*)- **24** *and* (±)-(3aR*,4S*,-5R*,7aR*)-3a,4,5,6,7,7a-*Hexahydro*-7a-*methyl*-7-*oxo*-5-*phenylthioindane*-4-*carboxylate* **26**.—*Method A*. To a solution of the 5:1 mixture of silyl enol ethers **20** and **22** (36 mg, 0.083 mmol) in THF (2.0 cm^3) at 0 °C was added 10% aq. $HClO_4$ (2.0 cm^3), and the mixture was stirred for 1 h at room temperature and then was thoroughly extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $NaHCO_3$ and brine, dried and evaporated to dryness under reduced pressure. Flash chromatography on silica gel with hexane–AcOEt (9:1 v/v) as eluent afforded the cis-*isomer* **26** (4.6 mg, 17%) as an oil; ν_{max}(neat)/cm^{-1} 1733 and 1704 (C=O); δ_H(500 MHz; $CDCl_3$) 1.09 (3 H, s, 7a-Me), 2.46 (1 H, dd, *J* 15.3 and 12.8, 6α-H), 2.47 (1 H, dd, *J* 12.8 and 12.8, 4-H), 2.70 (1 H, dd, *J* 15.3 and 4.4, 6β-H), 3.43 (1 H, ddd, *J* 12.8, 12.8, and 4.4, 5-H), 3.76 (3 H, s, OMe) and 7.31–7.50 (5 H, m, 5 × ArH); *m/z* 318 (M^+) (Found: M^+, 318.1290. $C_{18}H_{22}O_3S$ requires *M*, 318.1288).

Further elution with hexane–AcOEt (17:3 v/v) yielded a solid, recrystallisation of which from hexane–Et_2O provided the trans-*isomer* **24** (20.0 mg, 76%) as needles, m.p. 79.5–80 °C (Found: C, 67.65; H, 6.9, S, 10.0. $C_{18}H_{22}O_3S$ requires C, 67.9; H, 6.95; S, 10.05%); ν_{max}($CHCl_3$)/cm^{-1} 1737 and 1711 (C=O); δ_H(500 MHz; $CDCl_3$) 1.04 (3 H, s, 7a-Me), 2.53 (1 H, dd, *J* 14.8 and 1.9, 6α-H), 3.02 (1 H, dd, *J* 14.8 and 5.2, 6β-H), 3.18 (1 H, dd, *J* 11.3 and 4.0, 4-H), 3.66 (3 H, s, OMe), 4.07 (1 H, ddd, *J* 5.2, 4.0, and 1.9, 5-H), 7.25–7.33 (3 H, m, 3 × ArH) and 7.39–7.44 (2 H, m, 2 × Ar); *m/z* 318 (M^+).

Method B. To a stirred solution of the 1:2 mixture of compounds **14** and **16** (39.1 mg, 0.123 mmol) and Et_3N (0.12 cm^3, 0.86 mmol) in dry CH_2Cl_2 (4.0 cm^3) at room temperature was added TMSOTf (0.12 cm^3, 0.62 mmol), and the mixture was stirred for 15 min at room temperature. After dilution with CH_2Cl_2, the mixture was washed successively with saturated aq. $NaHCO_3$ and brine, dried and evaporated under reduced pressure to give a residue, which was dissolved in THF (1.5 cm^3). After addition of 10% aq. $HClO_4$ (1.5 cm^3), the mixture was stirred for 30 min at 0 °C. The same work-up, followed by purification as above, gave the *cis*-isomer **26** (11.8 mg, 35%) and the *trans*-isomer **24** (17.7 mg, 52%), which were identical with the above samples in all respects, respectively.

Methyl (±)-(3aR*,4S*,7aS*)-3a,4,7,7a-Tetrahydro-7a-*methyl*-7-*oxoindane*-4-*carboxylate* **28**.—To a stirred solution of the *trans*-indane **20** (14.4 mg, 0.0333 mmol) in THF (2.0 cm^3) at 0 °C was slowly added TBAF in THF (1 mol dm^{-3}; 0.07 cm^3, 0.07 mmol), and the mixture was stirred for 5 min at the same temperature. The mixture was poured into 10% aq. $KHSO_4$ and thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried and evaporated under reduced pressure to give a residue, which was subjected to flash chromatography on silica gel. Elution with hexane–AcOEt (9:1 v/v) yielded the *enone* **28** (3.2 mg, 46%) as a pale yellowish oil; ν_{max}(neat)/cm^{-1} 1734 (C=O) and 1684 (C=O); δ_H(500 MHz; $CDCl_3$) 0.99 (3 H, s, 7a-Me), 3.09–3.33 (1 H, m, 4-H), 3.76 (3 H, s, OMe), 5.99 (1 H, dd, *J* 9.8 and 2.9, 5-H) and 6.82 (1 H, dd, *J* 9.8 and 1.8, 6-H); *m/z* 208 (M^+) (Found: M^+, 208.1099. $C_{12}H_{16}O_3$ requires *M*, 208.1099).

Methyl (2E,9E)- **15** *and* (2E,9Z)-10-(4-*Methoxyphenylthio*)-7-*methyl*-8-*oxodeca*-2,9-*dienoate* **17**.—The epimeric mixture of alcohols **10** (184 mg, 1.18 mmol) was oxidised using TAPI[10] (1.75 g, 4.13 mmol) as above to give the keto aldehyde **11**, which was treated with 4-methoxy(thiophenyl) (0.1 cm^3, 0.81 mmol) as above to yield an (*E*)- and (*Z*)-mixture of sulfides **13** as an oil; ν_{max}(neat)/cm^{-1} 1730 and 1664 (C=O) and 1599 (C=C); δ_H(60 MHz; CCl_4) 1.06 [3 H (2:3), each d, each *J* 6.6, Me], 3.84 (3 H, s, OMe), 6.04 [0.4 H, d, *J* 15.0, (*E*)-C*H*=CHS], 6.45 [0.6 H, d, *J* 9.6, (*Z*)-C*H*=CHS], 6.71–7.58 [4.6 H, m, 4 × ArH and (*Z*)-CH=C*H*S] and 7.92 [0.4 H, d, *J* 15.0, (*E*)-CH=C*H*S], which was used in the following reaction without purification.

The above products **13** were treated for 15 h with methyl triphenylphosphoranylideneacetate (233 mg, 0.70 mmol) as above. Flash chromatography on silica gel with hexane–AcOEt (9:1 v/v) as eluent gave a 2:3 mixture of enones **15** and **17** (128 mg, 31% from **10**) as an oil. Separation of the two isomers was carried out by HPLC on Si 80-199-C5 (10 × 250 mm) with hexane–AcOEt (9:1 v/v; 4.0 cm^3 min^{-1}) as eluent to provide the (E,E)-*enone* **15** as an oil (Found: C, 65.35; H, 7.05, S, 9.1. $C_{19}H_{24}O_4S$ requires C, 65.5; H, 6.95; S, 9.2%); ν_{max}(neat)/cm^{-1} 1721 (C=O) and 1672 and 1651 (C=O and C=C); δ_H(500 MHz; $CDCl_3$) 1.04 (3 H, d, *J* 6.7, 7-Me), 2.14–2.19 (2 H, m, 4-H_2), 2.56 (1 H, tq, *J* 6.7 and 6.7, 7-H), 3.72 (3 H, s, CO_2Me), 3.85 (3 H, s, OMe), 5.80 (1 H, dt, *J* 15.9 and 1.9, 2-H), 5.96 (1 H, d, *J* 15.3,

9-H), 6.92–6.98 (3 H, m, 2 × ArH and 3-H), 7.39–7.43 (2 H, m, 2 × ArH) and 7.74 (1 H, d, *J* 15.3, 10-H); *m/z* 348 (M^+).

The second eluate afforded the (Z,E)-*enone* **17** as an oil; ν_{max}(neat)/cm^{-1} 1720 (C=O) and 1658 (C=O); δ_H(500 MHz; $CDCl_3$) 1.15 (3 H, d, *J* 7.3, 7-Me), 2.18–2.24 (2 H, m, 4-H_2), 2.60 (1 H, tq, *J* 7.3 and 6.7, 7-H), 3.72 (3 H, s, CO_2Me), 3.82 (3 H, s, OMe), 5.82 (1 H, dt, *J* 15.3 and 1.9, 2-H), 6.34 (1 H, d, *J* 9.2, 9-H), 6.89–6.92 (2 H, m, 2 × ArH), 6.95 (1 H, dt, *J* 15.3 and 7.3, 3-H), 7.22 (1 H, d, *J* 9.2, 10-H) and 7.41–7.44 (2 H, m, 2 × ArH); *m/z* 348 (M^+) (Found: M^+, 348.1379. $C_{19}H_{24}O_4S$ requires *M*, 348.1395).

Methyl (±)-(3aR*,4S*,5S*,7aS*)- **21** *and* (±)-(3aR*,4S*,5R*,7aR*)-7-(tert-*Butyldimethylsiloxy*)-3a,4,5,7a-*tetrahydro*-5-(4-*methoxyphenylthio*)-7a-*methylindane*-4-*carboxylate* **23**.—*Method A*. To a stirred solution of the (*E,E*)-enone **15** (20.7 mg, 0.06 mmol) and Et_3N (0.07 cm^3, 0.50 mmol) in dry CH_2Cl_2 (2.0 cm^3) at room temperature was added TBDMSOTf (0.07 cm^3, 0.31 mmol), and the mixture was stirred for 35 min at the same temperature. The mixture was poured into saturated aq. $NaHCO_3$ and thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. Flash chromatography on silica gel with hexane–AcOEt (98:2 v/v) as eluent provided a 5:1 mixture of the *tetrahydroindanes* **21** and **23** (21.6 mg, 79%) as a pale yellowish oil; ν_{max}(neat)/cm^{-1} 1735–1730 (C=O) and 1637–1635 (C=C); δ_H(500 MHz; $CDCl_3$) 0.13 and 0.14 [3 H (5:1), each s, SiMe], 0.15 and 0.19 [3 H (5:1), each s, SiMe], 0.87 and 1.05 [3 H (5:1), each s, 7a-Me], 0.89 and 0.91 [9 H (1:5), each s, SiBu^t], 2.28 (0.17 H, dd, *J* 12.0 and 11.0, 4-H), 2.93 (0.83 H, dd, *J* 11.6 and 4.9, 4-H), 3.34 and 3.70 [3 H (5:1), each s, CO_2Me], 3.78 and 3.80 [3 H (5:1), each s, OMe], 4.18 (0.83 H, dd, *J* 5.5 and 5.5, 5-H), 4.63 (0.83 H, d, *J* 4.9, 6-H), 4.68 (0.17 H, d, *J* 1.8, 6-H), 6.79–6.81 and 6.82–6.85 [2 H (5:1), each m, 2 × ArH] and 7.35–7.39 and 7.41–7.44 [2 H (5:1), each s, 2 × ArH]; *m/z* 462 (M^+), 323 ($M^+ - C_7H_7SO$) (Found: $M^+ - C_7H_7SO$, 323.2086. $C_{18}H_{31}O_3Si$ requires *m/z* 323.2042).

Method B. Treatment of the (*E,Z*)-enone **17** (10.0 mg, 0.029 mmol) with TBDMSOTf (0.03 cm^3, 0.13 mmol) in the presence of Et_3N (0.03 cm^3, 0.22 mmol) in dry CH_2Cl_2 (1.0 cm^3) as above gave a 5:1 mixture of tetrahydroindanes **21** and **23** (10.7 mg, 81%), which was identical with the above products in all respects.

Method C. Reaction of the 2:3 isomeric mixture of **15** and **17** (9.0 mg, 0.026 mmol) with TBDMSOTf (0.03 cm^3, 0.13 mmol) in the presence of Et_3N (0.03 cm^3, 0.22 mmol) in dry CH_2Cl_2 (1.0 cm^3) for 2 h at −10 °C, followed by the same work-up as above, provided a 7:1 mixture of tetrahydroindanes **21** and **23** (9.0 mg, 75%), whose ratio was determined by its 500 MHz ^{1}H NMR spectrum.

Methyl (±)-3aR*,4S*,5S*,7aS*)- **25** *and* (±)-(3aR*,4S*,5R*,7aR*)-3a,4,5,6,7,7a-*Hexahydro*-5-(4-*methoxyphenylthio*)-7a-*methyl*-7-*oxoindane*-4-*carboxylate* **27**.—The 5:1 isomeric mixture of silyl ethers **21** and **23** (14.0 mg, 0.03 mmol) was treated with 10% aq. $HClO_4$ (1.5 cm^3) in THF (1.5 cm^3) for 35 min at 0 °C as above. Flash chromatography of the raw product with hexane–AcOEt (85:15 v/v) as eluent yielded the *cis-indanone* **27** (1.7 mg, 16%) as a pale yellowish oil; ν_{max}(neat)/cm^{-1} 1735 and 1708 (C=O); δ_H(500 MHz; $CDCl_3$) 1.08 (3 H, s, 7a-Me), 2.38 (1 H, dd, *J* 15.9 and 12.9, 6α-H), 2.41 (1 H, dd, *J* 11.0 and 11.0, 4-H), 2.63 (1 H, dd, *J* 15.9 and 4.3, 6β-H), 3.26 (1 H, ddd, *J* 12.9, 11.0 and 4.3, 5-H), 3.80 (3 H, s, CO_2Me), 3.81 (3 H, s, OMe), 6.85–6.88 (2 H, m, 2 × ArH) and 7.40–7.44 (2 H, m, 2 × ArH); *m/z* 348 (M^+) (Found: M^+, 348.1390. $C_{19}H_{24}O_4S$ requires *M*, 348.1395).

Further elution gave the trans-*indanone* **25** (8.0 mg, 76%) as a solid; ν_{max}(neat)/cm^{-1} 1740 and 1714 (C=O); δ_H(500 MHz; $CDCl_3$) 1.04 (3 H, s, 7a-Me), 2.50 (1 H, dd, *J* 15.3 and 2.4, 6α-H), 2.96 (1 H, dd, *J* 15.3 and 5.5, 6β-H), 3.16 (1 H, dd, *J* 12.3 and 4.3, 4-H), 3.72 (3 H, s, CO_2Me), 3.80 (3 H, s, OMe), 3.89 (1 H, ddd, *J* 5.5, 4.3 and 2.4, 5-H), 6.83–6.86 (2 H, m, 2 × ArH) and 7.36–7.39 (2 H, m, 2 × ArH); *m/z* 348 (M^+) (Found: M^+, 348.1396).

Methyl (±)-(3aR*,4S*,7aS*)-3a,4,5,6,7,7a-*Hexahydro*-7a-*methyl*-7-*oxoindane*-4-*carboxylate* **29**.—*Method A*. A mixture of the *trans*-indanone **24** (24.1 mg, 0.076 mmol) and Raney Ni (W-2; 250 mg) in EtOH (2.0 cm^3) was stirred for 40 min at room temperature and then filtered through Celite. Evaporation of the filtrate under reduced pressure gave a residue, which was purified by flash chromatography on silica gel. Elution with hexane–AcOEt (85:15 v/v) afforded a solid, recrystallisation of which from hexane–Et_2O provided the *ketone* **29** (10.0 mg, 63%) as needles, m.p. 64–64.5 °C; ν_{max}($CHCl_3$)/cm^{-1} 1732 and 1708 (C=O); δ_H(500 MHz; $CDCl_3$) 1.06 (3 H, s, 7a-Me), 2.31 (1 H, ddd, *J* 15.3, 6.1 and 2.4, 6α-H), 2.64 (1 H, ddd, *J* 15.3, 13.4 and 6.7, 6β-H), 2.71 (1 H, ddd, *J* 11.6, 11.6 and 4.3, 4-H) and 3.70 (3 H, s, OMe); *m/z* 210 (M^+) (Found: M^+, 210.1256. $C_{12}H_{18}O_3$ requires *M*, 210.1255).

Method B. The mixture of the *trans*-4-methoxyphenyl sulfide **25** (7.0 mg, 0.02 mmol) and Raney Ni (W-2; 90 mg) in acetone (2.0 cm^3) was stirred for 6 h at room temperature and then filtered through Celite. Evaporation of the filtrate under reduced pressure gave a residue, which was purified as above to afford the ketone **29** (3.0 mg, 71%) as needles, m.p. 64–64.5 °C, identical with the above sample in all respects.

Methyl (±)-(3aR*,4S*,7aR*)-3a,4,5,6,7,7a-*Hexahydro*-7a-*methyl*-7-*oxoindane*-4-*carboxylate* **30**.—*Method A*. Reaction of the *cis*-indanone **26** (4.0 mg, 0.013 mmol) with Raney Ni (W-2; 50 mg) in acetone (2.0 cm^3) for 40 min at room temperature, followed by the same work-up as above, gave a residue, which was subjected to flash chromatography on silica gel. Elution with hexane–AcOEt (85:15 v/v) provided the cis-*ketone* **30** (2.5 mg, 95%) as a pale yellowish oil; ν_{max}(neat)/cm^{-1} 1733 and 1704 (C=O); δ_H(500 MHz; $CDCl_3$) 1.16 (3 H, s, 7a-Me), 2.35 (1 H, ddd, *J* 10.4, 8.2 and 4.2, 3a-H), 2.42 (1 H, ddd, *J* 16.4, 11.4 and 6.2, 6β-H), 2.43 (1 H, ddd, *J* 10.4, 10.4 and 3.4, 3-H), 2.53 (1 H, ddd, *J* 16.4, 5.0 and 5.0, 6α-H) and 3.72 (3 H, s, OMe); *m/z* 210 (M^+) (Found: M^+, 210.1256).

Method B. The *cis*-4-methoxyphenyl sulfide **27** (1.0 mg, 0.03 mmol) was transformed, using Raney Ni (W-2; 30 mg) in acetone (1.0 cm^3) as above, into the *cis*-ketone **30** (0.6 mg, 99%), identical with the above specimen in all respects.

Dimethyl 3-*Methyl*-2-*oxo*-7-*trimethylsiloxyheptylphosphonate* **31**.—To a stirred solution of dimethyl methylphosphonate (0.12 cm^3, 1.11 mmol) in dry THF (3.0 cm^3) at −78 °C was added BuLi in hexane (1.56 mol dm^{-3}; 0.57 cm^3, 0.89 mmol), and the mixture was stirred for 30 min at the same temperature. To the stirred solution was slowly added a solution of the lactone **4** (113 mg, 0.884 mmol) in dry THF (2.0 cm^3), and the mixture was stirred for 30 min at the same temperature. After addition of LDA solution (3.0 cm^3), prepared from $HNPr^i_2$ (0.13 cm^3, 0.93 mmol) and BuLi in hexane (1.56 mol dm^{-3}; 0.57 cm^3, 0.89 mmol), at −78 °C, the mixture was stirred for 30 min at the same temperature. After addition of TMSCl (0.23 cm^3, 1.81 mmol), the mixture was stirred for 30 min at the same temperature. The mixture was poured into cold, saturated aq. NH_4Cl and thoroughly extracted with $CHCl_3$. The extract was washed with brine, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. Chromatography on silica gel with benzene–acetone (9:1 v/v) as eluent yielded the *phosphonate* **31** (215 mg, 75%) as a pale yellowish oil; ν_{max}(neat)/cm^{-1}

1710 (C=O) and 1248 (P=O); δ_H(500 MHz; $CDCl_3$) 0.06 (9 H, s, $SiMe_3$), 1.07 (3 H, d, *J* 7.3, 3-Me), 2.68–2.75 (1 H, m, 3-H), 3.09 (2 H, d, *J* 22.5, 1-H_2), 3.52 (2 H, t, *J* 6.7, 7-H_2) and 3.75 [6 H, d, *J* 11.6, $P(OMe)_2$]; *m/z* 324 (M^+) (Found: M^+, 324.1522. $C_{13}H_{29}O_5PSi$ requires *M*, 324.1520).

(E)-2,6-*Dimethyl*-10-*trimethylsiloxydec*-3-*en*-5-*one* **32**.—To a stirred mixture of NaH in oil (60%; 62 mg, 1.55 mmol) in dry THF (10.0 cm^3) at 0 °C was slowly added a solution of the phosphonate **31** (499 mg, 1.54 mmol) in dry THF (5.0 cm^3). After being stirred for 20 min at the same temperature, followed by addition of a solution of isobutyraldehyde (0.17 cm^3, 1.87 mmol) in dry THF (5.0 cm^3), the resulting mixture was stirred for 15 min at the same temperature and then for 10 min at room temperature. The mixture was poured into cold, saturated aq. NH_4Cl and thoroughly extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (95:5 v/v) gave the *enone* **32** (342 mg, 82%) as an oil; ν_{max}(neat)/cm^{-1} 1693 and 1670 (C=O) and 1628 (C=C); δ_H(60 MHz; $CDCl_3$) 0.01 (9 H, s, $SiMe_3$), 0.98 (3 H, d, *J* 7.2, 6-Me), 1.03 (6 H, d, *J* 6.8, $CHMe_2$), 2.12–2.82 (2 H, m, 2- and 6-H), 3.32–3.72 (2 H, m, 10-H_2), 6.02 (1 H, br d, *J* 16.0, 4-H) and 6.77 (1 H, dd, *J* 16.0 and 6.4, 3-H); *m/z* 270 (M^+) (Found: M^+, 270.2015. $C_{15}H_{30}O_2Si$ requires *M*, 270.2013).

(E)-10-*Hydroxy*-2,6-*dimethyldec*-3-*en*-5-*one* **33**.—A mixture of the trimethylsilyl ether **32** (61.6 mg, 0.228 mmol) and TBAF in hexane (1 mol dm^{-3}; 0.45 cm^3, 0.45 mmol) in THF (2.0 cm^3) was stirred for 5 min at 0 °C. The reaction mixture was poured into 10% aq. $KHSO_4$ and thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. Chromatography on silica gel with hexane–AcOEt (7:3 v/v) yielded the *alcohol* **33** (45.5 mg, 100%) as an oil; ν_{max}(neat)/cm^{-1} 3430 (OH), 1691 and 1670 (C=O) and 1627 (C=C); δ_H(60 MHz; $CDCl_3$) 0.98 (3 H, d, *J* 7.0, 5-Me), 1.03 (6 H, d, *J* 6.4, $CHMe_2$), 2.06–3.00 (3 H, m, OH, 5-H and 9-H), 3.30–3.66 (2 H, m, 1-H_2), 5.93 (1 H, br d, *J* 15.6, 7-H) and 6.73 (1 H, dd, *J* 15.6 and 6.4, 8-H); *m/z* 198 (M^+) (Found: M^+, 198.1620. $C_{12}H_{22}O_2$ requires *M*, 198.1619).

Methyl (E,E)-7,11-*Dimethyl*-8-*oxododeca*-2,9-*dienoate* **34**.—The alcohol **33** (45.5 mg, 0.23 mmol) was oxidised with TAPI[10] (195 mg, 0.46 mmol) as above give to the keto aldehyde; ν_{max}(neat)/cm^{-1} 1725, 1692 and 1668 (C=O) and 1626 (C=C); δ_H(60 MHz; $CDCl_3$) 1.07 (3 H, d, *J* 6.6, 5-Me), 1.15 (6 H, d, *J* 7.0, $CHMe_2$), 6.07 (1 H, br d, *J* 16.2, 7-H), 6.90 (1 H, dd, *J* 16.2 and 6.4, 8-H) and 9.75–9.93 (1 H, m, CHO), which was used in the next reaction without purification.

A solution of the crude keto aldehyde and methyl triphenylphosphoranylideneacetate (70 mg, 0.21 mmol) in dry CH_2Cl_2 (2.0 cm^3) was stirred for 12 h at room temperature. After evaporation under reduced pressure, the residue was purified by flash chromatography on silica gel. Elution with hexane–AcOEt (9:1 v/v) afforded the (E,E)-*ester* **34** (45.9 mg, 79% from the alcohol **33**) as an oil; ν_{max}(neat)/cm^{-1} 1721 and 1690 (C=O), 1667 and 1660 (C=O and C=C) and 1623 (C=C); δ_H(500 MHz; $CDCl_3$) 1.06 (6 H, d, *J* 6.8, $CHMe_2$), 1.07 (3 H, d, *J* 7.3, 7-Me), 2.12–2.21 (2 H, m, 4-H_2), 2.41–2.50 (1 H, m, 11-H), 2.73 (1 H, tq, *J* 7.3 and 6.7, 7-H), 3.70 (3 H, s, OMe), 5.80 (1 H, dt, *J* 15.9 and 1.9, 2-H), 6.08 (1 H, dd, *J* 15.9 and 1.3, 9-H), 6.82 (1 H, dd, *J* 15.9 and 6.8, 10-H) and 6.92 (1 H, dt, *J* 15.9 and 7.3, 3-H); *m/z* 252 (M^+) (Found: M^+, 252.1725. $C_{15}H_{24}O_3$ requires *M*, 252.1724).

Methyl (E,E)-7-*Methyl*-8-*oxo*-10-*trimethylsilyldeca*-2,9-*dienoate* **36**.—The lactone **4** (131 mg, 1.02 mmol) was reduced with DIBAH in hexane (0.99 mol dm^{-3}; 1.14 cm^3, 1.13 mmol) at −78 °C as above to give the aldehyde **5** which was used in the following reaction without purification.

To a stirred solution of the stannylethene (*E*)-TMSCH=CHSnBu_3[17] (996 mg, 2.56 mmol) in dry THF (3.0 cm^3) at −78 °C was added BuLi in hexane (1.56 mol cm^{-3}, 1.31 cm^3, 2.04 mmol), and the mixture was stirred for 30 min at −23 °C. To the stirred mixture at −78 °C was slowly added a solution of the above aldehyde **5** in dry THF (3.0 cm^3), and the resulting mixture was stirred for 10 min at the same temperature. After being poured into cold, saturated aq. NH_4Cl, the mixture was thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried, and evaporated to dryness under reduced pressure. Chromatography on silica gel with hexane–AcOEt (7:3 v/v) as eluent gave the epimeric mixture of the diols **35** (110 mg, 47%) as an oil; ν_{max}(neat)/cm^{-1} 3430–3250 (OH) and 1622 (C=C); δ_H(90 MHz; $CDCl_3$) 0.05 (9 H, s, $SiMe_3$), 0.84 (3 H, d, *J* 4.2, 5-Me), 2.00 (1 H, br s, OH), 3.41–3.67 (2 H, m, 1-H_2), 3.82–4.71 (1 H, m, 6-H) and 5.88–5.97 (2 H, m, 7- and 8-H).

The above epimeric mixture of diols **35** (11.1 mg, 0.048 mmol) was oxidised with TAPI[10] (71.6 mg, 0.169 mmol) as above to give the keto aldehyde; ν_{max}(neat)/cm^{-1} 1724 (C=O) and 1688 and 1670 (C=O); δ_H(60 MHz; $CDCl_3$) 0.03 (9 H, s, $SiMe_3$), 0.98 (3 H, d, *J* 8.0, Me), 6.35 (1 H, d, *J* 18.0, =CHSi), 6.98 (1 H, d, *J* 18.0, C*H*=CHSi) and 9.62 (1 H, br s, CHO), which was used in the next reaction without purification.

A solution of the crude keto aldehyde and methyl triphenylphosphoranylideneacetate (15.8 mg, 0.0471 mmol) in dry CH_2Cl_2 (2.0 cm^3) was stirred for 12 h at room temperature and was then heated for 6 h under reflux. Evaporation of the solvent under reduced pressure gave a residue, which was subjected to flash chromatography on silica gel. Elution with hexane–AcOEt (9:1 v/v) yielded the (E,E)-*ester* **36** (11.2 mg, 82% from diol **35**) as an oil; ν_{max}(neat)/cm^{-1} 1727 (C=O) and 1670 and 1660 (C=O); δ_H(500 MHz; $CDCl_3$) 0.14 (9 H, s, $SiMe_3$), 1.09 (3 H, d, *J* 7.4, 7-Me), 2.15–2.24 (2 H, m, 4-H_2), 2.86 (1 H, tq, *J* 7.4 and 7.4, 7-H), 3.71 (3 H, s, OMe), 5.81 (1 H, br d, *J* 15.3, 2-H), 6.52 (1 H, d, *J* 18.9, 9-H), 6.93 (1 H, dt, *J* 15.3 and 6.7, 3-H) and 7.10 (1 H, d, *J* 18.9, 10-H); *m/z* 282 (M^+) and 267 (M^+ − Me) (Found: M^+ − Me, 267.1417. $C_{14}H_{23}O_3Si$ requires *m/z*, 267.1415).

Methyl (E,E)-7-*Methyl*-8-*oxo*-10-*phenylsulfinyldeca*-2,9-*dienoate* **37**.—To a stirred solution of $NaIO_4$ (25.0 mg, 0.117 mmol) in MeOH–water (1:2 v/v; 1.5 cm^3) at 0 °C was added a solution of the 1:2 mixture of the corresponding sulfides **14** and **16** (33.0 mg, 0.104 mmol) in MeOH (0.5 cm^3), and the mixture was stirred for 30 min at the same temperature and for 5 days at room temperature. After further addition of $NaIO_4$ (12.5 mg, 0.058 mmol), the mixture was stirred for 2 days at the same temperature. The mixture was then poured into water and thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried and evaporated to dryness under reduced pressure. Flash chromatography on silica gel with hexane–AcOEt (9:1 v/v) gave a 1:3.3 mixture of the starting sulfides **14** and **16** (11.7 mg, 36% recovery). Further elution with hexane–AcOEt (7:3 v/v) yielded the (E,E)-*sulfoxide* **37** (6.6 mg, 30%) as an oil; ν_{max}(neat)/cm^{-1} 1720 (C=O), 1695, 1677 and 1655 (C=O and C=C) and 1053 (S=O); δ_H(90 MHz; $CDCl_3$) 1.14 (3 H, d, *J* 6.2, 7-Me), 2.01–2.36 (2 H, m, 4-H_2), 2.50–2.82 (1 H, m, 7-H), 3.74 (3 H, s, OMe), 5.81 (1 H, dt, *J* 15.3 and 1.5, 2-H), 6.93 (1 H, dt, *J* 15.3 and 6.6, 3-H), 7.10 (1 H, d, *J* 12.9, 9-H) and 7.45 (1 H, d, *J* 12.9, 10-H); *m/z* 334 (M^+) (Found: M^+, 334.1239. $C_{18}H_{22}O_4S$ requires *M*, 334.1239).

Crystal Structure Analysis of Compound **24**.—A crystal with dimensions 0.20 × 0.25 × 0.30 mm was used for the data

collection on a Rigaku automated four-circle diffractometer, equipped with a rotating anode (45 kV, 200 mA), with use of graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). A summary of the crystal data and structure refinement details are given in Table 1. The structure was solved by direct methods with a RANTAN 81 program with some modification.[18] After the block-diagonal least-squares refinement for non-hydrogen atoms with anisotropic temperature factors, the hydrogen atoms were calculated geometrically and also verified from the difference Fourier map and then included in the refinement with isotropic temperature factors. The fractional atomic co-ordinates are given in Table 2. The remaining crystallographic tables have been deposited with the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC deposition scheme see section 5.6.3, 'Instructions for Authors', Issue 1.

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