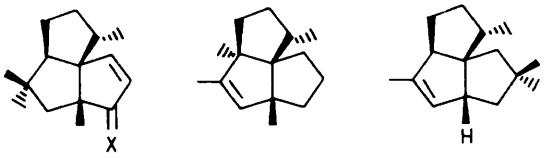
Stereoselective Total Synthesis of (±)-3-Oxosilphinene through Intramolecular Diels–Alder Reaction

Masataka Ihara, Akihiro Kawaguchi, Hitoshi Ueda, Masatoshi Chihiro, and Keiichiro Fukumoto*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan
Tetsuji Kametani
Institute of Medicinal Chemistry, Hoshi University, Ebara 2-4-41, Shinagawa-ku, Tokyo 142, Japan

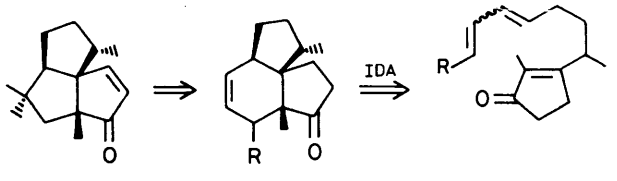
The angular tricyclopentanoid sesquiterpene (±)-3-oxosilphinene (**1**) was stereoselectively synthesized through intramolecular Diels–Alder reaction as the key step. On heating, the (*E,E*)-sulphenyltriene (**16**), derived from 3-bromo-2-methylcyclopent-2-enone (**13**), gave only one stereoisomer of the tricyclo[7.3.0.$0^{1,5}$]dodecene derivative (**17**) having all four contiguous asymmetric centres with the required stereochemistry. The cycloadduct (**17**) was converted into the racemate of the natural product (**1**) *via* ring contraction.

The structure of 3-oxosilphinene (**1**), isolated from the aerial parts of *Dugaldia hoopesii*, was determined by Bohlmann and his co-workers on the basis of careful spectral analyses.[1] The absolute configuration was deduced from the c.d. spectrum, assuming that the octant rule applies for the compound. Most of the existing strategies for the synthesis of angularly fused triquinanes, such as silphinene (**2**), isocomene (**3**), and pentalenene (**4**), sequentially construct each ring in the tricyclic



(**1**) X = O
(**2**) X = H_2 (**3**) (**4**)

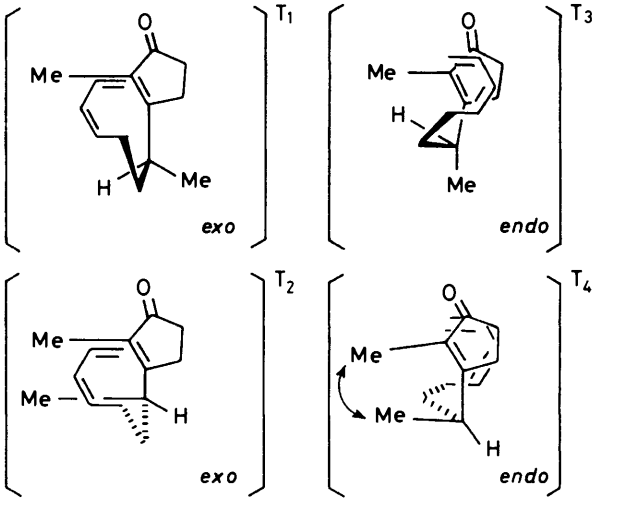
system,[2,3] with some notable exceptions.[4] We envisaged the synthesis of 3-oxosilphinene (**1**) through a tricyclo[7.3.0.$0^{1,5}$]-dodecene derivative (**5**) which could be constructed by the intramolecular Diels–Alder reaction of the trienes (**6**) (Scheme 1), and here we report our highly stereoselective total synthesis of the natural product (**1**).[5]



(**1**) (**5**) (**6**)

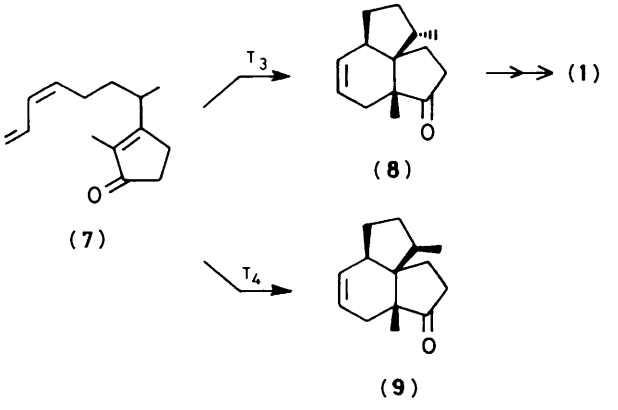
Scheme 1.

At the beginning of the work, the stereochemistry of the [4 + 2] cycloaddition was considered using Dreiding stereomodels. Since the triene (**6**) has one chiral centre, two pairs of *endo* and *exo* conformations are possible for the cycloaddition of (*Z*)- and (*E*)-trienes (**7**) and (**10**) respectively. In the case of the *exo* transients (T_1 and T_2) of the (*Z*)-isomer (**7**), the overlap of the orbitals of the diene and dienophile would be difficult due to the strain at the methylene chain. On the other hand, the *endo* transients (T_3 and T_4) may adopt a suitable conformation for the cycloaddition. The transient (T_3) would lead to the tricyclic



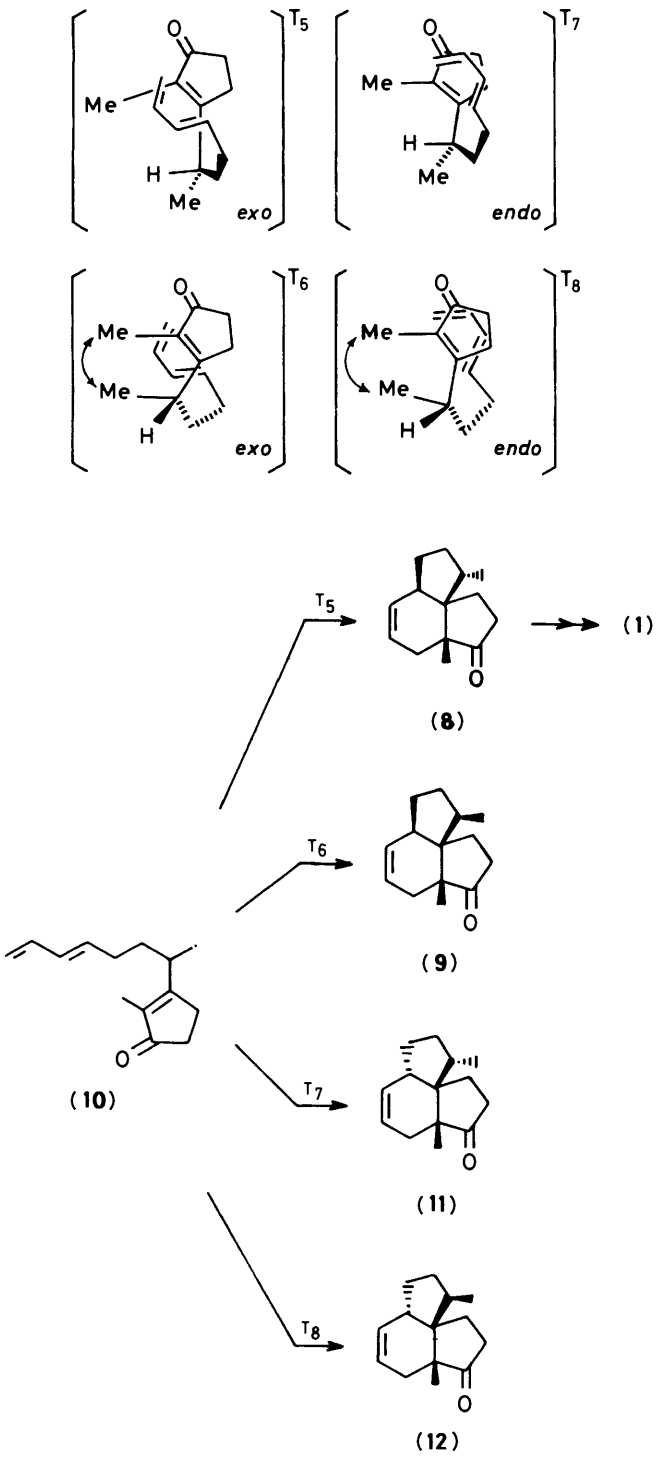
compound (**8**) possessing the right stereochemistry at the four contiguous asymmetric centres, while T_4 would give the unnatural isomer (**9**) (Scheme 2). It is further suggested that T_4 is more unstable because of the non-bonded interaction between the two methyl groups. Therefore the desired compound (**8**) would be the most preferred product of the cycloaddition of the (*Z*)-isomer.

Among the four possible intermediates (T_5—T_8) from the (*E*)-isomer (**10**) (Scheme 3), T_6 and T_8 would have higher potential

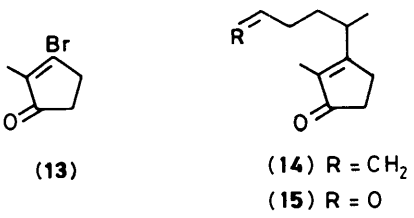


(**7**) (**8**) (**9**)

Scheme 2. Cycloaddition of the (*Z*)-triene (**7**)



Scheme 3. Cycloaddition of the (*E*)-triene (**10**)



The trienes (**7**) and (**10**) were easily prepared starting from 3-bromo-2-methylcyclopent-2-enone (**13**).[6] Reaction of the Grignard reagent, derived from 5-bromohex-1-ene,[7] with compound (**13**) in the presence of copper(I) bromide caused addition and elimination to give quantitatively the enone (**14**), oxidation of which with osmium tetraoxide and sodium periodate[8] produced the aldehyde (**15**) in 79% yield. Several methods are known for the construction of a 4-substituted 1,3-butadiene system from an aldehyde. For example, it was reported that the reaction of an aldehyde with the phosphorus ylide derived from an allyltriphenylphosphonium salt created *ca.* 1:1 mixture of the (*Z*)- and (*E*)-isomer.[9] On the other hand, Yamamoto and his co-workers recently developed the selective formation of (*Z*)- and (*E*)-dienes using allyldiphenylphosphine and its oxide, respectively.[10] Therefore the above three procedures were applied to the aldehyde (**15**). Thus the mixture of the trienes (**7**) and (**10**) was obtained in 31% yield on the reaction with allyltriphenylphosphonium bromide and methyllithium (Method A). The (*Z*)- and (*E*)-isomers were selectively synthesized in 51% yield on treatment with allyldiphenylphosphine and t-butyl-lithium in the presence of titanium tetraisopropoxide followed by iodomethane (Method B), and in 17% yield by the action with allyldiphenylphosphine oxide and n-butyl-lithium in the presence of hexamethylphosphoric triamide (Method C), respectively. These two isomers were inseparable on h.p.l.c. and were not distinguishable on n.m.r. analysis.

The intramolecular Diels–Alder reaction was conducted by heating the solutions of the above trienes in *o*-dichlorobenzene in sealed tubes at 200 °C for 45 h. The tricyclic compound (**8**) was obtained as a single stereoisomer in 23% yield from the mixture of the trienes (the product by Method A) and in 45% yield from the (*E*)-isomer (**10**) (the product by Method C). However, the reaction of the (*Z*)-isomer (**7**) gave no cyclized product. This fact indicated that the *endo*-mode cycloaddition was disfavoured because of the non-bonded interactions between the diene and the cyclopentenone ring. The planar structure of the product (**8**) was determined on the basis of its spectral data: in the i.r. spectrum, the disappearance of the absorption due to the α,β-unsaturated ketone and the appearance of the absorption due to the five-membered cyclic ketone at 1 735 cm^{-1}; in the n.m.r. spectrum, the change of the olefinic protons (5 H → 2 H) and the observation of the resonance due to the angular methyl group at δ 0.98 as a singlet; the molecular-ion peak at *m/z* 204 in the mass spectrum. The stereostructure (**8**), deduced from mechanistic considerations, was confirmed by the conversion of compound (**8**) into the natural sesquiterpene (**1**). The cycloaddition was examined under several reaction conditions, such as different temperatures and solvents, and in the presence of Lewis acids (aluminium trichloride, diethylaluminium chloride, trimethyl borate, and so on). The best result was obtained on heating the *o*-dichlorobenzene solution in a sealed tube at 200—220 °C as mentioned above.

In order to improve the transformation of the aldehyde (**15**) into the tricyclic compound (**8**), thermolyses of several (*E*)-trienes were tested. After several trials, the conversion was effectively carried out *via* the cycloaddition of the (*E*)-

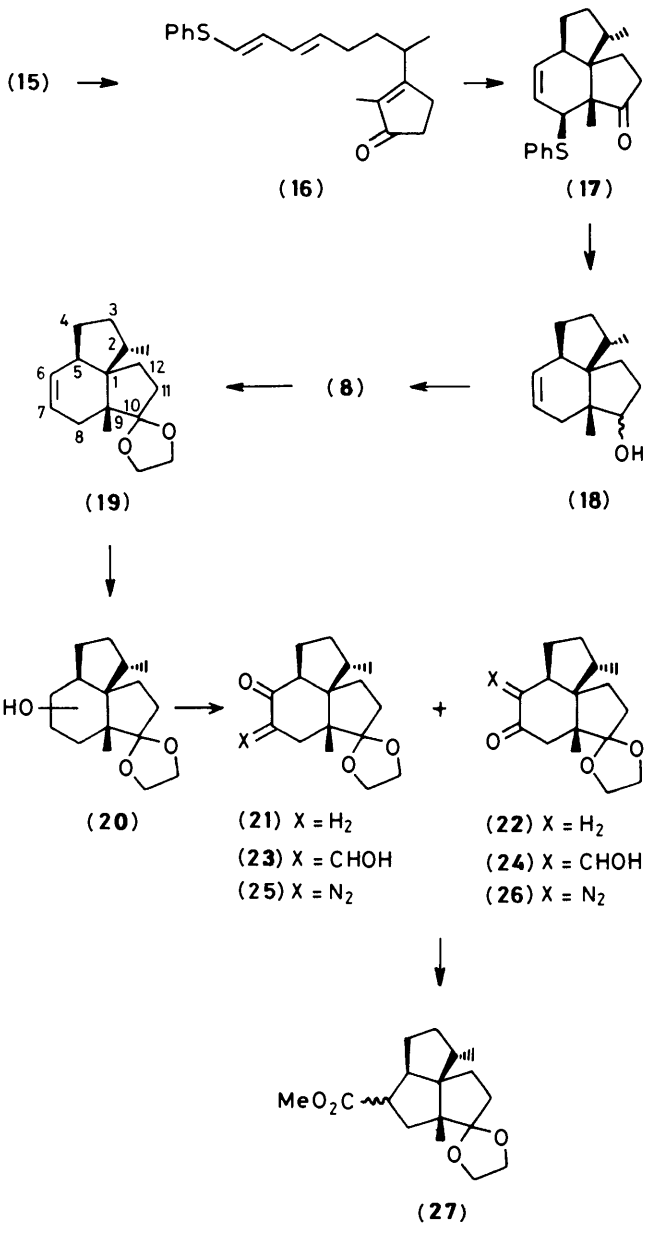
energies compared with those of T_5 and T_7, because a serious interaction between the two methyl groups exists, as in the case of the aforementioned intermediate T_4. It was assumed that the *exo*-mode T_5 leading to the required compound (**8**) would be the most preferable conformation since the *endo*-mode T_7 would have interactions between the diene and the cyclopentenone ring. On the basis of the above considerations, we decided to examine the intramolecular Diels–Alder reaction of both the (*Z*)- and (*E*)-trienes (**7**) and (**10**).

sulphenyltriene (**16**). Condensation of aldehyde (**15**) with diethyl 3-phenylthioprop-2-enylphosphonate[11] in the presence of n-butyl-lithium selectively afforded the (*E,E*)-isomer (**16**) in 78% yield. When an *o*-dichlorobenzene solution of compound (**16**) was heated in a sealed tube at 220 °C for 15 h the tricyclic compound (**17**), m.p. 97—99 °C, was obtained in 76% yield as a single isomer. The stereochemistry of the product is also deduced from consideration of the reaction mechanism. The sulphenyl group was readily removed in 88% overall yield by two steps, reduction using metallic calcium in liquid ammonia[12] followed by oxidation of the epimeric alcohols (**18**) with pyridinium chlorochromate (PCC) on alumina.[13] The product (**8**) was identical with the sample prepared as described above.

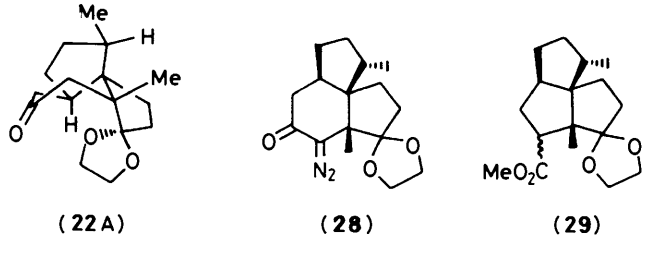
After extensive investigation, the ring contraction accompanied by the introduction of a substituent at the C-6 position was successfully carried out by Wolff rearrangement of the mixture of diazo ketones (**25**) and (**26**). First the ketone (**8**) was protected as the acetal (**19**) on reaction with ethylene glycol in the presence of toluene-*p*-sulphonic acid (PTSA) in 88% yield. The olefin (**19**) was treated with borane–dimethyl sulphide complex followed by a mixture of hydrogen peroxide and sodium hydroxide to give three alcohols (**20**) as a mixture, which was, without separation, oxidized with chromium(VI) oxide–pyridine complex.[14]

Two ketones (**21**) and (**22**), obtained in 78% yield from olefin (**19**) as a mixture in the ratio 2:3, were separable by silica gel column chromatography. The structure of compound (**21**) was assigned by the resonance due to the methine proton neighbouring the carbonyl group at δ 2.64—2.72, which appeared as a multiplet in the n.m.r. spectrum. The signals due to two methylene protons on the ethylenedioxy group of isomer (**22**) were observed at δ 3.64—3.98 as a multiplet, whereas those of isomer (**21**) were found at δ 3.90 as a broad singlet. This indicated that the ketone (**22**) adopted conformation (**22A**) in which one of the methylene groups would be made to resonate at higher field by presence of the carbonyl group. It was therefore expected that the C-8 position was very hindered and the formation of compound (**28**), which could be converted into the undesired regioisomer (**29**) on ring contraction, would be depressed. In fact, ketones (**21**) and (**22**) gave the hydroxymethylene compounds (**23**) and (**24**) in 88 and 100% yield, respectively. After conversion into the diazo ketones (**25**) and (**26**) on diazo-exchange using toluene-*p*-sulphonyl azide and triethylamine, irradiation of the products in methanol with a 400-W high-pressure lamp through a Pyrex filter[15] produced the same tricyclo[6.3.0.0^{1,5}]undecane derivative (**27**) (Scheme 4). Thus compound (**27**), m.p. 55—57 °C, was obtained in 88% overall yield from the mixture of two hydroxymethylene compound (**23**) and (**24**).

Finally the tricyclic ester (**27**), synthesized stereospecifically, was transformed into the racemate of the natural product (**1**). Methylation of compound (**27**) with lithium di-isopropylamide (LDA) and iodomethane occurred selectively from the less hindered side to furnish the trimethyl compound (**30**) in 80% yield. Reduction of the ester group of compound (**30**) with di-isobutylaluminium hydride (DIBAL), followed by oxidation of the resulting alcohol (**31**), m.p. 81—83 °C, with Collins' reagent gave, in 84% yield, the aldehyde (**32**), which was then subjected to Wolff–Kishner reduction to afford the tetramethyl compound (**33**) in 99% yield. After deprotection with 3.6% hydrochloric acid in acetone, the resulting ketone (**34**), obtained in 87% yield, was treated with LDA and then chlorotrimethylsilane. Oxidation of the resulting silyl enol ether with palladium acetate in the presence of *p*-benzoquinone[16] furnished (±)-3-oxosilphinene (**1**) in 84% overall yield. The n.m.r., i.r., and mass spectra of the synthetic compound, m.p. 50—51 °C, were consistent with reported data.[1] Thus the first total synthesis of the racemate of the angular triquinane (**1**) was achieved in a highly stereoselective manner (Scheme 5).

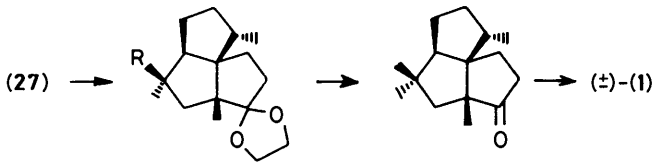


Scheme 4.



Experimental

General Methods.—M.p.s were measured on a YANACO micromelting point apparatus and are uncorrected. I.r. spectra



(30) R = CO_2Me
(31) R = CH_2OH
(32) R = CHO
(33) R = Me

(34)

Scheme 5.

were recorded for $CHCl_3$ solutions on a Hitachi 260-10 spectrophotometer. N.m.r. spectra were measured for $CDCl_3$ solutions on a JEOL PMX-60, a JEOL-PS-100, or a JNM-FX-400 spectrometer. Chemical shifts are reported as δ_H values relative to internal $SiMe_4$. Ordinary mass spectra were taken on a Hitachi M-52G instrument, and accurate mass spectra with a JEOL-JMS-01SG-2 spectrometer. All new compounds described in this section were homogeneous on t.l.c. Sodium sulphate was used to dry extracts.

3-(*Hex-5-en-2-yl*)-2-*methylcyclopent-2-enone* (**14**).—A solution of the Grignard reagent prepared from 5-bromohex-1-ene[7] (8.15 g, 50 mmol), activated magnesium (2.43 g, 100 mmol), and a catalytic amount of iodomethane in dry ether (130 ml) was slowly added to a stirred mixture of the enone (**13**)[6] (4.375 g, 25 mmol) and copper(I) bromide (0.72 g, 2.5 mmol) in dry tetrahydrofuran (THF) (120 ml) at −20 °C. The mixture was stirred for 2 h at the same temperature. After addition of saturated aqueous ammonium chloride (50 ml), the resulting mixture was extracted with ether. The extract was washed successively with 25% ammonia and saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was chromatographed on silica gel and eluted with n-hexane–ethyl acetate (9:1 v/v) to yield the *olefin* (**14**) (4.45 g, 100%) as an oil (Found: C, 80.55; H, 10.4. $C_{12}H_{18}O$ requires C, 80.85; H, 10.2%); $\nu_{max.}$ 1 690 cm^{-1} (C=O); δ_H 1.12 (3 H, d, *J* 7 Hz, CH*Me*), 1.68 (3 H, s, 2-Me), 2.39 (4 H, br s, 4- and 5-H_2), 2.94 (1 H, sextet, *J* 7 Hz, C*H*-Me), and 4.75—6.27 (3 H, m, CH=CH_2); *m/z* 178 (M^+).

4-(2′-*Methyl-3′-oxocyclopent-1′-enyl*)*pentanal* (**15**).—To a stirred mixture of the olefin (**14**) (1.78 g, 10 mmol) and osmium tetraoxide (130 mg, 0.5 mmol) in a mixture of ether (30 ml) and distilled water (30 ml) was added sodium periodate (4.28 g, 20 mmol) portionwise during 40 min at 24—26 °C. The mixture was stirred vigorously for 80 min at the same temperature, and was then extracted with ethyl acetate. The extract was washed successively with saturated aqueous sodium thiosulphate and saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was subjected to chromatography on silica gel. Elution with n-hexane–ethyl acetate (4:1 v/v) afforded the *aldehyde* (**15**) (1.377 g, 79%) as an oil (Found: C, 72.9; H, 9.3. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.95%); $\nu_{max.}$ 1 730 (C=O) and 1 695 cm^{-1} (C=O); δ_H 1.12 (3 H, d, *J* 7 Hz, CH*Me*), 1.68 (3 H, s, 2′-Me), 2.39 (4 H, br s, 4′- and 5′-H_2), 2.94 (1 H, sextet, *J* 7 Hz, C*H*Me), and 9.63 (1 H, s, CHO); *m/z* 180 (M^+).

(Z)- *and* (E)-2-*Methyl*-3-(*octa-5,7-dien-2-yl*)*cyclopent-2-enone* (**7**) *and* (**10**).—*Method A.* A suspension of allyltriphenylphosphonium bromide (215 mg, 0.56 mmol) in dry pentane (3 ml) was treated with methyl-lithium (1.5M solution in ether; 0.37 ml), and the resulting solution was stirred for 6 h. A solution of the aldehyde (**15**) (100 mg, 0.56 mmol) in dry ether (3 ml) was then added dropwise during 15 min, and the mixture was stirred for 2 h at room temperature. The resulting mixture was filtered and the filtrate was washed successively with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was chromatographed on silica gel. Elution with n-hexane–ethyl acetate (9:1 v/v) yielded a mixture of the *trienes* (**7**) and (**10**) (35 mg, 31%) as an oil (Found: C, 82.7; H, 9.8. $C_{14}H_{20}O$ requires C, 82.35; H, 9.85%); $\nu_{max.}$ 1 690 (C=O) and 1 640 cm^{-1} (C=O); δ_H 1.13 (3 H, d, *J* 7 Hz, CH*Me*), 1.68 (3 H, s, 2-Me), 2.40 (4 H, br s, 4- and 5-H_2), 2.93 (1 H, sextet, *J* 7 Hz, C*H*Me), and 4.84—6.72 (5 H, m, olefinic H); *m/z* 204 (M^+).

Method B. To a stirred solution of allyldiphenylphosphine (750 mg, 3.32 mmol) in dry THF (11 ml) was added dropwise a solution of t-butyl-lithium in dry pentane (2.2M solution; 1.51 ml, 3.32 mmol) at −78 °C, and the mixture was stirred at 0 °C for 30 min. Titanium tetraisopropoxide (0.99 ml, 3.36 mmol) was added dropwise to the mixture cooled to −78 °C, and the resulting reddish solution was stirred for 10 min at the same temperature. After addition of a solution of the aldehyde (**15**) (500 mg, 2.78 mmol) in dry THF (2 ml) during 5 min at −78 °C, the mixture was stirred at −78 °C for 10 min and then at 0 °C for 1 h. The resulting mixture was treated with iodomethane (0.21 ml, 3.34 mmol) at 0 °C, and was then allowed to warm to room temperature. After 2 h, the reaction mixture was filtered and the filtrate was washed with saturated aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel and eluted with n-hexane–ethyl acetate (9:1 v/v) to give the *triene* (**7**) (291 mg, 51%) as an oil; $\nu_{max.}$ 1 690 (C=O) and 1 640 cm^{-1} (C=C); δ_H 1.12 (3 H, d, *J* 7 Hz, CH*Me*), 1.68 (3 H, s, 2-Me), 2.40 (4 H, br s, 4- and 5-H_2), 2.88 (1 H, sextet, *J* 7 Hz, C*H*Me), and 4.88—6.72 (5 H, m, olefinic H); *m/z* 204 (M^+) (Found: M^+, 204.1485. $C_{14}H_{20}O$ requires *M*, 204.1512).

Method C. To a stirred solution of allyldiphenylphosphine oxide (756 mg, 3.12 mmol) and dry hexamethylphosphoric triamide (1.20 g, 6.7 mmol) in dry THF (5 ml) at −78 °C was added dropwise a solution of n-butyl-lithium in n-hexane (1.56M solution; 2.15 ml, 3.35 mmol) and the mixture was stirred for 10 min at the same temperature. A solution of the aldehyde (**15**) (500 mg, 2.78 mmol) in dry THF (2 ml) was added during 15 min. The resulting mixture was stirred at 0 °C for 30 min, then at room temperature for 2 h. Saturated aqueous ammonium chloride (5 ml) was added, and the mixture was stirred for a further 10 min, and then extracted with pentane. The extract was dried and evaporated to give a residue, which was chromatographed on silica gel and eluted with n-hexane–ethyl acetate (9:1 v/v) to afford the *triene* (**10**) (97 mg, 17%) as an oil; $\nu_{max.}$ 1 690 (C=CO) and 1 640 cm^{-1} (C=C); δ_H 1.10 (3 H, d, *J* 7 Hz, CH*Me*), 1.68 (3 H, s, 2-Me), 2.38 (4 H, br s, 4- and 5-H_2), 2.88 (1 H, sextet, *J* 7 Hz, C*H*Me), and 4.84—6.44 (5 H, m, olefinic H); *m/z* 204 (M^+) (Found: M^+, 204.1485. $C_{14}H_{20}O$ requires *M*, 204.1512).

(±)-(1RS,5RS,9RS,12SR)-5,12-*Dimethyltricyclo*[7.3.0.$0^{1,5}$]-*dodec-7-en-4-one* (**8**).—The mixture of (*E*)- and (*Z*)-triene (26 mg, 0.127 mmol), prepared by Method A, was dissolved in *o*-dichlorobenzene (3 ml) and the solution was heated in a sealed tube at 200 °C for 45 h. Evaporation of the solvent gave a residue, which was chromatographed on silica gel with n-hexane–ethyl acetate (9:1 v/v) as eluant to afford the *cycloadduct* (**8**) (6.0 mg, 23%) as an oil (Found: C, 81.55; H, 10.3. $C_{14}H_{20}O{\cdot}\frac{1}{8}H_2O$ requires C, 81.4; H, 9.9%); $\nu_{max.}$ 1 735 cm^{-1} (C=O); δ_H 0.98 (3 H, s, 5-Me), 1.08 (3 H, d, *J* 7 Hz, 12-Me), and 5.57 (2 H, br s, CH=CH); *m/z* 204 (M^+).

From the (*E*)-triene (53 mg, 0.26 mmol) prepared by Method C, the cycloadduct (**8**) (24 mg, 45%) was obtained by the same procedure as above.

(E,E)-2-*Methyl*-3-(8-*phenylthio-octa*-5,7-*dien*-2-*yl*)*cyclopent*-2-*enone* (**16**).—To a solution of Horner–Emmons reagent [prepared from diethyl (*E*)-3-phenylthioprop-2-enylphosphonate (1.0 g, 4.31 mmol) and n-butyl-lithium (1.56M solution in n-hexane; 2 ml, 3.13 mmol)] in dry THF (10 ml) at −78 °C was added dropwise a solution of the aldehyde (**15**) (537 mg, 2.98 mmol) in dry THF (2 ml). The resulting mixture was stirred at the same temperature for 1 h, then at −20 °C for 1 h, and then at room temperature for 2 h. After water (5 ml) had been added, the mixture was extracted with ether. The extract was dried and evaporated to give a residue, which was chromatographed on silica gel. Elution with n-hexane–ethyl acetate (4:1 v/v) yielded the *sulphenyl triene* (**16**) (730 mg, 78%) as an oil; $\nu_{max.}$ 1 680 (C=O) and 1 640 cm^{-1} (C=C); δ_H 1.13 (3 H, d, *J* 7 Hz, CH*Me*), 1.65 (3 H, s, 2-Me), 5.83—6.40 (4 H, m, olefinic H), and 7.28—7.63 (5 H, m, Ph); *m/z* 312 (M^+) (Found: M^+, 312.1569. $C_{20}H_{24}OS$ requires *M*, 312.1548).

(±)-(1RS,5RS,6SR,9RS,12SR)-5,12-*Dimethyl*-6-*phenylthiotricyclo*[7.3.0.$0^{1,5}$]*dodec*-7-*en*-4-*one* (**17**).—The triene (**16**) (623 mg, 2.00 mmol) was dissolved in *o*-dichlorobenzene (50 ml) and the solution was heated in a sealed tube at 200—220 °C for 15 h. Evaporation of the solvent afforded a residue, which was chromatographed on silica gel with n-hexane–ethyl acetate (95:5 v/v) as eluant to yield the *cycloadduct* (**17**) (473 mg, 76%) as a solid. Recrystallization from ether–n-hexane gave crystals, m.p. 97—99 °C (Found: C, 76.6; H, 8.0. $C_{20}H_{24}OS$ requires C, 76.9; H, 7.75%); $\nu_{max.}$ 1 735 cm^{-1} (C=O); δ_H 1.09 (3 H, d, *J* 7 Hz, 12-Me), 1.19 (3 H, s, 5-Me), 3.98 (1 H, br d, 6-H), 5.72—5.82 (2 H, m, CH=CH), and 7.30—7.54 (5 H, m, Ph); *m/z* 312 (M^+).

(±)-(1RS,5RS,9RS,12SR)-5,12-*Dimethyltricyclo*[7.3.0.$0^{1,5}$]-*dodec*-7-*en*-4-*ol* (**18**).—To a solution of the cycloadduct (**17**) (610 mg, 1.96 mmol) in a mixture of dry ether (3 ml) and liquid ammonia (20 ml) were quickly added calcium turnings (180 mg) and the mixture was stirred at −78 °C for 3 h. Ammonium chloride (3.0 g) was added portionwise, and the ether and liquid ammonia were allowed to evaporate off. The resulting residue was dissolved in water (10 ml), and the solution was extracted thoroughly with ether. The extract was dried and evaporated to give a residue, which was chromatographed on silica gel. Elution with n-hexane–ethyl acetate (4:1 v/v) afforded the *alcohols* (**18**) (399 mg, 100%) as an oil (Found: C, 78.0; H, 10.85. $C_{14}H_{22}O{\cdot}0.5H_2O$ requires C, 78.1; H, 10.75%); $\nu_{max.}$ 3 450 cm^{-1} (OH); δ_H 0.83 (3 H, s, 5-Me), 0.99 (3 H, d, *J* 7 Hz, 12-Me), 3.47—3.53 (1 H, m, 4-H), and 5.52—5.73 (2 H, m, CH=CH); *m/z* 206 (M^+).

(±)-(1RS,5RS,9RS,12SR)-5,12-*Dimethyltricyclo*[7.3.0.$0^{1,5}$]-*dodec*-7-*en*-4-*one* (**8**).—A mixture of the alcohols (**18**) (110 mg, 0.53 mmol) and PCC on alumina (1% w/w) (10 g) was stirred for 15 h at room temperature. The reaction mixture was filtered and the filtrate was washed successively with aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, and then evaporated. The residue was chromatographed on silica gel with n-hexane–ethyl acetate (9:1 v/v) as eluant to give the ketone (**8**) (96 mg, 88%) as an oil, whose spectral data and t.l.c. behaviour were identical with those of the sample prepared directly from (*E*)-triene (**10**).

(±)-(1RS,2SR,5RS,9RS)-10,10-*Ethylenedioxy*-2,9-*dimethyltricyclo*[7.3.0.$0^{1,5}$]*dodec*-6-*ene* (**19**).—A mixture of the ketone (**8**) (30 mg, 0.15 mmol), ethylene glycol (0.1 ml), and a catalytic amount of PTSA in dry benzene (5 ml) was heated at reflux for 24 h in a Dean–Stark apparatus. After having cooled, the reaction mixture was washed successively with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, and then evaporated to give a residue, which was chromatographed on silica gel. Elution with n-hexane–ether (95:5 v/v) yielded the *acetal* (**19**) (32 mg, 88%) as an oil (Found: C, 77.85; H, 10.05. $C_{16}H_{24}O_2$ requires C, 77.35; H, 9.75%); δ_H 0.82 (3 H, s, 9-Me), 0.88 (3 H, d, *J* 7 Hz, 2-Me), 3.84 (4 H, br s, OCH_2CH_2O), and 5.84 (2 H, br s, CH=CH); *m/z* 248 (M^+).

(±)-(1RS,2SR,5SR,9RS)-10,10-*Ethylenedioxy*-2,9-*dimethyltricyclo*[7.3.0.$0^{1,5}$]*dodecan*-6-*one* (**21**) *and* (±)-(1RS,2SR,5RS,9RS)-10,10-*Ethylenedioxy*-2,9-*dimethyltricyclo*[7.3.0.$0^{1,5}$]*dodecan*-7-*one* (**22**).—To a solution of the olefin (**19**) (550 mg, 2.22 mmol) in dry n-hexane (8 ml) at 0 °C was added borane–dimethyl sulphide complex (10M-solution; 0.4 ml, 4 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture cooled to 0 °C, was carefully treated in turn with ethanol (5 ml), 3M-aqueous sodium hydroxide (2.4 ml), and 30% aqueous hydrogen peroxide (0.12 ml). The resulting mixture was heated at 50 °C for 1 h. After having cooled, the reaction mixture was poured onto ice (10 g) and extracted with ether. The extract was dried and then evaporated to give a residue, which was dissolved in dry dichloromethane (5 ml). This solution was added to a suspension of Collins' reagent [prepared from chromium(VI) oxide (1.96 g, 19.6 mmol) and pyridine (3.2 ml, 39.62 mmol)] in dry dichloromethane (50 ml). The resulting mixture was stirred for 15 h at room temperature, and then treated with ether (50 ml). After filtration, the filtrate was washed successively with 10% aqueous copper(II) sulphate and saturated aqueous sodium chloride, and was then dried. Evaporation of the solvent gave a residue, which was chromatographed on silica gel with n-hexane–ethyl acetate (4:1 v/v) as eluant to yield the *ketone* (**21**) (91 mg, 16%), a mixture of ketones (**21**) and (**22**) (138 mg, 24%), and the *isomer* (**22**) (220 mg, 38%) as an oil.

For ketone (**21**) (Found: C, 73.05; H, 9.35. $C_{16}H_{24}O_3$ requires C, 72.7; H, 9.15%); $\nu_{max.}$ 1 710 cm^{-1} (C=O); δ_H 0.92 (3 H, s, 9-Me), 0.96 (3 H, d, *J* 6 Hz, 2-Me), 2.64—2.72 (1 H, m, 5-H), and 3.90 (4 H, br s, OCH_2CH_2O); *m/z* 264 (M^+).

For ketone (**22**) (Found: C, 72.05; H, 9.45. $C_{16}H_{24}O_3{\cdot}\frac{1}{8}H_2O$ requires C, 72.05; H, 9.15%); $\nu_{max.}$ 1 710 cm^{-1} (C=O); δ_H 1.00 (3 H, s, 9-Me), 1.07 (3 H, d, *J* 6 Hz, 2-Me), and 3.64—3.98 (4 H, m, OCH_2CH_2O); *m/z* 264 (M^+).

(±)-(1RS,2SR,5SR,9RS)-10,10-*Ethylenedioxy*-7-*hydroxymethylene*-2,9-*dimethyltricyclo*[7.3.0.$0^{1,5}$]*dodecan*-6-*one* (**23**).—A suspension of 60% sodium hydride (40 mg, 1.67 mmol) in dry ether (3 ml) was treated with methanol (0.1 ml). To this mixture was added dropwise a solution of the ketone (**21**) (100 mg, 0.38 mmol) in dry ether (3 ml) at 0 °C, and the mixture was stirred for 8 h at room temperature. After addition of methanol (3 ml), the mixture was stirred for a further 15 min, and was then extracted with ether after the addition of saturated aqueous ammonium chloride. The extract was dried and evaporated to give a residue, which was chromatographed on silica gel with n-hexane–ethyl acetate (9:1 v/v) as eluant to give the *hydroxymethylene compound* (**23**) (97 mg, 88%) as an oil; $\nu_{max.}$ 1 720 (C=O) and 1 640—1 580 cm^{-1} (enol); δ_H 0.89 (3 H, s, 9-Me), 1.00 (3 H, d, *J* 6 Hz, 2-Me), 3.92 (4 H, br s, OCH_2CH_2O), and 7.50 (1 H, br s, C=CH); *m/z* 292 (M^+) (Found: M^+, 292.1689. $C_{17}H_{24}O_4$ requires *M*, 292.1674).

(±)-(1RS,2SR,5SR,9RS)-10,10-*Ethylenedioxy*-6-*hydroxymethylene*-2,9-*dimethyltricyclo*[7.3.0.$0^{1,5}$]*dodecan*-7-*one* (**24**).—The *hydroxymethylene compound* (**24**) (11.1 mg, 100%) was prepared from the ketone (**22**) (9.5 mg, 0.036 mmol) by the same procedure as that of the isomer (**23**) (Found: C, 65.0; H, 8.1. $C_{17}H_{24}O_4{\cdot}\frac{5}{4}H_2O$ requires C, 64.85; H, 8.5%); $\nu_{max.}$ 1 720 (C=O) and 1 640—1 580 cm^{-1} (enol); δ_H 0.96 (3 H, s, 9-Me), 1.01 (3 H,

d, *J* 6 Hz, 2-Me), 3.68—3.92 (4 H, m, OCH_2CH_2O), and 8.03 (1 H, br d, *J* 5 Hz, C=CH); *m/z* 292 (M^+).

Methyl (±)-(1RS,2SR,5RS,8RS)-9,9-*Ethylenedioxy*-2,8-*dimethyltricyclo*[6.3.0.0^{1,5}]*undecane*-6-*carboxylate* (**27**).—A solution of the mixture of the hydroxymethylene compounds (**23**) and (**24**) (80 mg, 0.27 mmol) in dry dichloromethane (3 ml) was treated with triethylamine (0.07 ml, 0.5 mmol) and toluene-*p*-sulphonyl azide (70 mg, 0.36 mmol) at room temperature. The resulting mixture was stirred for 2 h at the same temperature. After addition of ether (5 ml), the mixture was subjected to chromatography on alumina (grade III) with ether as eluant to give the diazoketones (**25**) and (**26**) as a yellowish oil. The product was dissolved in dry methanol (5 ml) and the solution was irradiated for 30 min at 0 °C with a 400-W Hanovia lamp with a Pyrex filter. Evaporation of the solvent gave a residue, which was chromatographed on silica gel and eluted with n-hexane–ethyl acetate (7:1 v/v) to afford the *ester* (**27**) (49 mg, 88%) as crystals, m.p. 55—57 °C (Found: C, 69.2; H, 9.0. $C_{17}H_{26}O_4$ requires C, 69.35; H, 8.9%); $\nu_{max.}$ 1 725 cm^{-1} (C=O); δ_H 0.93 (3 H, d, *J* 6 Hz, 2-Me), 0.94 (3 H, s, 8-Me), 2.20—2.42 (1 H, m, 6-H), 3.63 (3 H, s, OMe), and 3.89 (4 H, br s, OCH_2CH_2O); *m/z* 294 (M^+).

(±)-(1RS,2SR,5SR,6RS,8RS)-9,9-*Ethylenedioxy*-2,6,8-*trimethyltricyclo*[6.3.0.0^{1,5}]*undecane*-6-*carboxylate* (**30**).—To a solution of LDA [prepared from di-isopropylamine (0.3 ml, 2.14 mmol) and n-butyl-lithium (1.56M-solution; 0.86 ml, 1.36 mmol)] in dry THF (3 ml) at −78 °C was added a solution of the ester (**27**) (100 mg, 0.34 mmol) in dry THF (1 ml). The reaction mixture was allowed to warm to −20 °C, and was stirred for 2 h. To this solution at −78 °C was added iodomethane (0.13 ml, 2.14 mmol), and the mixture was stirred for 2 h whilst being allowed to attain room temperature. The reaction mixture was then poured into saturated aqueous ammonium chloride and extracted with ether. The extract was washed with saturated aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel with n-hexane–ethyl acetate (7:1 v/v) as eluant to afford the *trimethyl compound* (**30**) (83.6 mg, 80%) as an oil; $\nu_{max.}$ 1 725 cm^{-1} (C=O); δ_H 0.95 (3 H, d, *J* 6 Hz, 2-Me), 1.03 (3 H, s, 8-Me), 1.25 (3 H, s, 6-Me), 3.60 (3 H, s, OMe), and 3.88 (4 H, br s, OCH_2CH_2O); *m/z* 308 (M^+) (Found: M^+, 308.1975. $C_{18}H_{28}O_4$ requires *M*, 308.1986).

(±)-(1RS,2SR,5SR,6RS,8RS)-(9,9-*Ethylenedioxy*-2,6,8-*trimethyltricyclo*[6.3.0.0^{1,5}]*undecan*-6-*yl*)*methanol* (**31**).—To a solution of the ester (**30**) (80 mg, 0.26 mmol) in dry ether (3 ml) at −78 °C was added dropwise a solution of DIBAL in toluene (1M-solution; 0.91 ml, 0.91 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 30 min. After addition of water (0.91 ml), the mixture was stirred for 1 h, and then filtered through Celite. The filtrate was washed with saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was chromatographed on silica gel. Elution with n-hexane–ethyl acetate (2:1 v/v) gave the *alcohol* (**31**) (72.8 mg, 100%) as crystals, m.p. 81—83 °C (Found: C, 72.1; H, 10.3. $C_{17}H_{28}O_3 \cdot \frac{1}{4}H_2O$ requires C, 71.65; H, 10.1%); $\nu_{max.}$ 3 450 cm^{-1} (OH); δ_H 0.95 (3 H, d, *J* 6 Hz, 2-Me), 1.03 (3 H, s, 8-Me), 1.04 (3 H, s, 6-Me), 3.25 (2 H, br s, CH_2OH), and 3.90 (4 H, br s, OCH_2CH_2O); *m/z* 280 (M^+).

(±)-(1RS,2SR,5SR,6RS,8RS)-9,9-*Ethylenedioxy*-2,6,8-*trimethyltricyclo*[6.3.0.0^{1,5}]*undecane*-6-*carbaldehyde* (**32**).—To a suspension of Collins' reagent [prepared from chromium(VI) trioxide (45 mg, 0.45 mmol) and pyridine (0.073 ml, 0.9 mmol)] in dry dichloromethane (1.5 ml) at room temperature was added dropwise a solution of the alcohol (**31**) (18 mg, 0.06 mmol) in dry dichloromethane (0.5 ml). After 3 min, ether (5 ml) was added, and the mixture was filtered. The filtrate was washed with 10% aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel with n-hexane–ethyl acetate (9:1 v/v) as eluant to give the *aldehyde* (**32**) (15 mg, 84%) as an oil; $\nu_{max.}$ 1 720 cm^{-1} (CHO); δ_H 0.97 (3 H, d, *J* 6 Hz, 2-Me), 1.07 (3 H, s, 8-Me), 1.11 (3 H, s, 6-Me), 3.90 (4 H, br s, OCH_2CH_2O), and 9.25 (1 H, s, CHO); *m/z* 278 (M^+) (Found: M^+, 278.1878. $C_{17}H_{26}O_3$ requires *M*, 278.1880).

(±)-(1RS,2SR,5RS,8RS)-9,9-*Ethylenedioxy*-2,6,6,8-*tetramethyltricyclo*[6.3.0.0^{1,5}]*undecane* (**33**).—A mixture of the aldehyde (**33**) (50 mg, 0.18 mmol) and hydrazine monohydrate (0.83 ml) in diethylene glycol (5 ml) was heated at 120 °C for 2 h. After removal of hydrazine and water, sodium hydroxide (0.7 g) was added. The resulting mixture was heated at 185 °C for 15 h, poured into water, and extracted with pentane. The extract was dried and evaporated to give a residue, which was chromatographed on silica gel and eluted with n-hexane–ether (98:2 v/v) to afford the *tetramethyl compound* (**33**) (47.2 mg, 99%) as an oil; δ_H 0.88 (3 H, s, 6α-Me), 0.91 (3 H, d, *J* 6 Hz, 2-Me), 0.96 (3 H, s, 6β-Me), 1.01 (3 H, s, 8-Me), and 3.90 (4 H, br s, OCH_2CH_2O); *m/z* 264 (M^+) (Found: M^+, 264.2075. $C_{17}H_{28}O_2$ requires *M*, 264.2088).

(±)-(1RS,5RS,8RS,11SR)-5,7,7,11-*Tetramethyltricyclo*-[6.3.0.0^{1,5}]*undecan*-4-*one* (**34**).—A solution of the acetal (**33**) (40 mg, 0.15 mmol) in acetone (5 ml) was treated with aqueous 3.6% hydrochloric acid (0.4 ml) at room temperature for 2 h. The mixture was neutralized with 10% aqueous sodium hydroxide and then extracted with pentane. The extract was dried and evaporated to give a residue, which was subjected to silica gel chromatography with n-hexane–ethyl acetate (95:5 v/v) as eluant to yield the *ketone* (**34**) (29.1 mg, 87%) as an oil (Found: C, 79.85; H, 11.05. $C_{15}H_{24}O \cdot \frac{1}{4}H_2O$ requires C, 80.1; H, 11.0%); $\nu_{max.}$ 1 735 cm^{-1} (C=O); δ_H 0.84 (3 H, s, 7α-Me), 0.90 (3 H, s, 7β-Me), 0.92 (3 H, s, 5-Me), 0.99 (3 H, d, *J* 6 Hz, 11-Me), and 2.32—2.52 (2 H, m, 3-H_2); *m/z* 220 (M^+).

(±)-3-*Oxosilphinene* (**1**).—To a solution of LDA [prepared from di-isopropylamine (0.064 ml, 0.46 mmol) and n-butyl-lithium (1.56M-solution; 0.29 ml, 0.46 mmol)] in dry THF (1 ml) at −78 °C was added a solution of the ketone (**34**) (10 mg, 0.045 mmol) in dry THF (1 ml). The resulting mixture was stirred for 1 h at −40 °C. To the above solution, cooled to −78 °C, was added a mixture of chlorotrimethylsilane (0.058 ml, 0.46 mmol) and triethylamine (0.016 ml, 0.12 mmol) in THF (1 ml) in one portion. The mixture was allowed to warm to room temperature and was stirred for 1 h. After addition of ice-cold saturated aqueous sodium hydrogen carbonate (1 ml), the mixture was extracted with ether. The combined extracts were washed with saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was dissolved in acetonitrile (2 ml). To the solution were added palladium(II) acetate (100 mg, 0.45 mmol) and *p*-benzoquinone (5 mg, 0.046 mmol), and the mixture was stirred for 10 h at room temperature. Evaporation of the solvent gave a residue, which was dissolved in benzene and the mixture was filtered. The filtrate was evaporated to give a residue, which was chromatographed on silica gel. Elution with n-hexane–ethyl acetate (95:5 v/v) yielded (±)-3-oxosilphinene (**1**) (8.1 mg, 84%) as crystals, m.p. 50—51 °C, whose i.r. (CCl_4), ^{1}H n.m.r. (400 MHz), and mass spectra were consistent with those of natural 3-oxosilphinene.[1]

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