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THE INTRAMOLECULAR DIELS-ALDER REACTIONS OF (*E*)- AND (*Z*)-METHYL 5-[2-METHYL-4-(TRIMETHYLSILYLOXY)-2,4-CYCLOPENTADIENYL]-2-PENTENOATE. A STEREOSELECTIVE SYNTHESIS OF (±)-SATIVENE *

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Abstract - The intramolecular Diels-Alder reactions of (*E*)- and (*Z*)-trimethylsilyl cyclopentadienyl ethers, (*E*)-6a and (*Z*)-6a, proceed with excellent stereo- and regioselectivity. Starting from the tricyclic keto ester 8, available from the former reaction, a stereoselective synthesis of (±)-sativene (26) is described.

Introduction.- The thermolysis of an isomeric mixture of 5-, 1-, and 2-(n-alkenyl)-1,3-cyclopentadienes (n>3), all readily interconvertible by [1,5]-hydrogen shifts, can afford, in principle, five different tricycloalkenes (cycloadducts I, II/II', and III/III') which result from the intramolecular [4+2] cycloadditions A, B/B', and C/C' respectively (*cf. Scheme 1*).[a]

When n=3, despite the low equilibrium concentration of the 5-isomer,[b] cycloaddition A is exclusively favoured to give 4-brexene (*i.e.* cycloadduct I, n=3) due to the highly strained transition states of the alternative cycloadditions: B/B' and C/C'. In contrast, when n=4 or 5 cycloaddition B is preferred, affording selectively the cycloadduct II.[c] It thus follows that access to the tricyclo alkanes IV is generally not possible *via* the intramolecular Diels-Alder reaction of (n-alkenyl)-cyclopentadienes when n>3.[d] However, a solution to this problem would be to ring expand I in one of

* Dedicated to Professor R.A. Raphael on the occasion of his 65th birthday.

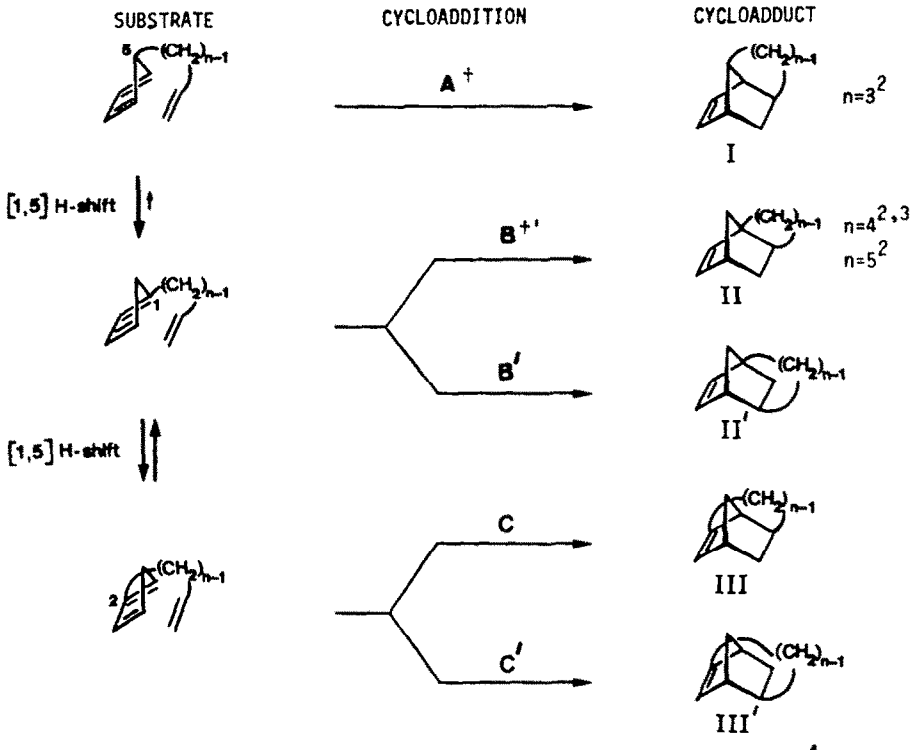
[a] For recent reviews of the intramolecular Diels-Alder reaction , *cf.*[1]

[b] For example, the equilibrium concentrations of 5-, 1-, and 2-methyl-1,3-cyclopentadiene, at 20°, are 1%, 44%, and 55% respectively, *cf.*[6]

[c] The intramolecular cycloadditions B', C, and C', as yet unreported, will only become possible when n is large enough to accommodate the severe torsional strain in their transition states.

[d] Recent work, *cf.*[4c] has shown that intramolecular cycloaddition A of a 5-substituted 4-(alkenyl)-cyclopentadiene competes effectively with [1,5]-hydrogen shifts when the dienophilic C,C-double bond is appropriately activated.

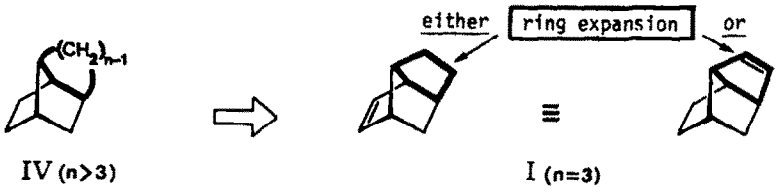
Scheme 1



† For type A cycloadditions of substituted (3-alkenyl)cyclopentadienes *cf.*[4]
+' For type B cycloadditions of substituted (4- or 5-alkenyl)cyclopentadienes *cf.*[5]

two possible ways as illustrated retrosynthetically in *Scheme 2*. This approach is evidently applicable to the synthesis of specifically functionalised tricycloalkanes structurally related to IV and, in this context, a stereoselective synthesis of racemic sativene (26), a naturally occurring sesquiterpene hydrocarbon, is now described in full.[e,f]

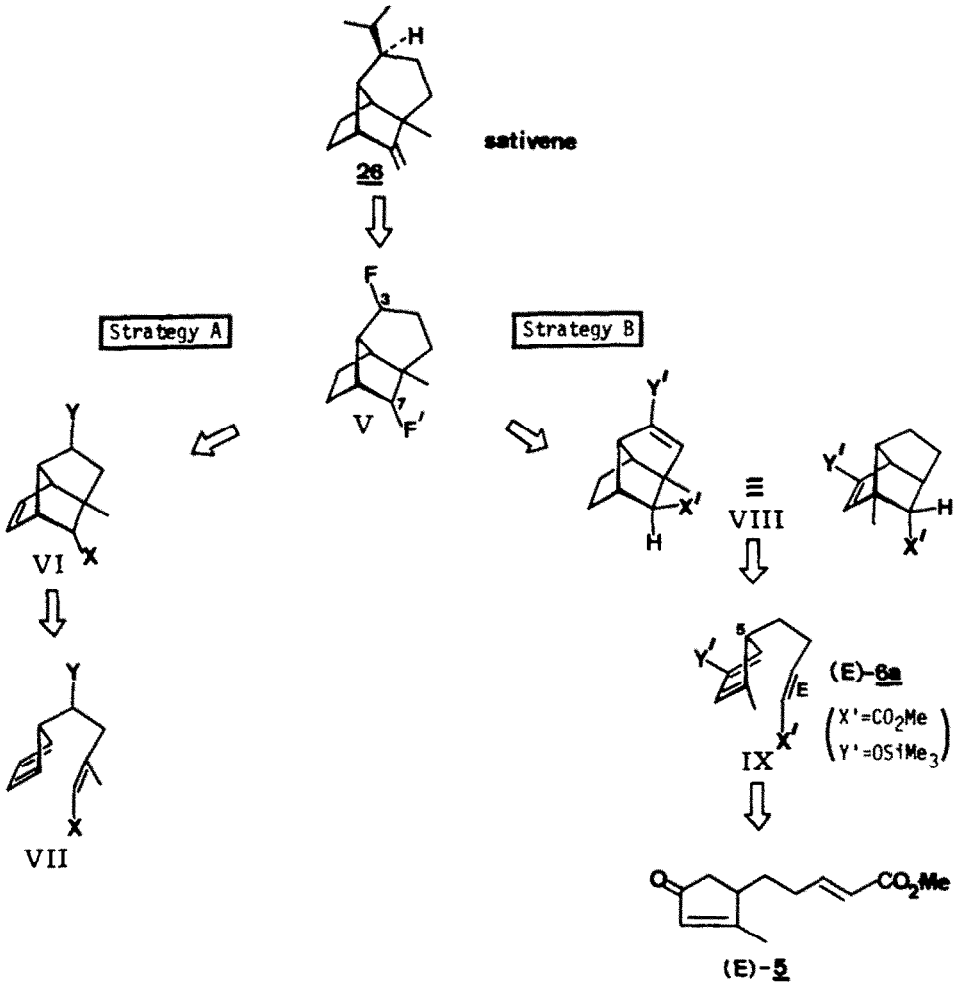
Scheme 2 *Retrosynthetic analysis*



Synthetic Strategy.- Retrosynthetic analysis of sativene (26) (*Scheme 3*) indicates the tricyclic structure V to be an ideal precursor: the carbon skeleton, including the C-6 methyl group, is complete and contains appropriate functionality, F and F', for the introduction of the β-C-3 isopropyl and the C-7 methylidene groups. Using the approach outlined above (*cf. Scheme 2*) two strategies thus presented themselves for access to V. Strategy A involves the intramolecular Diels-Alder

[e] For a preliminary account of this work, *cf.*[7]
[f] For previous syntheses of sativene, *cf.*[8]

Scheme 3 *Retrosynthetic analysis* *



* X, Y, F, and F' represent unspecified functionality

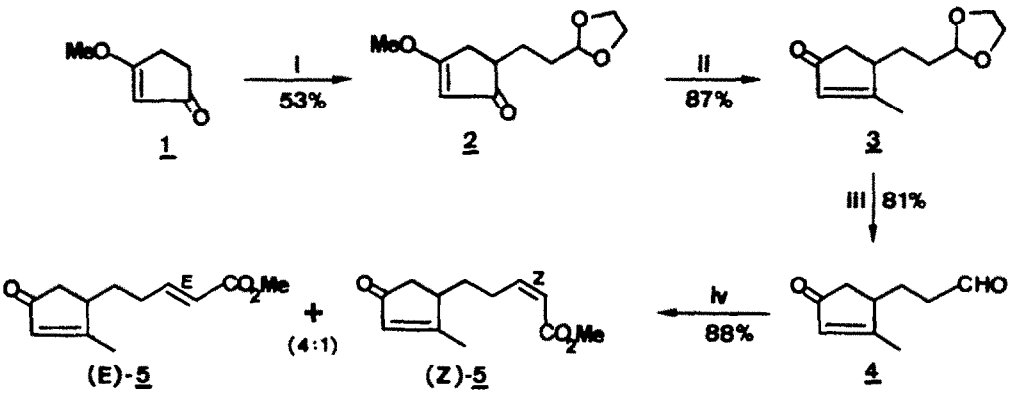
reaction of the 5-substituted cyclopentadiene VII[g] followed by ring expansion of the resulting cycloadduct VI. In contrast strategy B requires the intramolecular cycloaddition of the 1,3,5-trisubstituted cyclopentadiene IX[g] and ring expansion of the cycloadduct VIII. It was decided that the latter strategy was more feasible for two major reasons. Firstly the planned intramolecular cycloaddition is favoured by the fact that both the diene and dienophile components of IX are more reactive than those of VII. Secondly, VIII is readily amenable to a one-carbon ring expansion whereas the putative conversion of VI to V was considered to be less straightforward. Having selected strategy B the substituents X' and Y' were chosen to be carbomethoxy and trimethylsilyloxy groups in order to ensure the desired cycloaddition regiochemistry (*i.e.* IX → VIII).[4b] Thus the trimethylsilyl cyclopentadienyl ether (*E*)-6a and its logical precursor, the cyclopentenone (*E*)-5, became the first synthetic targets.

[g] For clarity only the 5-substituted isomer is depicted; VII is one of three, and IX one of five, possible cyclopentadienes.

Results and Discussion

Synthesis of (*E*)-5.- The four-step synthesis of (*E*)-5 from 3-methoxy-2-cyclopentenone (1) is summarised in *Scheme 4*. Kinetic deprotonation of 1 in tetrahydrofuran (THF)/hexane at -70° followed by the addition of 2-(2-iodoethyl)-1,3-dioxolane (5 mole equiv.) in hexamethylphosphoramide (HMPA) afforded 2 in 53% yield. For this transformation a low reaction temperature and an excess of the alkylating

Scheme 4



i) LDA/THF-hexane, -70° then $I(CH_2)_2CH(OCH_2)_2$ (5 mole equiv.)/HMPA, -70°;
ii) MeLi/Et_2O-THF, -60° then aqueous NH_4Cl; iii) aqueous HCl;
iv) $(MeO)_2P(O)CH_2CO_2Me$/THF, 0°.

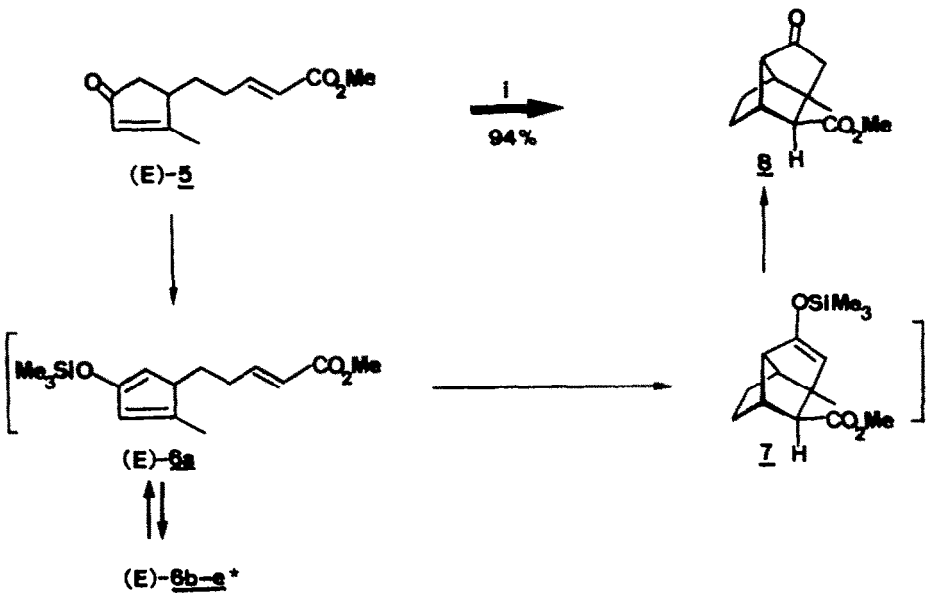
reagent are essential factors; requirements which are probably due to the instability and low reactivity of the lithium dienolate intermediate formed from 1. Treatment of 2 with methyllithium at -60° followed by an aqueous work-up gave the cyclopentenone 3 (87% yield) whose acetal group was hydrolysed with aqueous acid to furnish the ketoaldehyde 4. Finally, a Wadsworth-Emmons reaction using the sodium salt of methyl dimethylphosphonoacetate in THF at 0°[h] resulted in the formation of a 4:1 mixture (88% yield) of (*E*)- and (*Z*)-5 which was readily separated by column chromatography.

Formation and Intramolecular Diels-Alder Reaction of (*E*)-6a.- Treatment of (*E*)-5 with chlorotrimethylsilane (2.2 mole equiv.), triethylamine (2.5 mole equiv.) and anhydrous zinc chloride (0.1 mole equiv.)[9] in toluene at reflux during 72 h afforded directly, after either an aqueous or a non-aqueous work-up, the tricyclic ketoester 8 (m.p. 33-34°) in 94% yield (*cf. Scheme 5*). It is assumed that, out of the thermodynamic mixture of silyl cyclopentadienyl ethers (*E*)-6a-e[i] formed from (*E*)-5, only (*E*)-6a undergoes an intramolecular Diels-Alder reaction and is continually formed from (*E*)-6b-e *via* [1,5]-hydrogen shifts during the course of the reaction. The intermediacy of the cycloadduct 7 was confirmed by conducting the reaction under milder conditions (60°/4 h) whereupon, at partial conversion (*ca.* 15%), the presence of 7 could be verified by GC co-injection and ^{1}H-NMR spectral comparison with an authentic sample, independently prepared from 8 (*cf.* Experimental). Furthermore, a separate experiment demonstrated that 7 readily undergoes O-Si bond cleavage to give

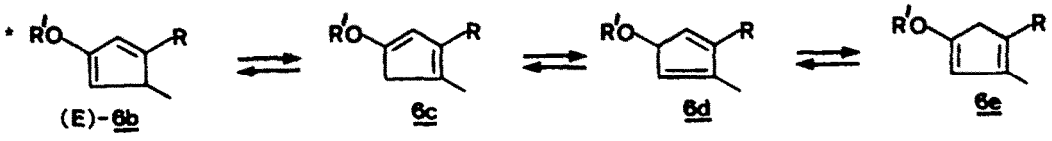
[h] A higher reaction temperature leads to undesired ring closure of (*E*)-5 and (*Z*)-5 to the bicyclic keto esters 10 and 11.

[i] (*E*)-6a is presumed to be a minor component of this mixture in which (*E*)-6c and (*E*)-6d are expected to be the major components. For the isomeric distribution of the trimethylsilyl cyclopentadienyl ethers derived from 3-ethyl-2-methyl-2-cyclopentenone using similar conditions, *cf.*[10]

Scheme 5



i) Me_3SiCl (2.2 mole equiv.)/Et_3N (2.5 mole equiv.)/anhydrous $ZnCl_2$ (0.1 mole equiv.) toluene, ↓, 72 h.

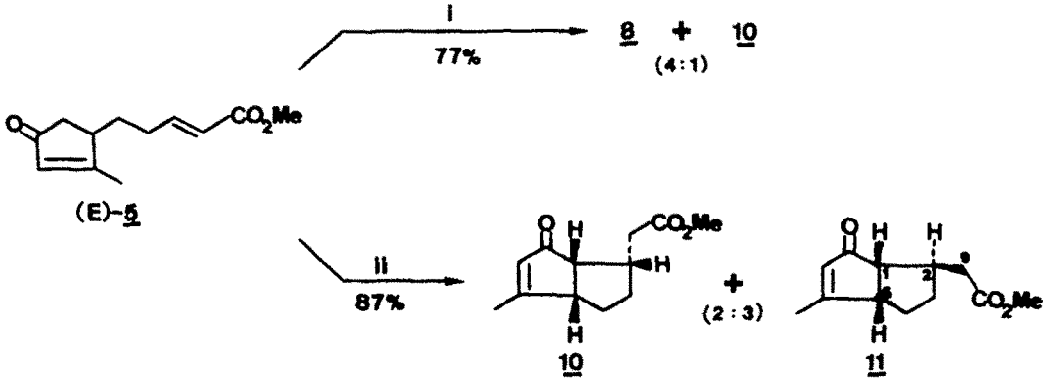


(R=CH_2CH_2CH=^{E}$CHCO_2Me$, R'=$SiMe_3$)

8 when treated with triethylamine hydrochloride in refluxing toluene in the presence of a catalytic amount of anhydrous zinc chloride.

An alternative access to (*E*)-6a, under kinetically controlled conditions, was also investigated Thus (*E*)-5 was treated with lithium diisopropylamide (LDA) at -70° in THF/hexane in the presence of

Scheme 6

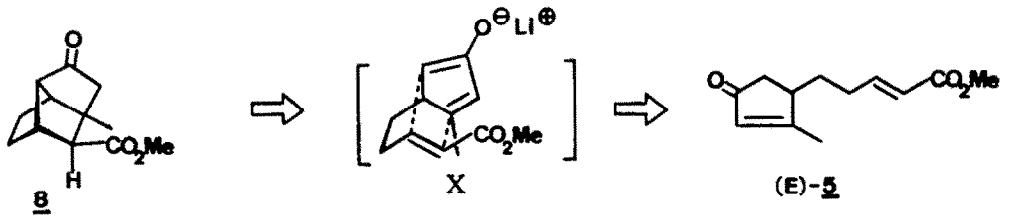


i) LDA (1 mole equiv.)/Me_3SiCl (excess)/THF-hexane, -70° then $H_3O^{\oplus}$; ii) LDA (1 mole equiv.) /THF-hexane, -70° then $H_3O^{\oplus}$.

an excess of chlorotrimethylsilane.[11] After 10 min at -70° a non-aqueous work-up followed by GC analysis indicated the major product to be 7 and subsequent acidic hydrolysis with aqueous HCl afforded a 4:1 mixture (77% yield) of 8 and the *cis*-fused bicyclooctane 10 (*cf. Scheme 6*).

Finally, another possible synthesis of 8 from (*E*)-5 was examined. The idea was that kinetic deprotonation of (*E*)-5 would form the lithium dienolate X which could then, in principle, undergo a double intramolecular Michael reaction[j] as indicated in *Scheme 7*. In the event treatment of (*E*)-5

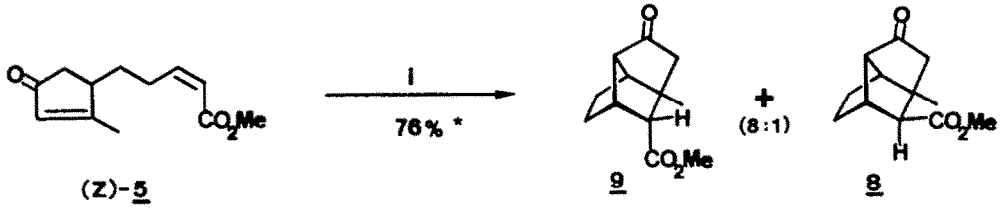
Scheme 7 Retrosynthetic analysis



with LDA at -70° in THF/hexane during 10 min followed by an aqueous quench and an extractive work-up afforded a 3:2 mixture of 11 and 10 in 87% yield[k] (*cf. Scheme 6*). Evidently the first Michael reaction, although efficient, is not stereoselective and the second step, ring closure to the desired tricyclic system, does not take place.[l] This approach to the synthesis of 8 was thus abandoned.

Formation and Intramolecular Diels-Alder Reaction of (*Z*)-6a.- Treatment of (*Z*)-5 with chlorotrimethylsilane, triethylamine and anhydrous zinc chloride under the same conditions as used for (*E*)-5 (*vide supra*) afforded a 8:1 mixture (76% yield[m]) of the epimeric keto esters 9 (m.p.

Scheme 8



i) Me_3SiCl (2.2 mole equiv.)/Et_3N (2.5 mole equiv.)/anhydrous $ZnCl_2$ (0.1 mole equiv./toluene, 4°, 72 h.

* yield calculated from converted (*Z*)-5 (*cf.* text)

[j] For examples of double intramolecular Michael reactions, *cf.*[12] and references quoted therein.

[k] The stereochemistries of 10 and 11 were assigned on the basis of their ^{1}H- NMR ($CDCl_3$) spectral data in which a major difference is the chemical shift and coupling of HC-1. In 10 this proton is a double doublet (δ 2.84), coupling with HC-5 (*J* 10 Hz) and HC-2 (*J* 6 Hz). In contrast, HC-1 in 11, shielded by *cis*-H_2C-9, appears as a double doublet at higher field (δ 2.52), coupling with HC-5 (*J* 6 Hz) and HC-2 (*J* 4 Hz). These stereochemical assignments were later corroborated by the conversion of 9 to 10 (*vide infra*).

[l] An experiment in which the reaction mixture was allowed to stand at room temperature during 16 h afforded an identical mixture of 10 and 11 (*ca.* 50% yield).

[m] This yield is calculated from converted (*E*)-5.

78-79°) and 8 (*ca.* 40% conversion) (*cf. Scheme 8*). Two observations are worthy of mention. Firstly, the transformation (*Z*)-5 → 9, believed to occur *via* a pathway analogous to that described previously for (*E*)-5 → 8, is slower than that with (*E*)-5 as substrate. Secondly, the partial formation of 8 from (*Z*)-5 indicates a *ca.* 10% loss of stereoselectivity which was not observed for (*E*)-5.

When (*Z*)-5 was treated with LDA at -70° in the presence of an excess of chlorotrimethylsilane followed by an aqueous work-up, using conditions identical with those employed for (*E*)-5, the only compounds identified (GC analysis) were unreacted (*Z*)-5 (40%) and 10 (*ca.* 6%). In addition treatment of (*Z*)-5 with LDA at -70° afforded a complex mixture from which only 10 and 11 (10:1 mixture, *ca.* 15% yield) could be identified.

Discussion.- The highly regio- and stereoselective transformations, (*E*)-5 → 8 and (*Z*)-5 → 9, are consistent with a mechanism which involves the concerted intramolecular Diels-Alder reactions of (*E*)-6a and (*Z*)-6a respectively.[n] The higher reaction rate of the former transformation would be thus a logical consequence of favourable secondary orbital interactions in the cycloaddition transition state where the carbomethoxy group is *endo* (in (*E*)-6a) rather than *exo* (in (*Z*)-6a). The slight loss in stereoselectivity exhibited by the formation of 9 from (*Z*)-5 may be an indication of a competing stepwise pathway or due to partial isomerisation of (*Z*)-6a-e to (*E*)-6a-e under the reaction conditions.[o] An alternative explanation of these results which would involve two consecutive intramolecular Mukaiyama-Michael reactions[p] cannot be excluded; indeed, the stereoselective formation of 10 from (*E*)- and (*Z*)-6a, albeit in low yields, are examples of this reaction. Compatible with either of these two mechanisms is the fact that when (*E*)-6a is selectively formed at low temperature it undergoes a remarkably smooth conversion to 7, whereas, under the same conditions, (*Z*)-6a remains essentially unchanged.[q]

Assuming kinetic control the poor stereoselectivity exhibited in the formation of 10 and 11 from (*E*)-5, *via* the intramolecular Michael reaction of X, is probably a consequence of the latter's conformational mobility. In contrast the low yields of 10 and 11 from the lithium dienolate of (*Z*)-5 show that the possible conformations available in this case are relatively less favoured towards cyclisation despite a marked preference for the formation of 10.

Synthesis of (±)-Sativene (26) from 8.- The synthesis of (±)-sativene (26) from 8 is described in *Scheme 9*. Protection of the ketone function in 8 as its ethylene acetal to give 12 (m.p. 45-46°) was followed by reduction to the alcohol 13. Aqueous acidic hydrolysis of the acetal group afforded the hydroxy ketone 14 (m.p. 131-133°) which was protected as its *tert*-butyldimethylsilyl ether 15 (m.p. 41-42°, 77% yield from 8). Formation of the silyl enol ether 16 *via* low temperature deprotonation of 15 (LDA/THF, -70°) followed by reaction of the intermediate lithium enolate with chlorotrimethylsilane afforded 16 (95% yield) which was treated with a zinc-copper couple and diiodomethane in refluxing ether[17] to furnish stereoselectively the (trimethylsilyloxy)cyclopropane 17[r] (77% yield).

[n] Both 8 and 9 are stable under the conditions of their formation. However, in methanolic sodium methoxide at reflux 9 is transformed to 10 (41%), the product of a retro-Michael reaction, and 8 (48%) which is stable under these conditions (*cf.* Experimental).

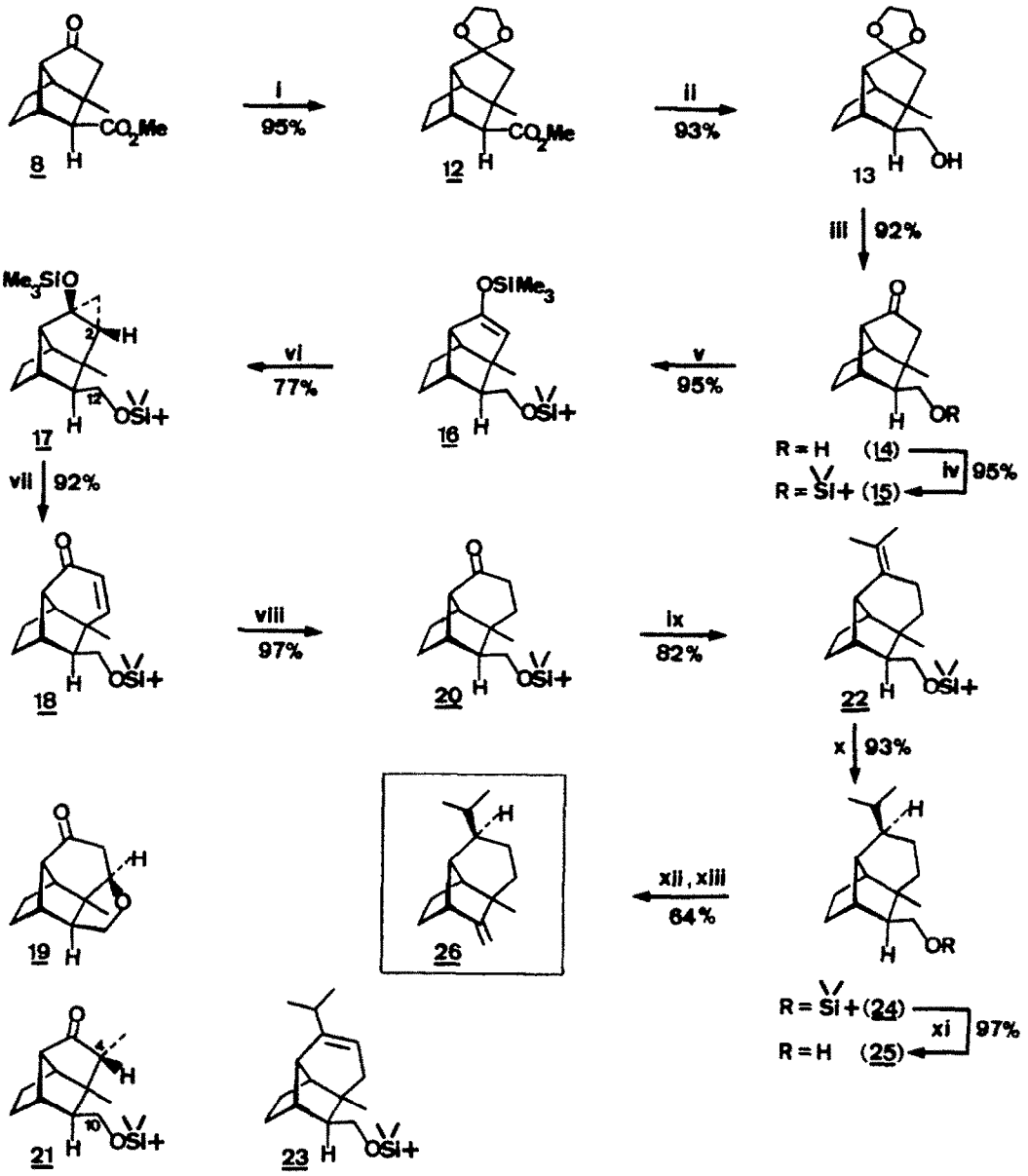
[o] Despite careful monitoring of the reaction by GC and ^{1}H-NMR analysis this isomerisation could not be detected.

[p] Usually effected under Lewis acid promotion the Mukaiyama-Michael reaction is the 1,4-addition of either a silyl enol ether or a silyl ketene acetal to a α,β-unsaturated carbonyl compound, *cf.*[13]; for recent work concerning the stereoselection of this reaction, *cf.*[14]; for examples of intramolecular versions, *cf.*[15]

[q] These low temperature reactions were effected in the presence of an excess of chlorotrimethylsilane which may possibly act as a Lewis acid catalyst; for a related activation of enones, *cf.*[16]

[r] The expected stereochemistry of 17, resulting from carbene addition on the less hindered *exo* face of 16, was confirmed by ^{1}H-NMR experiments in which a nuclear Overhauser effect (n.O.e.) was observed between H_2C-12 (δ_H 3.73) and HC-2 (δ_H 0.85). In addition the ^{13}C-NMR data, indicating the shielding of C-6 (δ_C 41.5) by C-3 (δ_C 11.5) and *vice versa*,[18] are consistent with the assigned stereochemistry.

Scheme 9 *Synthesis of (±)-eativene (26)*



i) $HO(CH_2)_2OH/H^{\oplus}$/toluene ↑↓; ii) $LiAlH_4/Et_2O$; iii) $H_3O^{\oplus}$; iv) *t*-$BuMe_2SiCl$/imidazole/DMF; v) LDA/THF, -70° then Me_3SiCl; vi) Zn-Cu couple/CH_2I_2/Et_2O ↑↓; vii) $FeCl_3$/pyridine-DMF-CH_2Cl_2; viii) H_2/Pd-C/EtOH; ix) $PH_3P{=}CMe_2$/DMSO-toluene, 60°; x) H_2/PtO_2/AcOH-AcOEt; xi) $H_3O^{\oplus}$; xii) Bu_3P/*o*-$O_2NC_6H_4SeCN$/pyridine/THF-HMPA; xiii) 30% aqueous H_2O_2/THF.

Following the procedure of Saegusa,[19] 17 was treated with anhydrous ferric chloride and pyridine in dimethylformamide (DMF)/CH_2Cl_2 to afford directly the ring expanded α,β-unsaturated ketone 18 (m.p. 74-75°; 92% yield).[s] Hydrogenation (5% Pd-C/H_2/ethanol) smoothly gave the tricyclic ketone 20 (m.p. 57-58°; 97% yield). The regioselective ring expansion of 15 to 20 had thus been efficiently accomplished in four steps (65% overall yield). Despite literature precedent in structurally related systems[20] basic hydrolysis (NaOH/methanol-water, 25°) of the trimethylsilyloxy group with concomitant cyclopropane ring opening was slow and non-selective, affording 20 in only 42% isolated yield, together with the isomeric tricyclic ketone 21[t] (m.p. 51-52°) as the principal side product (23%). Wittig reaction of 20 with the ylide prepared from isopropyltriphenylphosphonium iodide and potassium hydride in a solution of toluene and dimethylsulfoxide (DMSO) (60°/24 h) gave the tetrasubstituted alkene 22 (82% yield) which was hydrogenated (PtO_2/H_2/AcOH-AcOEt 3:1) to afford exclusively the *tert*-butyldimethylsilyl ether 24 (93% yield). GC analysis[u] during the course of this hydrogenation shows that 22 first isomerises to the isomeric trisubstituted alkene 23 which then undergoes stereoselective hydrogenation from the less hindered α-face. Finally deprotection of 24 by treatment with aqueous acid afforded the primary alcohol 25 (97% yield) which was converted into (±)-sativene (26) (64% yield) by using known methodology involving the intermediacy of a *o*-nitrophenylselenoxide.[21]

EXPERIMENTAL

All solvents were dried and distilled before use. Reactions involving air-sensitive reagents or substances were conducted under a N_2 atmosphere. LDA was freshly prepared from diisopropylamine (1.1 mole equiv.) and *n*-BuLi (*ca.* 15% solution in hexane (Chemetall) - analysis by Gilman's titration[22]) in THF at -30°. Work-up refers to: successive washing of the organic phase with water, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, drying over anhydrous Na_2SO_4, and removal of the solvent by distillation *in vacuo* (*i.v.*) using a rotary evaporator. Thin layer chromatography (TLC) was performed using Merck 0.25 mm (60 F 254) silica gel plates. Preparative column chromatography was carried out on silica gel (Merck, 0.06-0.20 mm). Gas chromatography (GC) (Hewlett-Packard 5890): capillary columns (10 m), Chrompack CPWAX 57CB and CP sil 5CB, 30 psi He. Melting points (m.p.) are uncorrected. Bulb-to-bulb distillation: Büchi GKR 50 apparatus with external temperature reading (bath). IR (Perkin-Elmer 297 spectrometer) spectra: liquid film unless otherwise specified, ν_{max} in cm-1. NMR spectra (Bruker WH 360 and Bruker HX 90) in $CDCl_3$, internal standard tetramethylsilane (δ = 0 ppm); abbreviations: *s* singlet, *d* doublet, *t* triplet, *q* quadruplet, *m* multiplet, br. broad, *J* spin-spin coupling constant (Hz). ^{1}H-NMR at 360 MHz, ^{13}C-NMR at 90.5 MHz. Mass spectra (MS) (Finnigan 4023c or Varian MAT 112); electron energy 70eV, signals are given in *m/z* (rel. %).

5-[2-(1,3-Dioxolan-2-yl)ethyl]-3-methoxy-2-cyclopentenone (2).- A solution of 3-methoxy-2-cyclopentenone (1) (9.6 g, 0.1 mol) in THF (75 ml) was added dropwise, during 30 min, to a mechanically stirred solution of LDA (0.11 mol) in THF/hexane 1:1 (150 ml) at -70°. After a further 30 min a solution of 2-(2-iodoethyl)-1,3-dioxolane (114 g, 0.5 mol) in HMPA (100 ml) was added dropwise during 45 min, maintaining the reaction temperature below -60°. After 72 h at -70° the mixture was poured into saturated aqueous NH_4Cl and extracted with AcOEt. Work-up and chromatography (AcOEt) gave 2 as a white crystalline solid (11.2 g, 53% yield). Sublimation (100-120° (bath)/0.01 Torr) of an aliquot afforded an analytical sample. M.p. 63-64°. Rf (AcOEt) 0.40.- IR ($CDCl_3$): 1695, 1600, 1360, 1240, 1165, 1135, 1030, 990.- ^{1}H-NMR: 1.52 (*m*, 1H); 1.72 (*m*, 2H); 1.96 (*m*, 1H); 2.31 (*m*, 1H); 2.53 (*m*, 1H); 2.77 (*m*, 1H); 3.80-4.00 (4H); 3.83 (*s*, 3H); 4.87 (*t*, *J* 4.5, 1H); 5.27 (*s*, 1H).- MS: 212 (4, M$^+$), 167 (14), 125 (12), 112 (78), 99 (14), 73 (100), 69 (12), 45 (17).- Found: C, 62.4; H 7.7. $C_{11}H_{16}O_4$ Requires: C, 62.3; H, 7.6.

[s] In an experiment in which basic conditions were not maintained during the aqueous work-up small amounts of the tetracyclic ketone 19 (b.p. 160-170° (bath)/0.3 Torr, Rf(CH_2Cl_2) 0.24) were isolated, formed presumably from 18 *via* hydrolysis of the *tert*-butyldimethylsilyl ether and ring closure of the resulting hydroxy ketone.- Spectral data of 19, IR: 1708, 1402, 1360, 1290, 1180, 792.- ^{1}H-NMR: 1.31 (*s*, 3H); 1.32 (*m*, 1H); 1.60 (*m*, 1H); 1.64-1.76 (3H); 2.23 (broad *s*, 1H); 2.29 (*d*, *J* 4, 1H); 2.37 (*dd*, *J* 16 and 1.5, 1H); 2.38 (*m*, 1H); 2.55 (*dd*, *J* 17 and 6, 1H); 3.14 (*dd*, *J* 10 and 7, 1H); 4.15 (*d*, *J* 7, 1H); 4.20 (*dd*, *J* 10 and 10, 1H).- ^{13}C-NMR: 212.3 (*s*), 81.7 (*d*), 72.2 (*t*), 59.2 (*d*), 53.5 (*d*), 52.5 (*s*), 47.2 (*d*), 45.2 (*t*), 44.7 (*d*), 30.1 (*t*), 22.8 (*t*), 21.7 (*q*).- MS: 192 (100, M$^+$), 174(18), 148 (46), 131 (54), 122 (61), 105 (66), 91 (70), 79 (70).

[t] The C-4 stereochemistry of 21 was confirmed by ^{1}H-NMR (n.O.e.) experiments in which irradiation of H_2C-10 (δ 3.46) results in a signal enhancement of HC-4 (δ 2.14).

[u] The GC retention times (column: CPsil 5CB, program: 160°(2 min) → 220° (5°/min)) of 22, 23, and 24 are 3.06, 2.45, and 2.88 min respectively.

4-[2-(1,3-Dioxolan-2-yl)ethyl]-3-methyl-2-cyclopentenone (3).- A solution of MeLi in ether (40 ml of a *ca.* 1.5M solution, *i.e.* 60 mmol (Fluka)) was added dropwise, during 30 min, to a stirred solution of 2 (10.6 g, 50 mmol) in THF (100 ml) at -70°. After 4 h at -70° the mixture was poured into saturated aqueous NH_4Cl and extracted with AcOEt. Work-up, chromatography (AcOEt), and bulb-to-bulb distillation *i.v.* gave 3 as a pale-yellow oil (8.5 g, 87% yield). Rf (AcOEt) 0.52. B.p. 120-140° (bath) /0.4 Torr.- IR: 1680, 1612, 1430, 1400, 1370, 1175, 1125, 1025.- ^{1}H-NMR: 1.44 (*m*, 1H; 1.66 (*m*, 2H); 1.94 (*m*, 1H); 2.11 (4H); 2.56 (*dd*, *J* 18 and 6.5, 1H); 2.82 (*m*, 1H); 3.82-4.02 (4H); 4.88 (*t*, *J* 5, 1H); 5.92 (*s*, 1H).- MS: 196 (1, M$^+$), 109 (12), 99 (23), 79 (100), 45 (19).- Found: C, 67.2; H, 8.1. $C_{11}H_{16}O_3$ Requires: C, 67.3; H, 8.2.

3-(2-Methyl-4-oxo-2-cyclopentenyl)propanal (4).- A mixture of 3 (8.23 g, 42 mmol), ether (100 ml) and 1N HCl (100 ml) was stirred vigorously during 3 h at room temperature. The mixture was then poured into an excess of saturated aqueous $NaHCO_3$ and continuously extracted with AcOEt. Work-up, chromatography (AcOEt), and bulb-to-bulb distillation *i.v.* gave 4 as a pale-yellow oil (5.2 g, 81% yield). B.p. 110-120° (bath)/0.2 Torr. Rf (AcOEt) 0.45.- IR: 1700, 1615, 1430, 1405, 1372, 1180, 1135.- ^{1}H-NMR: 1.53 (*m*, 1H); 2.03 (*dd*, *J* 16 and 2.5, 1H); 2.12 (*s*, 3H); 2.20 (*m*, 1H); 2.50 (*t*, *J* 9, 2H); 2.56 (*dd*, *J* 16 and 7, 1H); 2.82 (*m*, 1H); 5.95 (*s*, 1H); 9.82 (*s*, 1H).- MS: 152 (1, M$^+$), 124 (20), 109 (100), 96 (85), 80 (31), 67 (51).- Found: C, 70.9; H, 7.8. $C_9H_{12}O_2$ Requires: C, 71.0; H, 8.0.

Methyl (*E*)-5-(2-methyl-4-oxo-2-cyclopentenyl)-2-pentenoate ((*E*)-5) and methyl (*Z*)-5-(2-methyl-4-oxo-2-cyclopentenyl)-2-pentenoate ((*Z*)-5).- A solution of methyl dimethylphosphonoacetate (6.92 g, 38 mmol) in THF (20 ml) was added dropwise, during 30 min, to a slurry of NaH (*ca.* 55-60% dispersion in oil (Fluka); 840 mg, 35 mmol) in THF (130 ml) at room temperature. After 1 h the mixture was cooled to 0° and a solution of 4 (5 g, 33 mmol) in THF (20 ml) was added dropwise during 20 min. After a further 20 min at 0-5° the mixture was poured into saturated aqueous NH_4Cl (400 ml) and extracted with ether. Work-up afforded a crude 4:1 mixture of (*E*)-5 and (*Z*)-5 which was separated by chromatography (AcOEt/cyclohexane 1:1).- (*E*)-5, colourless oil (4.9 g, 71% yield). B.p. 142-144°/ 0.15 Torr. Rf (CH_2Cl_2) 0.10.- IR: 1710, 1655, 1620, 1435, 1380, 1275, 1030, 975, 920.- ^{1}H-NMR: 1.41 (*m*, 1H); 1.97 (*m*, 1H); 2.09 (*dd*, *J* 18.5 and 2.5, 1H); 2.10 (*s*, 3H); 2.24 (*m*, 2H); 2.56 (*dd*, *J* 18.5 and 6.5, 1H); 2.80 (*m*, 1H); 3.74 (*s*, 3H); 5.96 (*tt*, *J* 15 and 2, 1H); 5.94 (*s*, 1H); 6.96 (*dd*, *J* 15 and 7, 1H).- ^{13}C-NMR: 207.7 (*s*), 180.2 (*s*), 166.7 (*s*), 147.7 (*d*), 131.3 (*d*), 121.9 (*d*), 51.4 (*q*), 43.7 (*d*), 41.5 (*t*), 31.1 (*t*), 29.7 (*t*), 17.3 (*q*).- MS:208 (2, M$^+$), 177 (7), 148 (9), 134 (8), 109 (75), 96 (100), 81 (27), 67 (27).- Found: C, 69.0; H, 7.9. $C_{12}H_{16}O_3$ Requires: C, 69.2; H, 7.7. (*Z*)-5, colourless oil (1.2 g, 17% yield). B.p. 138-140°/0.15 Torr. Rf (CH_2Cl_2) 0.11.- IR: 1710, 1650, 1620, 1440, 1410, 1380, 1200, 1020, 822.- ^{1}H-NMR: 1.41 (*m*, 1H); 1.94 (*m*, 1H); 2.12 (*s*, 3H); 2.18 (*dd*, *J* 18.5 and 2.5, 1H); 2.58 (*dd*, *J* 18.5 and 7, 1H); 2.63 (*m*, 2H); 2.81 (*m*, 1H); 3.72 (*s*, 3H); 5.83 (*tt*, *J* 11 and 2, 1H); 5.93 (*s*, 1H); 6.23 (*tt*, *J* 11 and 7, 1H).- MS: 208 (1, M$^+$), 177 (3), 148 (3), 133 (4), 109 (100), 96 (28), 81 (20), 67 (15).- Found: C, 69.4; H, 7.8. $C_{12}H_{16}O_3$ Requires: C, 69.2; H, 7.7.

Methyl (1*RS*, 2*SR*, 3*RS*, 6*SR*, 7*RS*)-1-methyl-8-oxotricyclo[4.3.0.0^{3,7}]nonane-2-carboxylate (8).- A solution of (*E*)-5 (4.16 g, 20mmol) in toluene (20 ml) was added dropwise, during 10 min, to a stirred slurry of anhydrous $ZnCl_2$ (280 mg, 2 mmol) in a solution of Et_3N (5g, 50 mmol) in toluene at room temperature. Chlorotrimethylsilane (4.8 g, 44 mmol) was then added dropwise, during 15 min, and the mixture was heated under reflux (bath temperature: 130°) during 72 h. After cooling, the mixture was poured into saturated aqueous $NaHCO_3$ (150 ml) and extracted with ether. Work-up and distillation *i.v.* afforded 8 as a colourless oil (3.95 g (GC purity 97%), 92% yield), b.p. 114-116°/0.25 Torr. An aliquot was purified by chromatography (AcOEt/cyclohexane 1:1) to afford pure 8 as a white, crystalline solid, m.p. 33-34°. Rf (CH_2Cl_2) 0.17.- IR ($CDCl_3$): 1730 br., 1436, 1360, 1308, 1295, 1235, 1210.- ^{1}H-NMR: 1.32 (*s*, 3H); 1.50-1.80 (4H); 1.88 (AB system, *J* 17 and 2, 2H); 2.04 (br. *s*, 1H); 2.22 (br. *s*, 1H); 2.39 (br. *s*, 1H); 2.71 (br. *s*, 1H); 3.66 (*s*, 3H).- ^{13}C-NMR: 214.0 (*s*), 173.1 (*s*), 61.3 (*d*), 54.6 (*d*), 52.6 (*d*), 51.5 (*q*), 49.6 (*s*), 48.3 (*t*), 44.4 (*d*), 32.9 (*t*), 20.7 (*t*), 16.9 (*q*).- MS: 208 (25, M$^+$), 176 (29), 148 (60), 121 (28), 114 (25), 109 (100), 67 (58).- Found: C, 69.2; H, 7.8. $C_{12}H_{16}O_3$ Requires: C, 69.2; H, 7.7.

A solution of chlorotrimethylsilane (326 mg, 3 mmol) in THF (1 ml) was added dropwise to a stirred solution of LDA (0.55 mmol) in THF/hexane 5:1 (2.5 ml) at -70°. To this mixture at -70° was now added dropwise a solution of (*E*)-5 (104 mg, 0.5 mmol) in THF (0.5 ml). After 10 min at -70° Et_3N (500 mg, 5 mmol) was added and the mixture was poured into petroleum ether 30-50 (20 ml). Filtration (Hyflo) and removal of solvent afforded a colourless oil (*ca.* 150 mg) containing 7 as major component (*ca.* 62% yield, GC and ^{1}H-NMR analysis) which was dissolved in ether (5 ml) and stirred with 1N HCl (5 ml) during 16 h. Work-up and bulb-to-bulb distillation *i.v.* afforded a 4:1 mixture of 8 and 10 (93 mg (GC purity 86%), 77% yield).

Methyl (1*RS*, 2*RS*, 3*RS*, 6*SR*, 7*RS*)-1-methyl-8-oxotricyclo[4.3.0.0^{3,7}]nonane-2-carboxylate (9).- A solution of (*Z*)-5 (416 mg, 2 mmol) in toluene (2 ml) was added dropwise, during 10 min, to a stirred slurry of anhydrous $ZnCl_2$ (30 mg) in a solution of Et_3N (500 mg, 5 mmol) in toluene (8 ml) at room temperature. A solution of chlorotrimethylsilane (480 mg, 4.4 mmol) in toluene (2 ml) was then added dropwise, during 10 min, and the mixture was heated under reflux (bath temperature 130°) during 72 h. After cooling, the mixture was poured into saturated aqueous $NaHCO_3$ (30 ml) and extracted with ether. Work-up and bulb-to-bulb distillation *i.v.* afforded an oil (b.p. 120-150°/0.1 Torr) containing a 8:1 mixture of 9 and 8 which was separated by chromatography (CH_2Cl_2) to afford pure 9 as a white crystalline solid (145 mg, 35% yield). M.p. 78-79°. Rf (CH_2Cl_2) 0.26.- IR ($CDCl_3$): 1730 br., 1430, 1364, 1300, 1270, 1045, 1012.- ^{1}H-NMR: 1.32 (*s*, 3H); 1.55-1.72 (3H); 1.96 (*dd*, *J* 7 and 7, 1H); 1.99 (AB system, *J* 17, 2H); 2.25 (*d*, *J* 4, 1H); 2.35 (*d*, *J* 6, 1H); 2.42 (*m*, 1H); 2.63 (br. *s*, 1H); 3.64 (*s*, 3H).- ^{13}C-NMR: 215.1 (*s*), 172.4 (*s*), 62.1 (*d*), 56.1 (*t*), 55.0 (*d*), 51.2 (*q*), 49.6 (*d*), 46.9 (*s*), 44.6 (*d*), 28.1 (*t*), 21.0 (*t*), 15.1 (*q*).- MS: 208 (23, M$^+$), 176 (20), 148 (37), 121 (29), 114 (56), 109 (57), 96 (100), 79 (27), 67 (87).- Found: C, 69.2; H, 7.6. $C_{12}H_{16}O_3$ Requires: C, 69.2; H, 7.7.

(*Z*)-5 (104 mg, 0.5 mmol) was treated under conditions identical to those described previously for the conversion of (*E*)-5 to 8 and 10 (4:1 mixture), *i.e.* chlorotrimethylsilane (excess)/LDA/THF-hexane 5:1, -70°. Work-up and bulb-to-bulb distillation *i.v.* afforded a 8:1 mixture of (*Z*)-5 and 10 (82 mg (GC purity 75%), 59% yield).

Epimerisation of 9.- A solution of 9 (104 mg, 0.5 mmol) in methanol (3 ml) containing sodium methoxide (27 mg, 0.5 mmol) was refluxed during 72 h. The cooled mixture was poured into saturated aqueous NH_4Cl and extracted with ether. Work-up and bulb-to-bulb distillation *i.v.*(120-150° (bath)/0.1 Torr) afforded a colourless oil (95 mg) consisting of a mixture of 9 (3%), 8 (52%), and 10 (45%) (GC analysis).

Methyl (1*RS*, 2*SR*, 3*SR*, 6*SR*, 7*RS*)-1-methyl-8-oxo-9-(trimethylsilyloxy)tricyclo[4.3.0.$0^{3,7}$]non-9-ene-2-carboxylate (11).- A solution of chlorotrimethylsilane (550 mg, 5.1 mmol) in THF (2 ml) was added dropwise, during 10 min, to a stirred solution of LDA (1.1 mmol) in THF/hexane 5:1 (5 ml) at -70°. After 10 min at -70° a solution of 8 (208 mg, 1 mmol) in THF (1 ml) was added dropwise, during 5 min, maintaining the reaction temperature below -65°. After a further 10 min at -70° Et_3N (707 mg, 7 mmol) was added, the mixture was poured into saturated aqueous $NaHCO_3$ (30 ml) and then extracted with petroleum ether 30-50. Work-up and bulb-to-bulb distillation *i.v.* afforded 7 as a colourless oil (265 mg (GC purity 92%), 85% yield). B.p. 120-130° (bath)/0.2 Torr.- IR: 1730, 1606, 1340, 1250, 1198, 1174, 1128, 840, 754.- ^{1}H-NMR: 0.19 (*s*, 9H); 1.22 (*tt*, *J* 13 and 7, 1H); 1.30 (*s*, 3H); 1.33 (*m*, 1H); 1.69 (*m*, 1H); 1.75 (*m*, 1H); 2.04 (br. *s*, 1H); 2.05 (*s*, 1H); 2.33 (br. *s*, 1H); 2.54 (br. *s*, 1H); 3.60 (*s*, 3H); 4.38 (*s*, 1H).- ^{13}C-NMR: 174.2 (*s*), 158.8 (*s*), 105.2 (*d*), 65.9 (*d*), 56.5 (*d*), 56.3 (*d*), 55.4 (*s*), 51.1 (*q*), 41.2 (*d*), 33.9 (*t*), 19.3 (*t*), 16.1 (*q*), 0.10 (3 *q*).- MS: 280 (12, M$^+$), 249 (4), 221 (4), 181 (100), 168 (20), 73 (62).

Methyl (1*RS*, 5*SR*, 6*SR*)-(6-methyl-8-oxobicyclo[3.3.0]oct-6-ene-2-yl)acetate (10) and methyl (1*RS*, 5*SR*, 6*RS*)-(6-methyl-8-oxobicyclo[3.3.0]oct-6-ene-2-yl)acetate (11).- A solution of (*E*)-5 (208 mg, 1 mmol) in THF (1 ml) was added dropwise to a stirred solution of LDA (1.1 mmol) in THF/hexane 5:1 (5 ml) at -70°. After 10 min at -70° the mixture was poured into saturated aqueous NH_4Cl (10 ml) and extracted with ether. Work-up and bulb-to-bulb distillation *i.v.* (140-160° (bath)/0.1 Torr) gave a 2:3 mixture of 10 and 11 which was separated by column chromatography (AcOEt/cyclohexane 1:1).
10, colourless oil (70 mg, 34% yield). Rf (CH_2Cl_2) 0.12.- IR: 1740, 1695, 1625, 1430, 1380, 1150, 1015, 995, 920, 875.- ^{1}H-NMR: 1.03 (*m*, 1H); 1.70-1.80 (3H); 2.09 (*s*, 3H); 2.30 (*dd*, *J* 16 and 8, 1H); 2.44 (*m*, 1H); 2.75 (*dd*, *J* 16 and 7, 1H); 2.84 (*dd*, *J* 10 and 6, 1H); 3.20 (*m*,1H); 3.70 (*s*, 3H); 5.90 (*s*, 1H).- ^{13}C-NMR: 209.8 (*s*), 180.0 (*s*), 173.7 (*s*), 132.4 (*d*), 52.0 (*d*), 51.5 (*q*), 50.2 (*d*), 38.3 (*d*), 34.8 (*t*), 29.5 (*t*), 27.6 (*t*), 17.7 (*q*).- MS: 208 (15, M$^+$), 176 (27), 148 (52), 133(17), 120 (17), 109 (100), 91 (22).- Found: C, 69.0; H, 7.7. $C_{12}H_{16}O_3$ Requires: C, 69.2; H, 7.7.
11, colourless oil (110 mg, 53% yield). Rf (CH_2Cl_2) 0.11.- IR: 1740, 1695, 1620, 1430, 1380, 1020, 952, 912.- ^{1}H-NMR: 1.51 (*m*, 2H); 1.71 (*m*, 1H); 1.95 (*m*, 1H); 2.09 (*s*, 3H); 2.33 (*dd*, *J* 15 and 8, 1H); 2.47 (*m*, 1H); 2.52 (*dd*, *J* 6 and 4, 1H); 2.57 (*dd*, *J* 15 and 6, 1H); 3.20 (*m*, 1H); 3.69 (*s*, 3H); 5.80 (*s*, 1H).- ^{13}C-NMR: 210.4 (*s*), 180.2 (*s*), 172.7 (*s*), 129.6 (*d*), 56.9 (*d*), 51.5 (*q*), 49.8 (*d*), 38.7 (*d*), 38.7 (*t*), 31.6 (*t*), 27.2 (*t*), 17.8 (*q*).- MS: 208 (38, M$^+$), 176 (67), 148 (73), 134 (100), 108 (79), 91 (55).- Found: C, 69.1; H, 7.7. $C_{12}H_{16}O_3$ Requires: C, 69.2; H 7.7.

Methyl (1*RS*, 2*SR*, 3*RS*, 6*SR*, 7*RS*)-1-methyl-8-oxotricyclo[4.3.0.0^{3,7}]nonane-2-carboxylate ethylene acetal (12).- A solution of 8 (3.12 g, 15 mmol) and ethylene glycol (1.48 g, 24 mmol) in toluene (50 ml) containing *p*-TsOH (300 mg) was refluxed during 6 h with continuous removal of water formed during the reaction (Dean-Stark apparatus). The mixture was cooled and washed with saturated aqueous $NaHCO_3$. Work-up and distillation *i.v.* afforded 12 as a colourless oil, b.p. 112-114°/0.2 Torr, which crystallised at room temperature to a white crystalline solid (3.6 g, 95% yield). M.p. 45-46°. Rf (CH_2Cl_2) 0.32.- IR ($CDCl_3$): 2960, 2900, 1730, 1620, 1440, 1350, 1322, 1312, 1240, 1220, 1180, 1106, 1090, 1020, 860.- ^{1}H-NMR: 1.20(*s*, 3H); 1.40-1.65 (4H); 1.63 (*dd*, *J* 13 and 2, 1H); 1.78 (br. *s*, 1H); 1.94 (*d*, *J* 13, 1H); 1.95-1.99 (2H); 2.64 (br. *s*, 1H); 3.68 (*s*, 3H); 3.77-3.95 (4H).- ^{13}C-NMR: 173.7 (*s*), 113.4 (*s*), 64.9 (*t*), 63.8 (*t*), 55.5 (*d*), 54.0 (*d*), 52.1 (*d*), 51.2 (*q*), 49.4 (*s*), 46.0 (*t*), 40.7 (*d*), 32.8 (*t*), 20.5 (*t*), 17.6 (*q*).- MS: 252 (22, M$^+$), 237 (10), 193 (22), 184 (15), 153 (47), 139 (100), 86 (36).- Found: C, 66.5; H, 8.1. $C_{14}H_{20}O_4$ Requires: C, 66.6; H, 8.0.

(1*RS*, 2*RS*, 3*SR*, 6*SR*, 7*RS*)-2-(Hydroxymethyl)-3-methyltricyclo[4.3.0.0^{3,7}]nonan-5-one ethylene acetal (13).- A solution of 12 (3.3 g, 13 mmol) in ether (15 ml) was added dropwise, during 15 min, to a stirred slurry of $LiAlH_4$ (490 mg, 13 mmol) in ether (20 ml) at 0-5°. After 1 h at 5° the mixture was treated successively, under rapid stirring, with water (0.5 ml), 4N NaOH (0.5 ml), and water (1.5 ml). Filtration (Hyflo), evaporation of solvent, and bulb-to-bulb distillation *i.v.* afforded 13 as a colourless oil (2.7 g, 93% yield). B.p. 150-160° (bath)/0.1 Torr. Rf (CH_2Cl_2) 0.08, Rf (AcOEt) 0.69.- IR: 3400 br., 1460, 1440, 1335, 1300, 1200, 1080, 980, 940, 892, 840.- ^{1}H-NMR (+D_2O): 1.04 (*s*, 3H); 1.10 (*t*, *J* 7, 1H); 1.36-1.60 (4H); 1.55 (*dd*, *J* 14 and 2, 1H); 1.80 (*d*, *J* 14, 1H); 1.90 (*m*, 1H); 1.92 (br. *s*, 1H); 2.00 (br. *s*, 1H); 3.70 (*dd*, *J* 11 and 7, 1H; 3.80-3.96 (5H).- ^{13}C-NMR: 113.9 (*s*), 64.6 (*t*), 63.6 (*t*), 62.4 (*t*), 55.8 (*d*), 53.8 (*d*), 49.5 (*d*), 48.0 (*s*), 44.8 (*t*), 40.8 (*d*), 33.4 (*t*), 20.4 (*t*), 17.4 (*q*).- MS: 224 (10, M$^+$), 209 (15), 193 (25), 156 (51), 139 (100), 112 (56).- Found: C, 69.7 ; H, 9.0. $C_{13}H_{20}O_3$ Requires: C, 69.6; H, 9.0.

(1*RS*, 2*RS*, 3*SR*, 6*SR*, 7*RS*)-2-(Hydroxymethyl)-3-methyltricyclo[4.3.0.0^{3,7}]nonan-5-one (14).- A solution of 13 (2.5 g, 11 mmol) in ether (20 ml) was vigorously stirred with 1N HCl (50 ml) at room temperature during 16 h. Separation of the phases, extraction of the aqueous phase with ether, work-up, and chromatography (AcOEt/cyclohexane 1:1) afforded 14 as a white crystalline solid (1.85 g, 92% yield). Sublimation *i.v.* (140-150° (bath)/0.2 Torr) furnished an analytical sample of 14, m.p. 131-133°. Rf (AcOEt) 0.60.- IR ($CDCl_3$): 3625, 3450 br., 1730, 1420, 1380, 1280, 1078.- ^{1}H-NMR (+D_2O): 1.21 (*s*, 3H); 1.32 (*t*, *J* 7, 1H); 1.58-1.80 (4H); 1.80 (br. *s*, 1H); 1.84 (*d*, *J* 17, 1H); 2.16 (*d*, *J* 17, 1H); 2.17 (br. *s*, 1H); 2.31 (br. *s*, 1H); 3.50 (*d*, *J* 7, 2H).- ^{13}C-NMR: 218.0 (*s*), 62.3 (*t*), 61.3

(*d*), 56.0 (*d*), 49.0 (*d*), 47.6 (*s*), 47.6 (*t*), 46.1 (*d*), 33.9 (*t*), 20.7 (*t*), 17.1 (*q*).- MS: 180 (16, M+), 162 (15), 147 (9), 134 (13), 119 (10), 105 (10), 93 (17) 79 (19), 67 (100).- Found: C, 73.3; H, 9.0. $C_{11}H_{16}O_2$ Requires: C, 73.3; H, 9.0.

Compound 14 was also prepared from 12 without isolation of 13: a solution of 12 (126 mg, 0.5 mmol) in ether (2 ml) was added dropwise to a stirred slurry of $LiAlH_4$ (20 mg, 0.53 mmol) in ether (5 ml) at 0-5°. After 1 h at 5° the mixture was poured cautiously into cold 1N HCl (20 ml). Following the procedure described above (for 13 → 14) resulted in the isolation of 14 (80 mg, 89%), identical to an authentic sample.

(1*RS*, 2*RS*, 3*R*, 6*RS*, 7*RS*)-3-(*tert*-Butyldimethylsilyloxy)methyl-3-methyltricyclo[4.3.0.0^{2,7}]nonan-5-one (15).- A solution of *tert*-butyldimethylchlorosilane (1.8 g, 12 mmol) in DMF (6 ml) was added dropwise to a stirred solution of 14 (1.8 g, 10 mmol) and imidazole (880 mg, 12.9 mmol) in DMF (14 ml) at room temperature. After 3 h the mixture was poured into saturated aqueous NH_4Cl (100 ml) and extracted with ether. Work-up, chromatography (CH_2Cl_2), and bulb-to-bulb distillation *i.v.* (140-150° (bath)/0.2 Torr) afforded 15 as a colourless oil, which crystallised at room temperature to a white solid (2.8 g, 95% yield). M.p. 41-42°. Rf (CH_2Cl_2) 0.56.- IR: 1740, 1470, 1390, 1360, 1260, 1195, 1008.- ^{1}H-NMR: 0.02 (*s*, 6H); 0.88 (*s*, 9H); 1.20 (*s*, 3H); 1.30 (*t*, *J* 8, 1H); 1.50-1.75 (4H); 1.82 (*d*, *J* 17, 1H); 2.01 (br. *s*, 1H); 2.22 (*d*, *J* 17, 1H); 2.26 (br. *s*, 1H); 3.37 (*dd*, *J* 10 and 9, 1H); 3.53 (*dd*, *J* 10 and 7, 1H).- ^{13}C-NMR: 217.1 (*s*), 62.8 (*t*), 61.2 (*d*), 56.0 (*d*), 48.9 (*d*), 47.6 (*s*), 47.5 (*t*), 45.5 (*d*), 33.8 (*t*), 25.9 (3 *q*), 20.7 (*t*), 18.2 (*s*), 17.5 (*q*), -5.5 (2 *q*).- MS: 294 (0, M+), 279 (2), 237 (99), 207 (8), 145 (77), 105 (34), 93 (31), 75 (100).- Found: C, 69.1; H, 10.4. $C_{17}H_{30}O_2Si$ Requires: C, 69.3; H, 10.3.

(1*RS*, 3*RS*, 5*R*, 6*RS*, 7*RS*)-3-(*tert*-Butyldimethylsilyloxy)methyl-3-methyl-5-(trimethylsilyloxy)tricyclo[4.3.0.0^{3,7}]non-4-ene (16).- A solution of 15 (2.7 g, 9.5 mmol) in THF (10 ml) was added dropwise, during 10 min, to a stirred solution of LDA (10 mmol) in THF (prepared from 1.4 ml of BuLi and 1.4 ml of diisopropylamine in 40 ml of THF) at -70°. After 10 min at -70° a solution of chlorotrimethylsilane (2.2 g, 20 mmol) in THF (5 ml) was added dropwise during 5 min.. After a further 10 min at -70° Et_3N (3 g, 30 mmol) was added dropwise and the mixture was poured into pentane (160 ml). Filtration (Hyflo), evaporation of solvent, and bulb-to-bulb distillation *i.v.* gave 16 as a colourless oil (3.2 g, 95% yield). B.p. 140-160° (bath/0.05 Torr).- IR: 1608, 1460, 1340, 1246, 1216, 1078, 930, 890, 840, 766.- ^{1}H-NMR: 0.02 (*s*, 6H); 0.22 (*s*, 9H); 0.88 (*s*, 9H); 1.13 (*s*, 3H); 1.26 (2H); 1.37 (*t*, *J* 7, 1H); 1.62 (*m*, 1H); 1.70 (br. *s*, 1H); 1.75 (*m*, 1H); 1.99 (br. *s*, 1H); 2.19 (br. *s*, 1H); 3.38 (*m*, 2H); 4.46 (*s*, 1H).- ^{13}C-NMR: 156.6 (*s*), 106.1 (*d*), 66.5 (*d*), 64.4 (*t*), 56.2 (*d*), 54.2 (*d*), 53.2 (*s*), 41.6 (*d*), 34.8 (*t*), 25.9 (3 *q*), 19.0 (*t*), 18.1 (*s*), 16.1 (*q*), -0.06 (3 *q*), -5.4 (2 *q*).- MS: 366 (7, M+), 234 (8), 221 (17), 181 (95), 168 (100), 73 (96).- Found: C, 65.5; H, 10.4. $C_{20}H_{38}O_2Si_2$ Requires: C, 65.5; H, 10.5.

(1*RS*, 2*RS*, 4*RS*, 5*RS*, 6*SR*, 9*SR*, 10*SR*)-10-(*tert*-Butyldimethylsilyloxy)methyl-1-methyl-4-(trimethylsilyloxy)tetracyclo[4.4.0.0^{2,4}.0^{5,9}]decane (17).- A solution of 16 (2 g, 5.5 mmol) in ether (5 ml) was added dropwise, during 5 min, to a stirred slurry of freshly prepared Zn-Cu couple (22 mmol) in ether (20 ml) at room temperature. A solution of CH_2I_2 (2.95 g, 11 mmol) in ether (10 ml) was then added dropwise and the mixture was stirred under reflux during 20 h. Filtration of the cooled mixture (Hyflo), evaporation of solvent, flash chromatography[23] (CH_2Cl_2), and bulb-to-bulb distillation *i.v.* afforded 17 as a colourless oil (1.74 g (GC purity 92%), 77% yield). B.p. 150-160° (bath)/0.3 Torr. Rf (cyclohexane) 0.20.- IR: 1450, 1360, 1318, 1250, 1230, 1100, 1060, 924, 890, 840, 778.- ^{1}H-NMR: 0.01 (*s*, 6H); 0.13 (*s*, 9H); 0.46 (*m*, 1H); 0.84 (*m*, 1H); 0.85 (br, *s*, 1H); 0.91 (*s*, 9H); 1.03 (*s*, 3H); 1.14 (*t*, *J* 7, 1H); 1.22 (br. *s*, 1H); 1.24-1.50 (4H); 1.99 (br. *s*, 1H); 2.06 (br. *s*, 1H); 3.73 (*m*, 2H).- ^{13}C-NMR:63.1 (*t*), 59.7 (*s*), 54.4 (*d*), 52.3 (*d*), 46.7 (*s*), 46.5 (*d*), 41.5 (*d*), 33.1 (*t*), 26.1 (3 *q*), 23.7 (*d*), 19.6 (*t*), 18.3 (*s*), 15.5 (*q*), 11.2 (*t*), 0.93 (3 *q*), -5.2 (2 *q*).- MS: 380 (0.5, M+), 323 (20), 248 (18), 193 (90), 159 (100), 147 (83), 73 (98).

(1*RS*, 2*SR*, 6*SR*, 7*RS*, 8*RS*)-7-(*tert*-Butyldimethylsilyloxy)methyl-6-methyltricyclo[4.4.0.0^{2,8}]dec-4-en-3-one (18).- A solution of 17 (1.33 g (GC purity 92%), 3.2 mmol) in CH_2Cl_2 (5 ml) was added dropwise, during 10 min, to a stirred solution of $FeCl_3$ (1.7 g, 10.5 mmol) and pyridine (870 mg, 11 mmol) in DMF (20 ml) at 0°. The mixture was allowed to attain room temperature during 2 h and was then poured into saturated aqueous $NaHCO_3$ (100 ml). Extraction with petroleum ether 30-50, work-up, chromatography (CH_2Cl_2) and sublimation *i.v.* (140-150° /0.2 Torr) afforded 18 as a white crystalline solid (900 mg, 92% yield). M.p. 74-75°. Rf (CH_2Cl_2) 0.55.- IR ($CDCl_3$): 1670, 1460, 1250, 1140, 1085, 1070, 946, 908, 840, 780.- ^{1}H-NMR: -0.01 (*s*, 6H); 0.86 (*s*, 9H); 1.34 (*s*, 3H); 1.44-1.73 (5H); 1.90 (br. *s*, 1H); 2.33 (*d*, *J* 4, 1H); 2.43 (br. *s*, 1H); 3.06 (*t*, *J* 10.5, 1H); 3.50 (*dd*, *J* 10.5 and 6.5, 1H); 6.05 (*d*, *J* 9.5, 1H); 6.99 (*d*, *J* 9.5, 1H).- ^{13}C-NMR: 201.4 (*s*), 160.8 (*d*), 128.7 (*d*), 63.5 (*t*), 61.4 (*d*), 57.7 (*d*), 57.0 (*d*), 47.4 (*s*), 42.6 (*d*), 33.2 (*t*), 25.9 (3 *q*), 22.0 (*t*), 21.8 (*q*), 18.0 (*s*), -5.6 (2 *q*).- MS: 306 (0, M+), 249 (37), 231 (47), 195 (100), 177 (5), 157 (7), 75 (21).- Found: C, 70.9; H, 9.7. $C_{18}H_{30}O_2Si$ Requires: C, 70.5; H, 9.9.

(1*RS*, 2*SR*, 6*SR*, 7*RS*, 8*RS*)-7-(*tert*-Butyldimethylsilyloxy)methyl-6-methyltricyclo[4.4.0.0^{2,8}]decan-3-one (20).- A solution of 18 (840 mg, 2.7 mmol) in ethanol containing 5% Pd-C (100 mg) was hydrogenated at room temperature. After 6 h the mixture was filtered (Hyflo), the solvent evaporated, and the residue sublimed *i.v.* (150-160° (bath)/0.2 Torr) to afford 20 as a white crystalline solid (810 mg, 97% yield). M.p. 57-58°. Rf (CH_2Cl_2) 0.50.- IR ($CDCl_3$): 1700, 1465, 1260, 1143, 1090, 840, 780.- ^{1}H-NMR: 0.03 (*s*, 6H); 0.87 (*s*, 9H); 1.17 (*s*, 3H); 1.37 (*m*, 2H); 1.50-1.70 (3H); 1.78 (*m*, 1H); 1.96 (*m*, 1H); 2.10 (*d*, *J* 4, 1H); 2.14 (br. *s*, 1H); 2.25 (br. *s*, 1H); 2.41 (*m*, 2H); 3.43 (*m*, 2H).- ^{13}C-NMR: 214.7 (*s*), 63.6 (*t*), 59.6 (*d*), 54.4 (*d*), 48.2 (*d*), 46.2 (*d*), 42.5 (*s*), 36.9 (*t*), 32.7 (*t*), 28.0 (*t*), 25.9 (3 *q*), 25.1 (*q*), 22.5 (*t*), 18.1 (*s*), -5.5 (2 *q*).- MS: 308 (0, M+), 251 (100), 195 (28), 181 (18), 159 (36), 131 (16), 91 (15), 75 (40).- Found: C, 69.8; H, 10.8. $C_{18}H_{32}O_2Si$ Requires: C, 70.1; H, 10.5.

Direct preparation of 20 from 17. (1*RS*, 2*RS*, 3*SR*, 4*SR*, 6*SR*, 7*RS*)-2-(*tert*-Butyldimethylsilyloxy)methyl-3,4-dimethyltricyclo[4.3.0.0^{3,7}]nonan-5-one (21).- Aqueous 3N NaOH was added dropwise to a stirred solution of 17 (190 mg (GC purity 92%), 0.46 mmol) in methanol (2 ml) at 0-5°. The mixture was allowed to attain room temperature during 1 h, left at this temperature during 20 h, and then poured into water (10 ml). Extraction with ether and work-up gave a pale yellow oil (*ca.* 150 mg) which consisted of a 45:24:13 mixture (GC purity 82%) of 20, 21 and 17. Purification by chromatography (CH_2Cl_2) afforded 20 (60 mg, 42% yield), identical to an authentic sample, and 21 as a white crystalline solid (32 mg, 23% yield). M.p. 51-52° (ether/pentane). Rf (CH_2Cl_2) 0.54.- IR ($CDCl_3$): 1730, 1460, 1380, 1240, 1180, 1080, 1000, 920, 840, 770, 660.- ^{1}H-NMR: 0.02 (*s*, 6H); 0.87 (*s*, 9H); 1.02 (*d*, *J* 7, 3H); 1.11 (*s*, 3H); 1.35 (*t*, *J* 8, 1H); 1.55-1.75 (4H); 2.01 (br. *s*, 1H); 2.14 (*q*, *J* 7, 1H); 2.21 (br. *s*, 1H); 2.42 (br. *s*, 1H); 3.40 (*dd*, *J* 10 and 9, 1H); 3.53 (*dd*, *J* 10 and 7, 1H).- ^{13}C-NMR: 221.4 (*s*), 62.5 (*t*), 60.6 (*d*), 51.3 (*d*), 50.0 (*d*), 49.3 (*s*), 46.7 (*d*), 45.0 (*d*), 34.2 (*t*), 25.9 (3 *q*), 20.8 (*t*), 18.1 (*s*), 14.3 (*q*), 11.4 (*q*), -5.4 (2 *q*).- MS: 308 (0, M$^+$), 293 (1), 251 (70), 207 (11), 159 (91), 131 (38), 105 (40), 75 (100).- Found: C, 69.9; H, 10.6. $C_{18}H_{32}O_2Si$ Requires: C, 70.1; H, 10.5.

(1*RS*, 2*SR*, 6*SR*, 7*RS*, 8*SR*)-7-(*tert*-Butyldimethylsilyloxy)methyl-3-isopropylidene-6-methyltricyclo[4.4.0.0^{2,8}]decane (22).- DMSO (4 ml) was added dropwise to a stirred slurry of isopropyltriphenylphosphonium iodide (648 mg, 15 mmol) and KH (Alfa Products, 24.1% in oil, 12 mmol) in toluene (31 ml) at room temperature. To this dark red solution at 60° was now added dropwise a solution of 20 (740 mg, 2.4 mmol) in toluene (5 ml). After 24 h at 60° the mixture was cooled and poured into saturated aqueous NH_4Cl (100 ml) and extracted with ether. Work-up, chromatography (cyclohexane), and bulb-to-bulb distillation *i.v.* afforded 22 as a colourless oil (660 mg, 82% yield). B.p. 160-180° (bath)/0.3 Torr. Rf (CH_2Cl_2) 0.85, Rf (cyclohexane) 0.55.- IR: 1460, 1375, 1250, 1080, 840, 780.- ^{1}H-NMR: 0.00 (*s*, 6H); 0.88 (*s*, 9H); 1.05 (*s*, 3H); 1.22 (*m*, 2H); 1.36 (*m*, 1H); 1.47 (*m*, 1H); 1.55-1.82 (4H); 1.59 and 1.64 (2 *s*, 6H); 1.92 (br. *s*, 1H); 2.10 (*m*, 1H); 2.33 (*m*, 1H); 2.46 (br. *s*, 1H); 3.43 (*m*, 2H).- ^{13}C-NMR: 131.1 (*s*), 123.4 (*s*), 64.3 (*t*), 55.3 (*d*), 50.9 (*d*), 47.3 (*d*), 44.7 (*d*), 42.0 (*s*), 31.7 (*t*), 31.1 (*t*), 26.1 (*q*), 26.0 (3 *q*), 23.6 (*t*), 22.3 (*t*), 20.0 (2 *q*), 18.3 (*s*), -5.4 (2 *q*).- MS: 334 (0, M$^+$), 202 (77), 187 (31), 159 (35), 145 (25), 131 (35), 119 (36), 107 (52), 91 (30), 75 (100).- Found: C, 75.2; H, 11.6. $C_{21}H_{38}OSi$ Requires: C, 75.4; H, 11.4.

(1*RS*, 2*SR*, 3*SR*, 6*SR*, 7*RS*, 8*SR*)-7-(*tert*-Butyldimethylsilyloxy)methyl-3-isopropyl-6-methyltricyclo[4.4.0.0^{2,8}]decane (24).- A solution of 22 (600 mg, 1.8 mmol) in AcOH/AcOEt 3:1 (6 ml) containing PtO_2 (100 mg) was hydrogenated at room temperature. After 24 h the mixture was filtered (Hyflo), the solvent evaporated, and the residual oil dissolved in ether. This ethereal solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous aqueous NaCl. Work-up, chromatography (cyclohexane), and bulb-to-bulb distillation *i.v.* afforded 24 as a colourless oil (560 mg, 93% yield). B.p. 160-180° (bath)/0.2 Torr. Rf (cyclohexane) 0.58.- IR: 1460, 1250, 1080, 840, 780, 665.- ^{1}H-NMR: 0.04 (*s*, 6H); 0.88 (2 *d*, *J* 7, 6H); 0.89 (*s*, 9H); 0.98 (*s*, 3H); 1.00-1.70 (12H); 1.75 (br. *s*, 1H); 1.91 (br. *s*, 1H); 3.75 (*m*, 2H).- ^{13}C-NMR: 63.1 (*s*), 54.5 (*d*), 51.5 (*d*), 50.1 (*d*), 43.5 (*d*), 42.7 (*d*), 41.0 (*s*), 35.2 (*t*), 35.0 (*t*), 34.0 (*d*), 26.5 (*t*), 26.1 (3 *q*), 23.3 (*q*), 22.1 (*t*), 21.3 (*q*), 21.0 (*q*), 18.3 (*s*), -5.2 (2 *q*).- MS: 336 (0, M$^+$), 279 (10), 203 (20), 147(7), 115 (11), 95 (11), 81 (13), 75 (100).- Found: C, 74.7; H, 11.9. $C_{21}H_{40}OSi$ Requires: C, 74.9; H, 12.0.

(1*RS*, 2*SR*, 3*SR*, 6*SR*, 7*RS*, 8*SR*)-(3-Isopropyl-6-methyltricyclo[4.4.0.0^{2,8}]dec-7-yl)methanol (25).- A mixture of 24 (500 mg, 1.5 mmol), THF (5 ml), and 1N HCl (5 ml) was stirred during 4 h at room temperature and then poured into saturated aqueous $NaHCO_3$ (50 ml). Extraction with ether, work-up, chromatography (CH_2Cl_2), and bulb-to-bulb distillation *i.v.* afforded 25 as a colourless oil (320 mg, 97% yield). B.p. 150-160° (bath)/0.2 Torr. Rf (CH_2Cl_2) 0.37.- IR ($CDCl_3$): 3625, 3400 br., 2960, 2880, 1460, 1370, 1000.- ^{1}H-NMR (+D_2O): 0.89 (2 *d*, *J* 7 6H); 1.00 (*s*, 3H); 1.00-1.75 (12H); 1.80 (br. *s*, 1H); 1.99 (br. *s*, 1H); 3.73 (*dd*, *J* 10.5 and 5.5, 1H); 3.85 (*dd*, *J* 10.5 and 9, 1H).- ^{13}C-NMR: 62.9 (*t*), 55.4 (*d*), 51.2 (*d*), 50.2 (*d*), 43.5 (*s*), 42.5 (*d*), 41.2 (*d*), 35.2 (*t*), 35.1 (*t*), 33.9 (*d*), 26.3 (*t*), 23.2 (*q*), 22.0 (*t*), 21.2 (*q*), 20.9 (*q*).- MS: 222 (2, M$^+$), 204 (8), 189 (8), 179 (23), 161 (51), 150 (39), 135 (68), 119 (41), 105 (76), 95 (84), 81 (100), 67 (59).- Found: C, 80.9; H, 11.8. $C_{15}H_{26}O$ Requires: C, 81.0; H, 11.8.

(1*RS*, 2*SR*, 3*SR*, 6*RS*, 8*SR*)-3- Isopropyl-6-methyl-7-methylidenetricyclo[4.4.0.0^{2,8}]decane ((±)-sativene, 26).- A solution of tributylphosphine (202 mg, 1 mmol) in THF (1 ml) was added dropwise to a stirred solution of 25 (111 mg, 0.5 mmol) and *o*-nitrophenylselenocyanate (260 mg, 1 mmol) and pyridine (0.5 ml) in THF/HMPA 4:1 (2.5 ml) at 25°. After 16 h at reflux the mixture was poured into saturated aqueous NH_4Cl (10 ml) and extracted with ether. Work-up afforded a crude product which was filtered through silica gel (20 g) (eluent: CH_2Cl_2). The filtrate was concentrated *i.v.*, the residue dissolved in THF (5 ml), and 30% aqueous H_2O_2 (0.5 ml) was added. The mixture was stirred during 16 h at room temperature and then poured into petroleum ether 30-50. Work-up, chromatography (cyclohexane), and bulb-to-bulb distillation *i.v.* afforded 26 as a colourless oil (65 mg, 64% yield). B.p. 110-120° (bath)/0.1 Torr. Rf (cyclohexane) 0.79.- IR ($CDCl_3$): 3060, 2940, 1660, 1460, 1375, 880.- ^{1}H-NMR: 0.88 (2 *d*, *J* 7, 6H); 1.03 (*s*, 3H); 1.14-1.70 (11H); 1.83 (*s*, 1H); 2.61 (br. *s*, 1H); 4.44 (*s*, 1H); 4.76 (*s*, 1H).- ^{13}C-NMR: 163.5 (*s*), 98.9 (*t*), 51.7 (*d*), 49.4 (*d*), 47.3 (*d*), 45.3 (*s*), 43.3 (*d*), 40.1 (*t*), 33.1 (*d*), 32.6 (*t*), 25.5 (*t*), 22.4 (*t*), 21.2 (*q*), 21.0 (*q*), 20.9 (*q*).- MS: 204 (48, M$^+$), 189 (24), 175 (7), 161 (73), 147 (18), 133 (39), 119 (36), 108 (100).

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