Annulation by Sequential Double Michael Reaction; Synthesis of Decalones and Its Application to the Syntheses of ε-Cadinene, Khusitone and Khusilal

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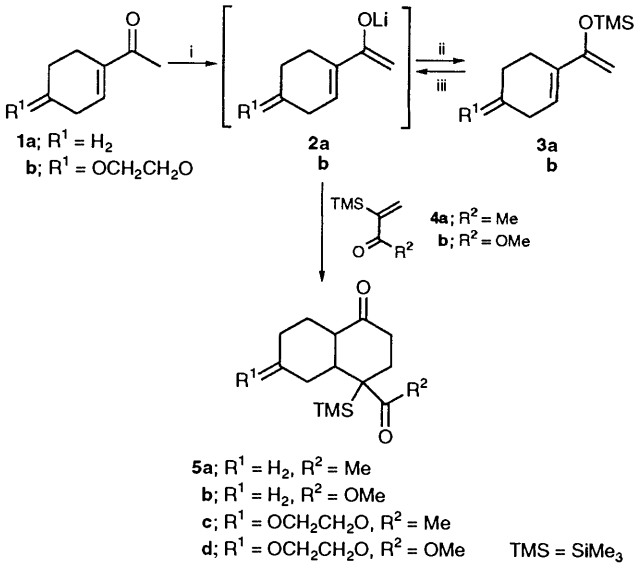
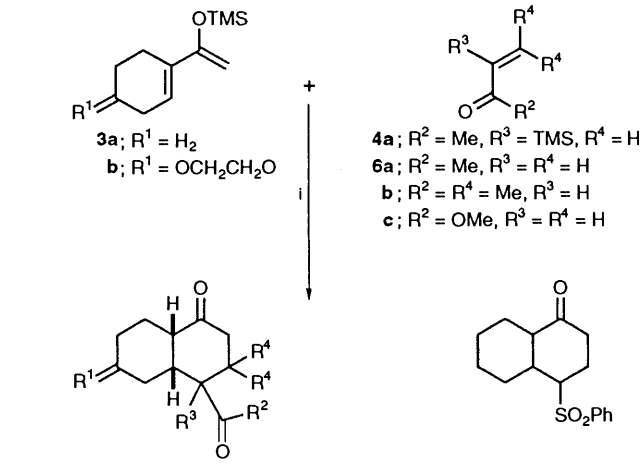
Reaction of the kinetic enolates or the trimethylsilyl enol ethers of 1-acetylcyclohexenes with α,β-unsaturated carbonyl compounds affords 4-substituted 1-decalone derivatives under basic or Lewis acidic conditions. The reaction with acrylates of chiral alcohols has achieved 70% diastereoselection. Application of these reactions has enabled syntheses of ε-cadinene, khusitone and khusilal to be accomplished.

A one-pot annulation by sequential multiple carbon–carbon bond-forming reaction offers an efficient opportunity for the construction of polycarbocyclic compounds. Various anionic, radical and cationic reactions have a potential to inaugurate such a sequential reaction, in the case where anionic, radical or cationic species are regenerated on the product after the first reaction. In particular, the Michael reaction has the ability to propagate sequentially, enabling annulation by multiple carbon–carbon bond formation providing that at least one intramolecular reaction is involved in the succeeding process. One of the characteristic features of annulation by sequential Michael reaction is formation of six-membered rings, affording either linearly condensed or bridged carbocyclic compounds. The result is in sharp contrast with the sequential radical reaction which gives linearly fused five-membered carbocyclic compounds. Decalin, a linearly fused six-membered carbocyclic molecule, is one of the most widespread carbon frameworks among natural products, especially in terpenoids and polyketides.[1] Our ongoing research interest in the annulation by sequential Michael reaction[2] as well as our synthetic study of natural products having a decalin framework[3] result herein in the synthesis of 1-decalone derivatives by the sequential double Michael reaction[4] and application of the reaction towards syntheses of three *trans*-decalin terpenoids, ε-cadinene, khusitone and khusilal.



Scheme 1 *Reagents:* i, LDA, THF; ii, TMSCl; iii, MeLi, THF



Scheme 2 *Reagents:* i, Lewis acid, CH_2Cl_2

Results and Discussion

1-Decalones **5** *from the Kinetic Enolates* **2**.—The reaction of the kinetic enolate **2a** or **2b**, which was generated by treatment of 1-acetylcyclohexene **1a** or the ketal **1b** with lithium diisopropylamide (LDA) at −78 °C, with an α-trimethylsilyl-α,β-unsaturated carbonyl compound **4a**[5] or **4b**,[6] afforded the 1-decalones **5a–d** (Scheme 1, Table 1).[7] The kinetic enolate **2a** or **2b** was also generated by MeLi cleavage of the trimethylsilyl enol ether **3a**[8] or **3b** (*vide infra*), and there enolates reacted with compound **4a** or **4b** to give the decalones **5** in relatively low yield (Table 1, entries 2, 5, 8 and 10). In these reactions, the presence of an α-trimethylsilyl group in the α,β-unsaturated carbonyl compound **4a** or **4b** is an essential factor for the reaction to proceed since the reaction with methyl vinyl ketone **6a** or methyl acrylate **6c** gave no decalone derivative.

1-Decalones **5** *from the Trimethylsilyl Enol Ethers* **3**.—The double Michael reaction of the trimethylsilyl enol ethers **3** with α,β-unsaturated carbonyl compounds was also promoted by Lewis acids. Thus, the reaction of the trimethylsilyl enol ether **3a** with α,β-unsaturated carbonyl compounds **4a**, **6a–c** in the presence of a Lewis acid afforded the decalones **5a,e–g**. The trimethylsilyl enol ether **3b** also reacted, to give the decalone **5h** (Scheme 2, Table 2).[9] Among the Lewis acids examined, diethylaluminium chloride (Et_2AlCl) (3 mol equiv.) gave the highest and most reproducible yields. The decalones **5a**, **5e**, and

Table 1 Double Michael reaction of the kinetic enolates **2** of 1-acetylcyclohexenes **1** with α-trimethylsilyl-α,β-unsaturated carbonyl compounds **4**

Entry	1-Acetylcyclohexene	α,β-Unsaturated carbonyl compound	Reaction conditions	Product yield (%)
1	**1a**	**4a**	*a*	**5a** (26)
2	**3a**	**4a**	*b*	**5a** (9)
3	**1b**	**4a**	*a,c*	**11a** (9)
4	**1a**	**4b**	*a*	**5b** (62) + **12a** (8)
5	**3a**	**4b**	*b*	**5b** (39)
6	**1b**	**4a**	*a*	**5c** (30)
7	**1b**	**4b**	*a*	**5d** (71) + **12b** (5)
8	**3b**	**4b**	*b*	**5d** (18) + **12b** (9)
9	**1b**	**4b**	*a,d*	**5d** (24) + **11b** (5)
10	**3b**	**4a**	*b*	**5c** (trace)

[a] An acetylcyclohexene **1** was treated with LDA. [b] A silyl enol derivative **3** was cleaved by MeLi. [c] Reaction was quenched at −10 °C in 3.6 h. [d] Reaction was quenched at −45 °C in 1 h.

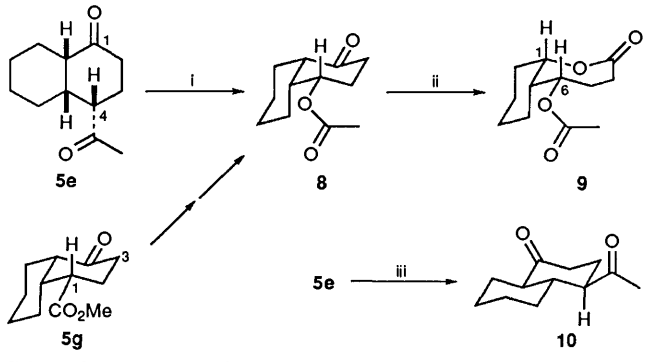
Table 2 Double Michael reaction of the trimethylsilyl enol derivatives **3** of 1-acetylcyclohexenes **1** with α,β-unsaturated carbonyl compounds **4** and **6**

Entry	Trimethylsilyl enol compound	α,β-Unsaturated carbonyl compound **4** or **6**	Lewis acid[a]	Product	Yield (%)[b]
1	**3a**	**4a**	Et_2AlCl	**5a**	64
2	**3a**	**6a**	$TrClO_4$[c]	**5e**	21
3	**3a**	**6a**	$TiCl_2(OPr^i)_2$	**5e**	22
4	**3a**	**6a**	$EtAlCl_2$	**5e**	24
5	**3a**	**6a**	Et_2AlCl	**5e**	56
6	**3a**	**6a** + dimethyl fumarate	Et_2AlCl	**5e**	34
7	**3a**	**6b**	Et_2AlCl	**5f**	51[d]
8	**3a**	**6c**	Et_2AlCl	**5g**	64
9	**3a**	**6c**	Et_2AlCl[e]	**5g**	51
				+**13**	9
				+**14**	4
10	**3b**	**4a**	$TiCl_2(OPr^i)_2$	**5c**	12
				+**15**	19
11	**3b**	**6a**	$TiCl_2(OPr^i)_2$[f]	**5h**	34[d]
12	**3a**	vinyl sulfone	Et_2AlCl	**7**	21[d]

[a] 3 mol equiv. [b] A single isomer was obtained. [c] A catalytic amount (10 mol%). [d] A mixture of two isomers was obtained. [e] 1 mol equiv. [f] Reaction was quenched at −50 °C in 1.5 h.

5g thus obtained were found to be spectroscopically and chromatographically pure. In this case, the presence of the α-trimethylsilyl group in the unsaturated carbonyl compounds is not always required, because methyl vinyl ketone **6a** and methyl acrylate **6c** provided the corresponding decalones **5e**, **5g** or **5h** in comparable yields (Table 2, entries 5, 8, 9 and 11).

Assignment of the Relative Stereochemistry of the Decalones **5e** *and* **5g**.—The ^1H NMR signal that appears at the lowest field (δ 2.97) among the methine protons was assigned to be 4-H in the decalone **5e**. The coupling pattern of the proton at C-4 shows one axial–axial and two axial–equatorial couplings (dt, *J* 11.8, 4.1 Hz) and indicates that the decalone **5e** has the *cis*-steroidal conformation. The signal at δ 2.6 was assigned to the 8a-H proton which appeared as a broad singlet (triplet-like). In order to confirm this stereochemical assignment, the decalone **5e** was transformed into the acetate **8** and the acetoxy lactone **9** by the Baeyer–Villiger oxidation (Scheme 3). The decalone **5e** was heated in dichloromethane with *m*-chloroperbenzoic acid (MCPBA) under reflux for 24 h to give the acetoxy decalone **8** whose methine proton at C-4 (δ 5.26) exhibited half-height width of 31 Hz, indicating the axial orientation of 4-H. Prolonged heating (62 h) provided the acetoxy lactone **9** whose two signals at δ 4.61 (1-H, $w_{\frac{1}{2}}$ 8.8 Hz) and 4.98 (6-H, $w_{\frac{1}{2}}$ 30 Hz) (1 H each) indicated the equatorial nature of 1-H and the axial nature of 6-H, respectively. These results established that the decalone **5e** had the *cis*-steroidal conformation. Treatment of

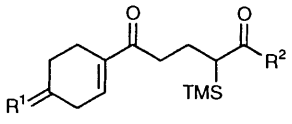


Scheme 3 *Reagents and conditions:* i, MCPBA, CH_2Cl_2, reflux, 24 h; ii, MCPBA, CH_2Cl_2, 62 h; iii, MeONa, MeOH, room temperature

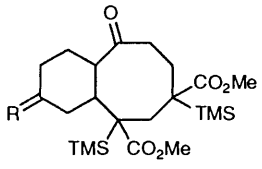
the decalone **5e** with sodium methoxide in methanol produced the more stable *trans*-decalone **10** having an equatorial acetyl group at C-4.

The ^1H NMR spectrum of the decalone **5g** was fully assigned by decoupling and 2D measurements, indicating that the signal due to 1-H at δ 2.94 has coupling constants 12.9 (doublet) and 3.9 Hz (triplet) and the signal due to 4a-H at δ 2.6 appears as broad singlet (triplet-like, see Experimental section). Since the decalone **5g** was transformed into the acetoxy decalone **8** (see Experimental section), the conformation of the decalone **5g** was determined to be also *cis*-steroidal.

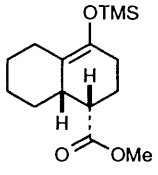
Reaction Pathway.—When the reaction of the kinetic enolate **2b** with the α-trimethylsilyl-α,β-unsaturated carbonyl compound **4a** or **4b** was quenched at low temperature, the single Michael adduct **11a** or **11b** was obtained, respectively (Table 1, entries 3 and 9). Moreover, the bicyclo[6.4.0]dodecane derivative **12a** or **12b**, a triple Michael reaction product, was isolated as a minor product in the reaction of methyl 2-trimethylsilylpropenoate **4b** (Table 1, entries 4, 7 and 8). In the Et_2AlCl-assisted reaction of the trimethylsilyl enol ether **3b** with methyl vinyl ketone **6a**, the presence of an equimolar amount of dimethyl fumarate, which is known as a good dienophile in the Diels–Alder reaction, did not affect the reaction, which gave only the decalone **5e** in 34% yield (Table 2, entry 6). The dicarbonyl compound **15** (19%) derived from the single Michael reaction was also obtained along with the decalone **5c** (12%) in the $TiCl_2(O^iPr)_2$-assisted reaction between the trimethylsilyl enol ether **3b** and 3-trimethylsilylbut-3-en-2-one **4a** (Table 2, entry 10). Careful separation of the reaction products enabled the isolation of a triple Michael reaction product **14** along with the decalone **5g** in Et_2AlCl-mediated annulation (Table 2, entry 9). These results indicate that the present annulation proceeds *via* a sequential double Michael reaction either under the basic or Lewis acidic reaction conditions. The isolation of the trimethylsilyl enol ethers **13** and **14** indicates that the reaction involves a silyl-transfer process.



11a; $R^1 = OCH_2CH_2O$, R^2 = Me
b; $R^1 = OCH_2CH_2O$, R^2 = OMe
c; $R^1 = H_2$, R^2 = OMe



12a; R = H_2
b; R = OCH_2CH_2O



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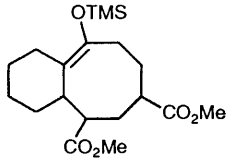

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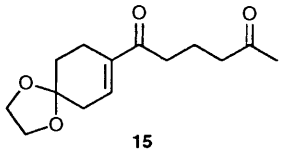

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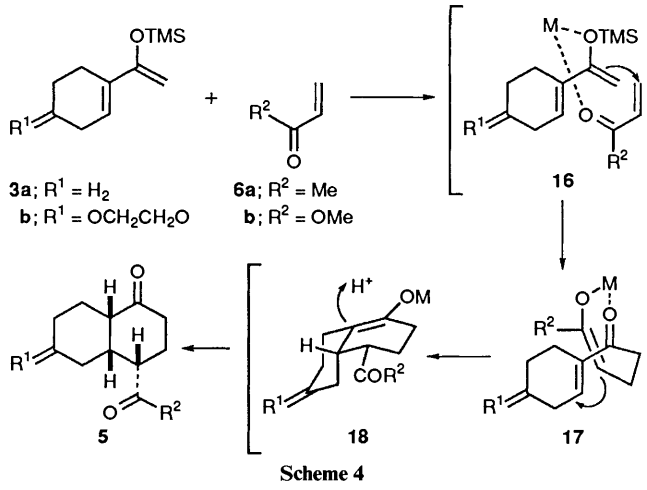
The formation of the *cis*-steroidal conformation is explained as follows. The double Michael reaction would proceed *via* chelation of the metal cation between the enolate or the ether oxygen of the trimethylsilyl enol ether and the carbonyl oxygen of the α,β-unsaturated carbonyl compound (Scheme 4, **16** → **17**). Owing to this chelation, an α,β-unsaturated carbonyl compound reacts *via* an s-*cis* conformation. As a result, the intermediary trimethylsilyl enol ether or metal enolate **18** is generated, having an equatorial acetyl or methoxycarbonyl group. Axial protonation to this intermediate **18** furnishes the decalone **5** having the *cis*-steroidal conformation.

Asymmetric Double Michael Reaction.—As described above, stereoselective formation of the *cis*-steroidal conformation was explained by the chelation-controlled transition-state model followed by axial protonation. Chelation-controlled arrangement of the two reactants, the trimethylsilyl enol ethers **3** and the α,β-unsaturated carbonyl compound **4** or **6**, suggests that



3a; $R^1 = H_2$
b; $R^1 = OCH_2CH_2O$

6a; R^2 = Me
b; R^2 = OMe

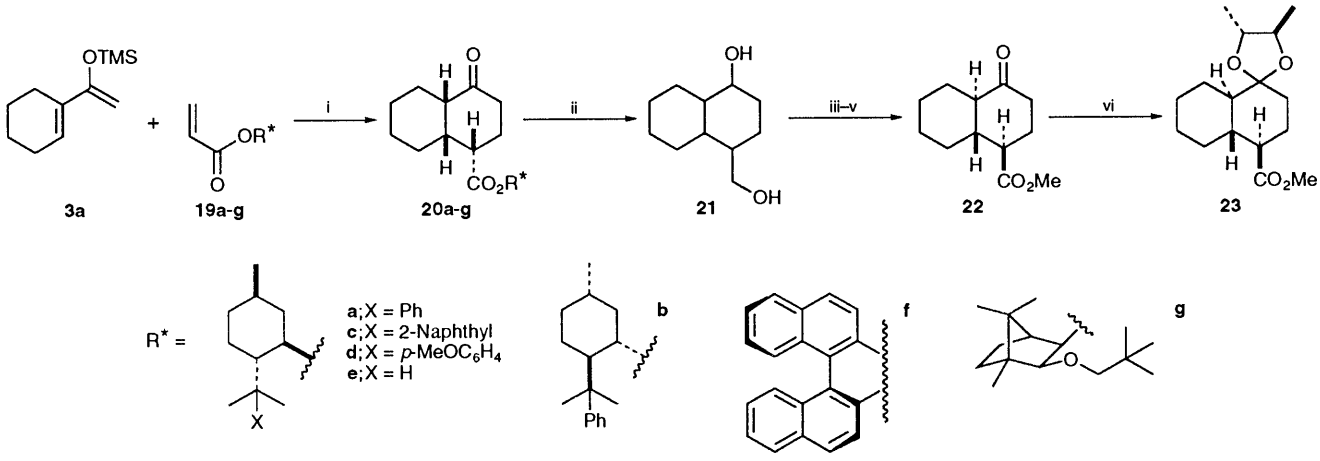
16 **17** **18** **5**

Scheme 4

chirality would be introduced in a decalone molecule if a chiral α,β-unsaturated carbonyl compound were used for the reaction.[10]

Acrylates **19a–g** having (−)-menthol, (+)- or (−)-8-phenylmenthol,[11] (−)-binaphthol, and (−)-2-neopentyloxybornan-3-ol[12] and so on as chiral auxiliaries were employed for examination of the asymmetric double Michael reaction, which was carried out in the presence of Et_2AlCl as mentioned above. The diastereoselectivity of this reaction was determined as follows (Scheme 5). The chiral auxiliary was removed quantitatively by reduction of the resulting diastereoisomeric mixture of the corresponding decalone **20a–g** with lithium aluminium hydride (LAH) to give the diol **21**. Direct hydrolysis with alkali to the keto acid failed. Jones oxidation, followed by esterification with diazomethane, transformed the diol **21** into the keto ester, which isomerised into the thermodynamically more stable *trans*-decalone **22** by NaOMe-mediated epimerisation. The enantiomeric excess of the keto ester **22** was determined by medium-pressure liquid chromatography (MPLC) analysis of the (2*R*,3*R*)-butane-2,3-diol acetal **23**. The acetal **23** from racemic **22** revealed baseline separation. As seen in Table 3, 70% chiral induction was observed in 60% chemical yield in the case where (−)- or (+)-8-phenylmenthol was used as a chiral auxiliary (Table 3, entries 1 and 2). Diastereoselectivity was not improved even if the bulkiness (entry 3) or the site of chelation (entry 4) was increased in a chiral auxiliary. Diastereoisomeric enrichment by MPLC was achieved by isolation of the *cis*-steroidal diastereoisomer of **20a** in 45% yield in entry 1. In this case, the diastereoisomeric excess (d.e.)-value of the acetal **23** was 97%.

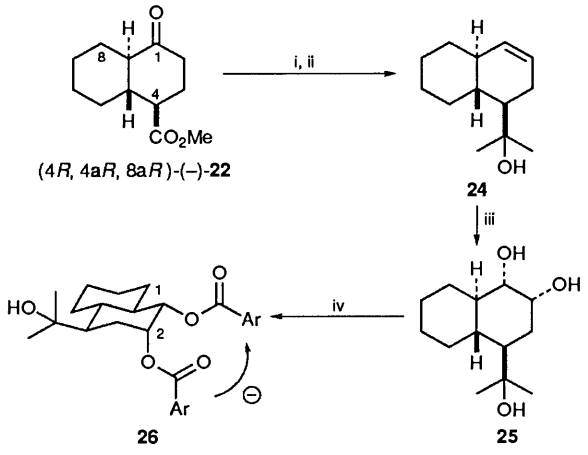
The absolute stereostructure of the (−)-decalone **22** derived from (−)-8-phenylmenthyl acrylate was determined by the exciton chirality method (Scheme 6).[13] (−)-Decalone **20a** enriched to 97% d.e. by MPLC resolution was converted into the (−)-keto ester **22** as described in Scheme 5. The double bond was introduced regioselectively at C-1 by the Shapiro reaction to give the olefin **24** in 55% yield. Subsequent *cis*-dihydroxylation with osmium tetraoxide occurred exclusively from the α-side of the olefin **24** and benzoylation of the resulting secondary glycol **25** afforded the bis-*p*-methoxybenzoate **26** (63% overall yield from the olefin **24**). The relative configuration of the two benzoyloxy groups of the dibenzoate **26** was found to be *cis*-α on the basis of ^1H NMR spectroscopy in which 1-H appeared at δ 4.91 (dd, *J* 10.6, 2.7 Hz) and 2-H at δ 5.60 (br s). The CD spectrum of the dibenzoate **26** showed exciton-split Cotton effects of negative first (Δε −16.0 at 266 nm) and positive second (Δε +7.8 at 246 nm) signs. This result demonstrates that the chirality between two long axes of the transition moments of the benzoate chromophores constitutes a counterclockwise screw sense as shown in the structure **26**.



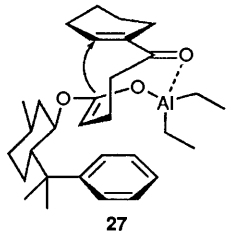
Scheme 5 *Reagents:* i, Et_2AlCl, CH_2Cl_2; ii lithium aluminium hydride (LAH); iii, Jones' reagent, acetone; iv, CH_2N_2, ether; v, MeONa, MeOH; vi, (2*R*,3*R*)-butane-2,3-diol, toluene-*p*-sulfonic acid (PTSA), benzene

Table 3 Asymmetric double Michael reaction of the trimethylsilyl enol derivative **3a** of 1-acetylcyclohexene **1a** with chiral acrylates **19**

Entry	R* = Chiral auxiliary in **19**	Yield of **20** (%)	$[\alpha]_D$ of **22** (10^{-1} deg cm^2 g^{-1})	Diastereoisomeric excess of the reaction (%)
1	**a**; (−)-8-phenylmenthyl	64	−23.4	70
2	**b**; (+)-8-phenylmenthyl	62	+24.9	73
3	**c**; (−)-8-(2-naphthyl)menthyl	64	−22.9	64
4	**d**; (−)-8-(*p*-methoxyphenyl)menthyl	44	−21.5	62
5	**e**; (−)-menthyl	54	0	0
6	**f**; (−)-1′-binaphthyl-2,2′-diyl	80	−1.4	2.3
7	**g**; (−)-*cis*-2-neopentyloxybornan-3-yl	63	+2.0	17



Scheme 6 *Reagents and conditions:* i, $TsNHNH_2$, EtOH, reflux; ii, MeLi, ether, reflux; iii, OsO_4, *N*-methylmorpholine *N*-oxide, Bu^{t}OH, water; iv, *p*-methoxybenzoyl chloride, 4-(dimethylamino)pyridine, 60 °C



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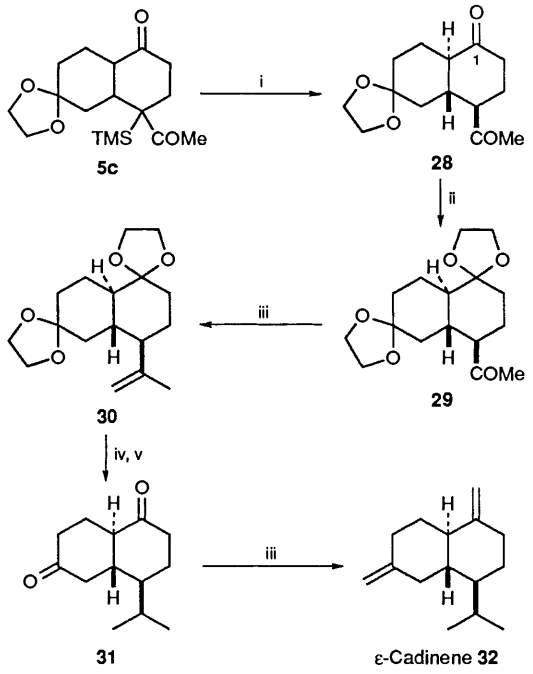
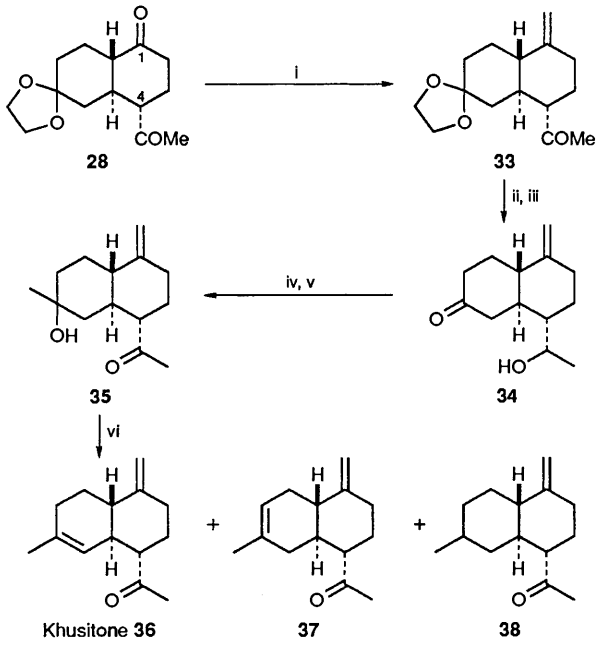
Thus, the absolute stereostructure of the (−)-decalone **22** was determined to be 4*R*, 4a*R*, 8a*R* as depicted in Scheme 6. The absolute stereostructure is understood by assuming that the second Michael addition took place from the *re* face of the cyclohexene moiety of **27**.

Synthesis of ε-*Cadinene* **32**.—ε-Cadinene **32**, one of the constituents of ylang-ylang oil,[14] was synthesized starting from the decalone **5c** obtained by the basic double Michael reaction (Table 1, entry 6) or the decalone **5h** by the Lewis acid-assisted double Michael reaction (Table 2, entry 11) (Scheme 7).[9] The trimethylsilyl enol ether **3b** was prepared by the Diels–Alder reaction of 1-methoxy-3-(trimethylsiloxy)buta-1,3-diene[15] and methyl vinyl ketone **6a** followed by conventional treatment with LDA and chlorotrimethylsilane. Treatment of the decalone **5c** with NaOMe (93%) resulted in ready removal of the trimethylsilyl group and isomerisation to the more stable *trans*-decalone **28** having an equatorial acetyl group at C-4. The selective protection of the carbonyl group at C-1 by using a limited amount of ethylene glycol gave the bis-acetal **29** (73%) whose ^{1}H NMR coupling constants of 4-H (td, *J* 11.5, 3.7 Hz) were diagnostic to confirm the equatorial nature of the acetyl group in a *trans*-decalin stereochemistry. Prolonged heating with a large excess of methylenetriphenylphosphorane furnished the isopropenyl group at C-4 of the bis-acetal **30** (81%). Catalytic hydrogenation followed by deprotection of the acetal afforded the 1,6-diketone **31** (66%) which was transformed into ε-cadinene **32** (75%) by Wittig methylenation. The spectral data of synthetic **32** (NMR, IR and mass) were identical with those reported.[16]

Synthesis of Khusitone **36**.—Khusitone **36** is a rare C_{14}-terpenoid isolated from north Indian vetiver oil and is antipodal to cadinane terpenoids.[17] Synthesis had started from the decalone **28** previously used for the synthesis of ε-cadinene **32** (Scheme 8).[7] Regioselective Wittig olefination with an equimolar amount of methylenetriphenylphosphorane provided the *exo*-methylene compound **33** in 45% yield. Reduction of the acetyl group with LAH, followed by deprotection of the acetal, yielded a diastereoisomeric mixture of the hydroxy ketone **34** (87%). Addition of methyllithium, followed by



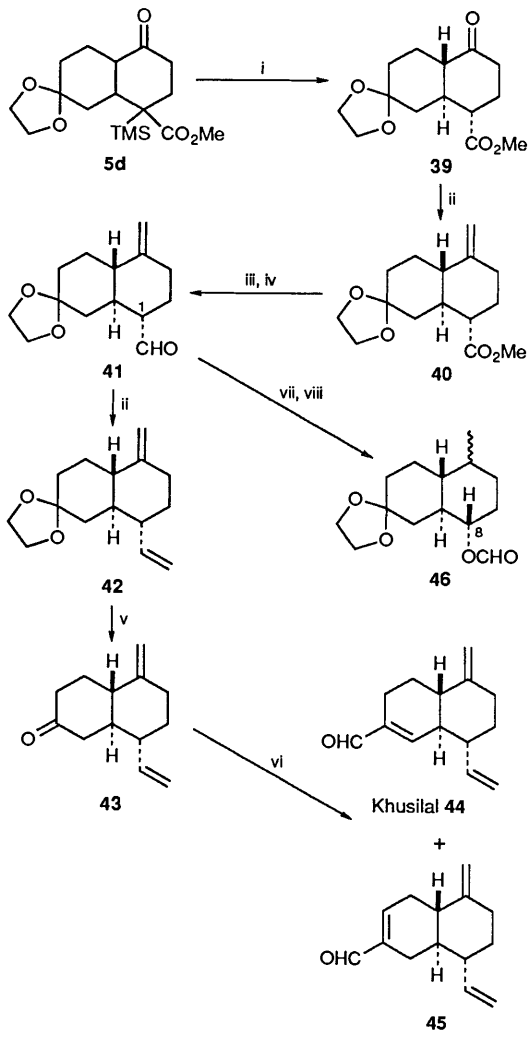
Scheme 7 *Reagents:* i, MeONa, MeOH; ii, $(CH_2OH)_2$, PTSA, benzene; iii, $Ph_3P{=}CH_2$, THF; iv, H_2, 10% Pd–C; v, PTSA, aq. THF



Scheme 8 *Reagents:* i, $Ph_3P{=}CH_2$, THF; ii, LAH, ether; iii, PTSA, aq. acetone; iv, MeLi, ether; v, Jones' reagent, acetone; vi, $POCl_3$, pyridine

oxidation of the secondary alcohol back to an acetyl group, gave the keto alcohol **35** (32%). Dehydration with phosphorus trichloride oxide furnished khusitone **36** along with an inseparable mixture of double-bond isomers **37** and **38** (a combined yield 51%, **36**:**37**:**38** 2:3:1). The spectral properties of synthetic **36** (NMR and IR) matched with those reported values.

Synthesis of Khusilal **44**.—Khusilal **44** is also a C_{14}-terpenoid isolated from north Indian vetiver oil.[18] The double Michael adduct **5d** was employed as the starting material (Table 1, entry 7) (Scheme 9).[19] Treatment of the decalone **5d** with NaOMe at 40 °C for 4.4 h resulted in smooth removal of the trimethylsilyl group at C-1 and isomerisation to the more stable *trans*-



Scheme 9 *Reagents:* i, MeONa, MeOH; ii, $Ph_3P{=}CH_2$, THF; iii, LAH, ether; iv, $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; v, PPTS, aq. acetone; vi, CH_2Cl_2, BuLi, $LiClO_4$, $CaCO_3$, HMPA; vii, H_2, 10% Pd-C; viii, MCPBA, CH_2Cl_2

decalone **39** whose methoxycarbonyl group at C-1 occupies an equatorial position as determined by the ^1H NMR spectrum with two methine protons at δ 2.4 (td, J 12, 5.8 Hz) and 2.58 (ddd, J 12.4, 10.6, 3.5 Hz) with two axial–axial couplings. Wittig condensation of ketone **39** proceeded to give the *exo*-methylene ester **40** (94%). LAH reduction of the methoxycarbonyl group at C-1 followed by Swern oxidation afforded the unstable aldehyde **41**. After catalytic hydrogenation of the exocyclic olefin at C-4 of the aldehyde **41**, Baeyer–Villiger oxidation provided the formate **46** whose proton at C-8 appeared at δ 4.3–4.7 with a half-height width of 22 Hz. This result established the stereochemistry at C-1 of the aldehyde **41**. Then the formyl group at C-1 in compound **41** was transformed into a vinyl group by Wittig methylenation to give the volatile acetal **42** which was deprotected to furnish the ketone **43** (80% overall yield from the *exo*-methylene ester **40**). Finally, the requisite α,β-unsaturated aldehydic moiety was introduced to the ketone **43** according to the one-pot procedure using dichloromethyllithium[20] to furnish khusilal **44** (21%) along with its regioisomer **45** (25%). The spectral data of khusilal **44** (NMR and IR) agreed with those reported.

Thus, the present one-pot annulation proceeds *via* sequential double Michael reaction and provides a useful method for the preparation of substituted 1-decalones with defined stereochemistry under either of alternative and complementary reaction conditions, namely basic or acidic conditions, in

acceptable yields. Both enantiomers of optically active decalones have been obtained in ~70% diastereoselective and 60% chemical yields. The utility of the decalones as starting materials for terpenoid synthesis has been exemplified by the syntheses of ε-cadinene **32**, khusitone **36** and khusilal **44**.

Experimental

All m.p.s were determined with a Mitamura Riken hot-stage apparatus and are uncorrected. IR spectra were recorded on a JASCO A-3 spectrophotometer for solutions in tetrachloromethane. ^{1}H NMR spectra were obtained for solutions in deuteriochloroform with JEOL GX-400 (400 MHz), Bruker CXP-300 (300 MHz), JEOL PS-100 (100 MHz), JEOL FX 90Q (90 MHz) and JEOL PMX-60 (60 MHz) instruments with tetramethylsilane as internal standard. *J*-Values are given in Hz. Mass spectra were run on a JEOL JMS-DX300 spectrometer with a JMA-3500 data system. Specific rotations, $[\alpha]_D$, were determined on a JASCO DIP-4S polarimeter for solutions in chloroform, and are given in 10^{-1} deg cm^2 g^{-1}. The circular dichroic spectrum was measured on a JASCO J-400X spectrophotometer. The UV spectrum was obtained on a JASCO UVDEC-505 spectrophotometer. Medium-pressure liquid chromatography (MPLC) was carried out on a JASCO PRC-50 instrument with a silica gel-packed column. Microanalyses were carried out in the microanalytical laboratory of this Institute. Ether refers to diethyl ether. Anhydrous sodium sulfate was used for the drying of organic extracts. Tetrahydrofuran (THF) was distilled from LAH before use. Upon typical work-up, product was extracted with solvent (2 × 20 cm^3 for 1–10 mmol scale reaction). The organic layer was washed once with water and once with brine. After drying over sodium sulfate, the solvent was evaporated off under reduced pressure.

General Procedure for the Reaction of the Kinetic Enolates **2** *of* 1-*Acetylcyclohexenes* **1** *with* α,β-*Unsaturated Carbonyl Compounds* **4**.—*Method I.* To a stirred solution of diisopropylamine in anhydrous THF at 0 °C under nitrogen was added BuLi (1.5 mol dm^{-3} solution in hexane). After the mixture had been stirred for 10 min, a solution of the 1-acetylcyclohexene **1** in THF was added to the mixture at −85 °C, and the solution was stirred for 30 min at that temperature. A solution of an α,β-unsaturated carbonyl compound **4** in THF was added and the resulting solution was stirred overnight, with gradual raising of the reaction temperature to ambient. Aq. ammonium chloride was added to quench the reaction and the product was extracted with ether. Purification by MPLC gave the corresponding 1-decalone **5**.

Method II. To a stirred solution of a trimethylsiloxyvinyl compound **3** in THF was added MeLi (0.89 mol dm^{-3} solution in ether) at 0 °C under nitrogen. After the mixture had been stirred at room temperature for 30 min, a solution of an α,β-unsaturated carbonyl compound **4** in THF was added and the mixture was stirred overnight at room temperature. The reaction was quenched by the addition of aq. ammonium chloride and the product was extracted with ether. Purification by MPLC afforded the corresponding 1-decalone **5**.

4-[1-(*Trimethylsiloxy*)*vinyl*]*cyclohex*-3-*enone* 1-*Ethylene Ketal* **3b**.—A solution of 1-methoxy-3-(trimethylsiloxy)buta-1,3-diene[15] (3.24 cm^3, 15 mmol) and methyl vinyl ketone **6a** (1.25 cm^3, 15 mmol) in anhydrous benzene (6 cm^3) was heated at reflux under nitrogen for 18 h, when pent-3-en-2-one **6a** (0.38 cm^3, 0.45 mmol) was added. After the mixture had been heated at reflux for 6 h, the resulting solution was cooled to room temperature. A solution of butan-2-one ethylene ketal (2.9 g, 25 mmol) and toluene-*p*-sulfonic acid (PTSA) (100 mg) in benzene (5 cm^3) was added and the resulting solution was heated at 50 °C for 2 h. The reaction was quenched by addition of aq. $NaHCO_3$ and the product was extracted with chloroform (50 cm^3 × 2). The organic layer was washed successively with water and brine. Evaporation of the solvents left an oil, which was purified by column chromatography on SiO_2 to give 4-*acetylcyclohex*-3-*enone* 1-*ethylene ketal* **1b** (1.25 g, 85%); ν_{max}/cm^{-1} 1735, 1715, 1670 and 1640; δ(60 MHz) 1.6–1.9 (2 H, m), 2.27 (3 H, s, COMe), 2.3–2.7 (4 H, m), 3.96 (4 H, s, OCH_2CH_2O) and 6.69 (1 H, m, 3-H) (Found: C, 65.7; H, 7.9. $C_{10}H_{14}O_3$ requires C, 65.9; H, 7.7%).

A solution of LDA was prepared from diisopropylamine (1.25 cm^3, 8.9 mmol) in THF (10 cm^3) and BuLi (1.45 mol dm^{-3} solution in hexane; 5.7 cm^3, 8.2 mmol) at 0 °C under nitrogen. To a stirred solution of LDA at −85 °C was added a solution of 4-acetylcyclohex-3-enone 1-ethylene ketal (1.25 g, 6.85 mmol) in THF (7 cm^3). The mixture was stirred for 30 min and then chlorotrimethylsilane (1.3 cm^3, 10.3 mmol) was added in one portion. After being stirred for 1 h, the reaction mixture was quenched at −55 °C by addition of aq. $NaHCO_3$. The product was extracted with ether (50 cm^3 × 2) and the organic layer was washed successively with water and brine. Evaporation of ether followed by evaporative distillation (0.1 mmHg at 85 °C), afforded the siloxyvinyl compound **3b** (1.45 g, 83%); δ(60 MHz) 0.21 (9 H, s, $SiMe_3$), 1.6–2.0 (2 H, m), 2.2–2.6 (4 H, m), 3.93 (4 H, s, OCH_2CH_2O), 4.17 (1 H, s), 4.32 (1 H, s) and 6.01 (1 H, t-like, *J* 4, 3-H).

General Procedure for the Reaction of the Trimethylsiloxyvinyl Derivatives **3** *of* 1-*Acetylcyclohexenes* **1** *with* α,β-*Unsaturated Carbonyl Compounds* **4** *or* **6**.—*Method III.* To a stirred solution of a Lewis acid in dichloromethane were added successively at −85 °C a solution of an α,β-unsaturated carbonyl compound **4** or **6** and a solution of the trimethylsilyl enol ether **3**, both in dichloromethane. The reaction temperature was raised gradually and the mixture was stirred at room temperature overnight. After the addition of aq. potassium carbonate, the resulting suspension was filtered through a Celite pad. The product was extracted with ether, and the extracts were concentrated to give an oil, which was subjected to MPLC to give the pure 1-decalone **5**.

4-*Acetyl*-3,4,4a,5,6,7,8,8a-*octahydro*-4-(*trimethylsilyl*)*naphthalen*-1(2H)-*one* **5a**. Method I: 26%, Method II: 9%; ν_{max}/cm^{-1} 1710, 1680, 1440, 1360, 1260m, 1190 and 1085; δ(60 MHz) 0.18 (9 H, s, $SiMe_3$), 0.8–2.9 (14 H, m) and 2.20 (3 H, s, COMe); *m*/*z* 266 (M$^+$, 74%), 251 (25), 237 (22), 223 (100), 176 (17), 143 (19), 75 (36) and 73 (100) (Found: M$^+$, 266.1696. $C_{15}H_{26}O_2Si$ requires M, 266.1701).

Methyl decahydro-4-*oxo*-1-(*trimethylsilyl*)*naphthalene*-1-*carboxylate* **5b**. Method I: 62%, Method II: 39%; ν_{max}/cm^{-1} 1720, 1710, 1260, 1170, 1120 and 840; δ(60 MHz) 0.12 (9 H, s, $SiMe_3$), 0.9–3.0 (14 H, m) and 3.72 (3 H, s, OMe); *m*/*z* 283 (M$^+$ + 1, 18%), 282 (M$^+$, 9), 239 (36), 178 (100), 135 (95), 89 (23) and 73 (19) (Found: M$^+$, 282.1652. $C_{15}H_{26}O_3Si$ requires M, 282.1651).

4-*Acetyl*-3,4,4a,7,8,8a-*hexahydro*-4-(*trimethylsilyl*)*naphthalene*-1,6(2H,5H)-*dione* 6-*ethylene ketal* **5c**. Method I: 30%, Method II: trace; ν_{max}/cm^{-1} 1710, 1680, 1255, 1145, 1095 and 840; δ(60 MHz) 0.29 (9 H, s, $SiMe_3$), 1.3–2.9 (12 H, m), 2.17 (3 H, s, COMe) and 3.90 (4 H, s, OCH_2CH_2O); *m*/*z* 324 (M$^+$, 13%), 167 (18), 99 (100), 86 (53) and 73 (45) (Found: M$^+$, 324.1758. $C_{17}H_{28}O_4Si$ requires M, 324. 1757).

Methyl 7-*ethylenedioxydecahydro*-4-*oxo*-1-(*trimethylsilyl*)-*naphthalene*-1-*carboxylate* **5d**. Method I: 71%, Method II: 18%; ν_{max}/cm^{-1} 1720, 1710, 1255, 1150, 1100 and 840; δ(60 MHz) 0.13 (9 H, s, $SiMe_3$), 1.1–2.9 (12 H, m), 3.71 (3 H, s, OMe) and 3.92 (4 H, s, OCH_2CH_2O); *m*/*z* 340 (M$^+$, 27%), 267 (13), 183 (25), 99 (100), 86 (43), 73 (49) and 58 (49) (Found: M$^+$, 340.1707. $C_{17}H_{28}O_5Si$ requires M, 340.1706).

4α-*Acetyl*-3,4,4aβ,5,6,7,8,8aβ-*octahydronaphthalen*-1(2H)-*one* **5e**. Method III: 56%, m.p. 85–86 °C (Found: C, 74.2; H, 9.3. $C_{12}H_{18}O_2$ requires C, 74.33; H, 9.3%); ν_{max}/cm^{-1} 1710, 1460, 1450, 1350 and 1185; δ(300 MHz) 0.8–2.5 (13 H, m), 2.22 (3 H, s, COMe), 2.6 (1 H, br s, 8a-H) and 2.97 (1 H, dt, *J* 11.8, 4.1, 4β-H).

4-*Acetyl*-3,4,4aβ,5,6,7,8,8aβ-*octahydro*-3,3-*dimethylnaphthalen*-1(2H)-*one* **5f**. Method III: 33%; ν_{max}/cm^{-1} 1720, 1710, 1450, 1400, 1365 and 1355; δ(300 MHz) 0.91 (3 H, s, Me), 1.09 (3 H, s, Me), 1.0–2.0 (10 H, m), 2.08 (1 H, d, *J* 13, B part of AB type q, 2-H), 2.39 (1 H, d, *J* 13, A part of AB type q, 2-H), 2.25 (3 H, s, COMe) and 2.81 (1 H, d, *J* 9.1, 4-H). The *trans* isomer of **5f**, 4-*acetyl*-3,4,4aβ,5,6,7,8,8aα-octahydro-3,3-dimethylnaphthalen-1(2*H*)-one, was also isolated: 18%; ν_{max}/cm^{-1} 1705, 1450, 1350 and 1310; δ(300 MHz) 1.00 (3 H, s, Me), 1.04 (3 H, s, Me), 1.0–2.8 (12 H, m), 2.26 (3 H, s, COMe) and 3.01 (1 H, d, *J* 13.3, 4-H).

Methyl 1,2,3,4,4aβ,5,6,7,8,8aβ-*decahydro*-4-*oxonaphthalene*-1α-*carboxylate* **5g**. Method III: 64%, m.p. 88–89 °C; ν_{max}/cm^{-1} 1740, 1715, 1440 and 1220; δ(400 MHz) 1.05 (1 H, qd, *J* 12.9, 3.2, 8α-H), 1.12–1.25 (2 H, m, 5-H_2), 1.27–1.34 (1 H, br d, 8β-H), 1.38 (1 H, qt, *J* 12.7, 3.9, 6α-H), 1.46 (1 H, br, $w_{\frac{1}{2}}$ 18, 7α-H), 1.71 (1 H, br d, *J* 13, 7β-H), 2.04–2.11 (2 H, m, 2-H_2), 2.24 (1 H, br d, *J* 12.7, 6β-H), 2.28 [1 H, m, B part of AB type q, 3β-H, became doublet (*J* 14.3) by irradiation at δ 2.1], 2.4 [1 H, dt, *J* 14.3, 3.2, A part of AB type q, 3α-H, became doublet (*J* 14.3) by irradiation at δ 2.1], 2.54 (1 H, m, $w_{\frac{1}{2}}$ 23, 8a-H), 2.59 (1 H, br s, $w_{\frac{1}{2}}$ 9.5, 4a-H), 2.94 [1 H, dt, *J* 12.9, 3.9, 1-H, became doublet (*J* 3.9) by irradiation at δ 2.1] and 3.69 (3 H, OMe); *m*/*z* 210 (M^+, 62%), 155 (41), 128 (100), 100 (91), 81 (45) and 41 (46).

4-*Acetyl*-3,4,4a,7,8,8a-*hexahydronaphthalene*-1,6(2H,5H)-*dione* 6-*ethylene ketal* **5h**. Method III: 34%, $TiCl_2(OPr^i)_2$ (3 mol equiv.) was used instead of Et_2AlCl at −78 °C overnight to give a mixture of two isomers; the less polar major isomer had δ(60 MHz) 1.0–3.3 (13 H, m), 2.18 (3 H, s, COMe) and 3.87 (4 H, s, OCH_2CH_2O); the more polar minor isomer had δ(60 MHz) 1.0–3.0 (13 H, m), 2.16 (3 H, s, COMe) and 3.8 (4 H, s, OCH_2CH_2O), which were identical with those of the decalone **28**.

3,4,4a,5,6,7,8,8a-*Octahydro*-4-(*phenylsulfonyl*)*naphthalen*-1(2H)-*one* **7**. Method III: 21% (a mixture of two isomers); the less polar isomer had ν_{max}/cm^{-1} 3020, 1715, 1450, 1310, 1150 and 1090; δ(60 MHz) 0.7–3.4 (15 H, m), 7.4–7.8 (3 H, m, ArH) and 7.8–8.3 (2 H, m, ArH); the more polar isomer had ν_{max}/cm^{-1} 3020, 1715, 1450, 1310, 1150 and 1090; δ(60 MHz) 0.8–3.0 (14 H, m), 3.0–3.7 (1 H, br), 7.4–7.8 (3 H, m) and 7.8–8.2 (2 H, m).

4α-*Acetoxy*-3,4,4a,5,6,7,8,8a-*octahydronaphthalen*-1(2H)-*one* **8**.—*Method I:* A solution of the decalone **5e** (20 mg, 0.1 mmol) and MCPBA (80%; 33 mg, 0.15 mmol) in dichloromethane (2 cm^3) was heated under reflux under nitrogen for 24 h. After addition of water, the product was extracted with ether. The extract was treated with diazomethane. Evaporation of the ether followed by MPLC separation of the residue afforded the acetoxydecalone **8** (1 mg) along with recovered starting material (19 mg).

Method II: A mixture of the keto ester **5g** (110 mg, 0.52 mmol), ethylene glycol (0.14 cm^3, 2.6 mmol), and PTSA (10 mg, 0.05 mmol) in anhydrous benzene (10 cm^3) was heated under reflux using a Dean–Stark water separator for 1 h. After cooling to room temperature, the mixture was poured into cold aq. sodium hydrogen carbonate. The product was extracted with ether. Evaporation of the solvents followed by MPLC purification gave methyl 4-ethylenedioxy-1,2,3,4,4a,5,6,7,8,8aβ-decahydronaphthalene-1α-carboxylate (89 mg, 67%).

To a stirred solution of ketal (89 mg, 0.35 mmol) in anhydrous ether (2 cm^3) at 0 °C was added LAH (15 mg, 0.39 mmol) and the mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of water. The ethereal layer was separated, and evaporation of the ether left 3,4,4aβ,5,6,7,8,8aβ-octahydro-4-(hydroxymethyl)naphthalen-1(2*H*)-one ethylene ketal (75 mg, 95%).

To a stirred slurry of the alcohol (75 mg, 0.33 mmol) and molecular sieves 4 Å (380 mg) in dichloromethane (3 cm^3) at 0 °C was added pyridinium dichromate (98%; 380 mg, 1 mmol) and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was filtered through a short column of silica gel with the aid of ether. Evaporation of the solvents followed by MPLC purification gave 4-ethylenedioxy-1,2,3,4,4aβ,5,6,7,8,8aβ-decahydronaphthalene-1α-carbaldehyde (44 mg, 59%).

A solution of the aldehyde (22 mg, 0.1 mmol) and MCPBA (80%; 63 mg, 0.3 mmol) in dichloromethane (4 cm^3) was stirred at room temperature for 6 h. The resulting solution was poured into cold aq. sodium hydrogen carbonate. The product was extracted with ether. MPLC purification gave 3,4,4aβ,5,6,7,8,8aβ-octahydro-4-(formyloxy)naphthalen-1(2*H*)-one 1-ethylene ketal (9 mg, 38%); ν_{max}/cm^{-1} 1725, 1175 and 1105; δ(60 MHz) 0.9–2.3 (14 H, m), 3.95 (4 H, s, OCH_2CH_2O), 5.13 (1 H, br s, $w_{\frac{1}{2}}$ 16, 4-H) and 8.10 (1 H, s, CHO).

A solution of the formate (63 mg, 0.26 mmol) and PTSA (10 mg, 0.02 mmol) in THF (3 cm^3)–water (0.5 cm^3) was heated under reflux for 4 h. After cooling to room temperature, the resulting solution was poured into cold aq. sodium hydrogen carbonate. The product was extracted with ether. Evaporation of the solvents gave an oil, which was treated with acetic anhydride (0.2 cm^3) and pyridine (2 cm^3) overnight at room temperature. After being stirred for 30 min with ice chips, the product was extracted with ether. The organic layer was washed with aq. copper sulfate and evaporated to dryness. MPLC separation afforded the acetoxydecalone **8** (15 mg, 27%); ν_{max}/cm^{-1} 1740, 1720 and 1245; δ(60 MHz) 0.8–2.8 (14 H, m), 2.07 (3 H, s, COMe) and 5.26 (1 H, br s, $w_{\frac{1}{2}}$ 31, 4-H); *m*/*z* 209 ($M^+ - 1$, 3%), 167 (52) and 150 (100).

6α-*Acetoxy*-cis-2-*oxabicyclo*[5.4.0]*undecan*-3-*one* **9**.—A solution of the decalone **5e** (20 mg, 0.1 mmol) and MCPBA (80%; 44 mg, 0.2 mmol) in dichloromethane (4 cm^3) was heated under reflux under nitrogen for 62 h. After addition of water, the product was extracted with ether. The extract was treated with diazomethane. Evaporation of the ether, followed by MPLC separation of the residue, afforded the acetoxy lactone **9** (9 mg, 39%). The acetoxy lactone **9** had ν_{max}/cm^{-1} 1740, 1720, 1275, 1240, 1175 and 1040; δ(100 MHz) 1.0–2.4 (11 H, m), 2.08 (3 H, s, COMe), 2.4–2.8 (2 H, m, 4-H_2), 4.61 (1 H, br s, $w_{\frac{1}{2}}$ 8.8, 1-H) and 4.98 (1 H, dt, *J* 10.5, 5.5, 6-H); *m*/*z* 226 (M^+, 0.1%), 165 (100), 138 (35), 124 (35), 112 (34), 85 (50) and 80 (62).

4β-*Acetyl*-3,4,4aβ,5,6,7,8,8aα-*octahydronaphthalen*-1(2H)-*one* **10**.—To a solution of NaOMe prepared from sodium hydride (50%; 10 mg, 0.2 mmol) in anhydrous MeOH (4 cm^3) was added a solution of the decalone **5e** (20 mg, 0.1 mmol) in MeOH (1 cm^3) at room temperature under nitrogen. The mixture was stirred at room temperature for 72 h and MeOH was evaporated off under reduced pressure at room temperature. The residue was extracted with ether. MPLC purification gave the decalone **10** (14 mg, 70%); δ(300 MHz) 0.95–1.3 (4 H, m), 1.55–1.8 (5 H, m), 1.95–2.2 (3 H, m), 2.2 (3 H, s, COMe), 2.4–2.46 (2 H, m) and 2.71 (1 H, td, *J* 11.5, 3.5, 4α-H).

Trapping of 1-(4′-*Ethylenedioxycyclohex*-1′-*enyl*)-4-(*trimethylsilyl*)*hexane*-1,5-*dione* **11a**, *the Single Michael Adduct by Basic Double Michael Reaction.*—A solution of LDA was prepared from diisopropylamine (0.18 cm^3, 1.3 mmol) and BuLi (1.62 mol dm^{-3} solution in hexane; 0.74 cm^3, 1.2 mmol) at

0 °C under nitrogen. To the stirred solution of LDA at −85 °C was added a solution of the acetylcyclohexene **1b** (182 mg, 1.0 mmol) in anhydrous THF (2 cm^3). After the mixture had been stirred for 30 min, a solution of 3-(trimethylsilyl)but-3-en-2-one **4a**[5] (170 mg, 1.2 mmol) in THF (2 cm^3) was added. The resulting solution was stirred for 3.5 h and the reaction was quenched at −10 °C by addition of water. The aqueous layer was neutralised by 1 mol dm^{-3} HCl. The product was extracted with ether. Evaporation of the solvents, followed by MPLC separation of the residue, afforded the *single Michael adduct* **11a** (30 mg, 9%); ν_{max}/cm^{-1} 1720, 1670, 1640, 1370, 1120 and 845; δ(60 MHz) 0.10 (9 H, s, $SiMe_3$), 1.4–2.9 (11 H, m), 2.06 (3 H, s, COMe), 3.97 (4 H, s, OCH_2CH_2O) and 6.71 (1 H, br t, 2′-H); *m/z* 325 (M^+ + 1, 12%), 324 (M^+, 46), 223 (18), 143 (63), 86 (78) and 73 (100) (Found: M^+, 324.1753. $C_{17}H_{28}O_4Si$ requires M, 324.1757).

Trapping of Methyl 5-(4′-Ethylenedioxycyclohex-1′-enyl)-5-oxo-2-(trimethylsilyl)pentanoate **11b**, *the Single Michael Adduct by Basic Double Michael Reaction.*—In the same manner, the reaction of the acetylcyclohexene **1b** (91 mg, 0.5 mmol) with methyl 2-(trimethylsilyl)propenoate **4b**[6] (95 mg, 0.6 mmol) afforded the decalone **5d** (41 mg, 24%), recovered acetylcyclohexene **1b** (23 mg, 25%) and the single Michael adduct **11b** (9 mg, 5%); ν_{max}/cm^{-1} 1710, 1670, 1640, 1250 and 845; δ(60 MHz) 0.08 (9 H, s, $SiMe_3$), 1.5–2.9 (11 H, m), 3.62 (3 H, s, OMe), 3.96 (4 H, s, OCH_2CH_2O) and 6.70 (1 H, br t, 2′-H); *m/z* 340 (M^+, 9%), 308 (24), 99 (17), 86 (100), 73 (38) and 55 (27) (Found: M^+, 340.1707. $C_{17}H_{28}O_5Si$ requires M, 340.1706).

Isolation of Dimethyl 7-Oxo-2,4-bis(trimethylsilyl)bicyclo[6.4.0]dodecane-2,4-dicarboxylate, the Triple Michael Reaction Product **12a**.—According to Method I of the general procedure of the double Michael reaction, the reaction of acetylcyclohexene **1a** (124 mg, 1.0 mmol) with methyl 2-(trimethylsilyl)propenoate **4b**[6] (190 mg, 1.2 mmol) afforded the single Michael adduct **11c** (15 mg, 5%), the double Michael adduct **5b** (176 mg, 62%), and the triple Michael adduct **12a** (24 mg, 6%). The single Michael adduct **11c** had ν_{max}/cm^{-1} 1715, 1670, 1255, 1120 and 850; δ(60 MHz) 0.08 (9 H, s, $SiMe_3$), 1.0–3.0 (13 H, m), 3.65 (3 H, s, OMe) and 6.88 (1 H, br s, 2′-H).

The *triple Michael adduct* **12a** had ν_{max}/cm^{-1} 1720, 1435, 1255, 1220, 1120 and 840; δ(60 MHz) 0.19 (18 H, s, 2 × $SiMe_3$), 0.8–2.8 (16 H, m) and 3.67 (6 H, s, 2 × OMe); *m/z* 440 (M^+, 10%), 159 (28) 109 (34), 89 (29), 73 (100) and 55 (49) (Found: M^+, 440.2400. $C_{22}H_{40}O_5Si_2$ requires M, 440.2413).

Isolation of Dimethyl 11-Ethylenedioxy-7-oxo-2,4-bis(trimethylsilyl)bicyclo[6.4.0]dodecane-2,4-dicarboxylate **12b**, *the Triple Michael Reaction Product.*—According to Method I of the general procedure of the double Michael reaction, the reaction of the acetylcyclohexene **1b** (182 mg, 1.0 mmol) with methyl 2-(trimethylsilyl)propenoate **4b** (185 mg, 1.2 mmol) afforded the double Michael adduct **5d** (292 mg, 71%), and the triple Michael adduct **12b** (25 mg, 5%); ν_{max}/cm^{-1} 1715, 1250 and 840; δ(60 MHz) 0.09 (9 H, s, $SiMe_3$), 0.12 (9 H, s, $SiMe_3$), 0.9–3.0 (14 H, m), 3.62 (6 H, s, 2 × OMe) and 3.90 (4 H, s, OCH_2CH_2O); *m/z* 498 (M^+, 24%), 340 (13), 235 (13), 159 (30), 99 (100), 73 (96) and 55 (49) (Found: M^+, 498.2474. $C_{24}H_{42}O_7Si_2$ requires M, 498.2469).

Competitive Double Michael Reaction of the Trimethylsiloxy Compound **3a**[8] *with Methyl Vinyl Ketone* **6a** *and Dimethyl Fumarate.*—To a stirred solution of Et_2AlCl (1 mol dm^{-3} solution in hexane; 0.5 cm^3, 0.5 mmol) in anhydrous dichloromethane (3 cm^3) at −80 °C was added a solution of the trimethylsiloxy compound **3a**[8] (98 mg, 0.5 mmol), methyl vinyl ketone **6a** (42 mm^3, 0.5 mmol), and dimethyl fumarate (72 mg, 0.5 mmol) in dichloromethane (3 cm^3) under nitrogen. The resulting solution was stirred overnight with gradual warming to room temperature. The reaction was quenched by the addition of aq. potassium carbonate. The precipitate was removed by filtration. The product was extracted with ether. MPLC separation gave the decalone **5e** (33 mg, 34%).

Isolation of Dimethyl 7-(Trimethylsiloxy)bicyclo[6.4.0]dodec-7-ene-2,4-dicarboxylate **14**, *a Triple Michael Product.*—To a stirred suspension of ground molecular sieves (4 Å, 120 mg) in dichloromethane (3 cm^3) at −20 °C was added successively a solution of methyl acrylate **6c** (174 mm^3, 2 mmol) in dichloromethane (1.5 cm^3), a solution of the siloxy compound **3a**[8] (196 mg, 1 mmol) in dichloromethane (1.5 cm^3), and Et_2AlCl (1 mol dm^{-3} solution in hexane; 0.2 cm^3, 0.2 mmol) under nitrogen. The resulting suspension was stirred at −10–0 °C overnight. The reaction was quenched by addition of aq. potassium carbonate and the precipitate was removed by suction filtration through a Celite pad. Extraction with ether, followed by MPLC separation, afforded the decalone **5g** (142 mg, 50%), methyl 1,2,3,5,6,7,8,8aβ-octahydro-4-(trimethylsiloxy)naphthalene-1α-carboxylate **13** (24 mg, 14%); δ(60 MHz) 0.17 (9 H, $SiMe_3$), 0.7–3.1 (14 H, m) and 3.68 (3 H, s, OMe), and the diester **14** (14 mg, 4%); δ(60 MHz) 0.15 (9 H, $SiMe_3$), 0.9–3.5 (17 H, m) and 3.66 (6 H, s, 2 × OMe).

Treatment of the siloxy compound **13** with Et_2AlCl in dichloromethane at −10 °C gave the decalone **5g** quantitatively.

To a stirred solution of the diester **14** (14 mg, 0.04 mmol) in THF (1 cm^3) at 0 °C was added tetrabutylammonium fluoride (1 mol dm^{-3} in THF; 0.05 cm^3, 0.05 mmol). After being stirred for 20 min, the reaction mixture was quenched by addition of aq. ammonium chloride. Extraction with ether, followed by MPLC purification, provided *dimethyl 7-oxobicyclo[6.4.0]dodecane-2,4-dicarboxylate* (10 mg, 89%); ν_{max}/cm^{-1} 1730, 1700, 900, 715 and 645; δ(60 MHz) 0.8–2.6 (17 H, m), 3.36 (1 H, m), 3.67 (3 H, s, OMe) and 3.72 (3 H, s, OMe); *m/z* 296 (M^+, 4%), 222 (24), 209 (26), 128 (44), 124 (68) and 99 (100) (Found: M^+, 296.1626. $C_{16}H_{24}O_5$ requires M, 296.1624).

Trapping of 1-(4′-Ethylenedioxycyclohex-1′-enyl)hexane-1,5-dione **15**, *the Single Michael Adduct in the Lewis Acid-promoted Double Michael Reaction.*—To a stirred solution of $TiCl_2(OPr^i)_2$ (3 mmol) in anhydrous dichloromethane (5 cm^3) was added a solution of 3-(trimethylsilyl)but-3-en-2-one **4a**[5] (185 mg, 1.3 mmol) in dichloromethane (2 cm^3) and a solution of the trimethylsiloxy compound **3b** (257 mg, 1 mmol) in dichloromethane (2 cm^3) successively at −85 °C under nitrogen. The reaction was quenched at −18 °C in 3.5 h by addition of aq. potassium carbonate. Titanium hydroxide was removed by filtration through a Celite pad. The product was extracted with ether. After evaporation of the solvents, the residue was separated by MPLC to give the decalone **5c** (38 mg, 11.7%), the acetylcyclohexene **1b**, (43 mg, 17%), and the *single Michael adduct* **15** (48 mg, 19%) which exhibited ν_{max}/cm^{-1} 1710, 1665, 1640, 1365 and 1115; δ(60 MHz) 1.5–2.0 (4 H, m), 2.28 (3 H, s, COMe), 2.2–3.0 (8 H, m), 3.97 (4 H, s, OCH_2CH_2O) and 6.71 (1 H, br t, 2′-H); *m/z* 252 (M^+, 6%), 167 (7), 86 (100), 55 (16), 53 (17) and 43 (32) (Found: M^+, 252.1370. $C_{14}H_{20}O_4$ requires M, 252.1362).

Asymmetric Double Michael Reaction.—The reaction conditions of the double Michael reaction were the same as reported above for Method III employing an equimolar amount of the trimethylsiloxy compound **3a**,[8] the chiral acrylates **19a–g**, and 3

mol equiv. of Et_2AlCl in dichloromethane, at −80 °C to room temperature. The reaction according to Method I or II resulted in decomposition of the chiral acrylate **19a**.

Determination of the Diastereoisomeric Excess of Compound **22**.—*Decahydro-4-(hydroxymethyl)naphthalen-1-ol* **21**. To a stirred slurry of LAH (80 mg, 2.1 mmol) in anhydrous ether (8 cm^3) was added a solution of the keto ester **20g** (440 mg, 1.05 mmol) in ether (6 cm^3). The resulting slurry was heated under reflux for 1 h. The reaction was quenched by addition of water at 0 °C and the organic layer was filtered through anhydrous sodium sulfate. Evaporation of ether, followed by column chromatography, left the *diol* **21** (190 mg, 98%); ν_{max}/cm^{-1} 3600, 3450, 1445 and 1210; δ(60 MHz) 0.7–2.0 (15 H, m), 3.56 (2 H, br d, *J* 5, CH_2OH) and 4.06 (1 H, m, 1-H); *m/z* 184 (M^+, 2%), 166 (21), 148 (36), 135 (73), 93 (48), 91 (48), 81 (55), 79 (66), 67 (100) and 55 (65) (Found: M^+, 184.1467. $C_{11}H_{20}O_2$ requires M, 184.1464). The yields of the diol **21** from other keto esters are as follows: 90% from **20a**; 99% from **20b**; 91% from **20c**; 77% from **20d**; 89% from **20f**. (For yield from the acid **20e**, see below.)

Methyl decahydrooxonaphthalene-1-carboxylate **22**. To a stirred solution of the diol **21** derived from the keto ester **20g** (190 mg, 1.03 mmol) in acetone (5 cm^3) at 0 °C was added Jones' reagent dropwise. After the solution became orange, it was stirred for 1.5 h, and then water was added. The product was extracted with ethyl acetate. After evaporation of the solvent, the residue was dissolved in ether and treated with diazomethane. Evaporation of the ether left the keto ester (178 mg, 82%). A solution of the keto ester in anhydrous methanol (5 cm^3) was added to a solution of sodium methoxide (2.2 mmol) in methanol (3 cm^3) at 0 °C under nitrogen. The resulting solution was heated at 30 °C overnight. Aq. ammonium chloride was added to the solution and the product was extracted with ethyl acetate. Evaporation of the solvent, followed by MPLC purification, left the *keto ester* **22** (117 mg, 47% from the diol **21**), $[\alpha]_D$ +2.0 (*c* 1.03); ν_{max}/cm^{-1} 1730, 1705 and 1160; δ(60 MHz) 0.8–2.8 (15 H, m) and 3.67 (3 H, s, OMe); *m/z* 210 (M^+, 100%), 151 (51), 150 (81), 142 (52), 133 (69), 128 (51), 109 (89), 100 (93), 83 (68), 81 (57) and 79 (53) (Found: M^+, 210.1262. $C_{12}H_{18}O_3$ requires M, 210.1256). The overall yield and specific rotational value of the keto ester **22** from the diol **21** derived from other sources are as follows: **20a**, 65%, −23.4 (*c* 0.80); **20b**, 57%, +24.9 (*c* 1.11); **20c**, 63%, −22.9 (*c* 1.38); **20d**, 45%, −21.5 (*c* 0.646); **20e**, 54% from **20e**; **20f**, 44%, −1.4 (*c* 1.31).

Methyl 4-[(2R,3R)-butane-2,3-diyldioxy]decahydronaphthalene-1-carboxylate **23**. A mixture of the keto ester **22** (derived from a major diastereoisomer of **20a** separated by MPLC; 105 mg, 0.5 mmol) (2*R*,3*R*)-butane-2,3-diol (93 mm^3, 0.6 mmol), and PTSA (20 mg) in anhydrous benzene (8 cm^3) was heated under nitrogen under reflux using a Dean–Stark water separator. After being stirred for 1 h, the reaction was quenched by addition of aq. sodium hydrogen carbonate. The product was extracted with ether. Evaporation of the ether left the *acetal* **23** (137 mg, 96%), $[\alpha]_D$ −27.8 (*c* 1.37) (Found: C, 68.5; H, 9.4%; M^+, 282.1836. $C_{16}H_{26}O_4$ requires C, 68.1; H, 9.3%; M, 282.1831); ν_{max}/cm^{-1} 1720, 1450, 1430, 1160 and 1090; δ(60 MHz) 0.7–2.5 (15 H, m), 1.20 (3 H, d, *J* 6, Me), 1.25 (3 H, d, *J* 6, Me), 3.3–4.0 (2 H, m, OCHCHO) and 3.69 (3 H, s, OMe); *m/z* 282 (M^+, 6%), 181 (73), 127 (100), 114 (46), 81 (13) and 55 (37). The acetal **23** was analysed by MPLC [column SiO_2; solvent ethyl acetate–hexane (1 : 7), flow rate 20 cm^3 min^{-1}; resolution factor (1.1)] and the diastereoisomeric excess was 97.4%. The d.e.s of the acetal derived from substrates **20a–g** are listed in the Table 3.

Determination of the Absolute Stereochemistry.—*2-(1,2,4a,5,6,7,8,8a-Octahydro-1-naphthyl)propan-2-ol* **24**. A stirred mixture of the (−)-keto ester **22** (400 mg, 1.89 mmol, enriched to 97% d.e. by MPLC separation of **20a**) and toluene-*p*-sulfonohydrazide (352 mg, 1.9 mmol) in ethanol (2 cm^3) was heated under reflux for 2 h. After evaporation of the ethanol under reduced pressure, anhydrous THF (4 cm^3) and MeLi (0.73 mol dm^{-3} solution in ether; 12 cm^3, 8.8 mmol) were added successively to the mixture at 0 °C under nitrogen. After being stirred for 1 h, the reaction mixture was quenched by addition of aq. ammonium chloride. The product was extracted with ether. MPLC purification gave the olefinic alcohol **24** (202 mg, 55%), $[\alpha]_D$ −9.4 (*c* 0.62); ν_{max}/cm^{-1} 3600, 3450, 1445, 1385, 1370, 1090 and 915; δ(60 MHz) 0.8–2.5 (14 H, m), 1.20 (6 H, s, 2 × Me) and 5.2–5.8 (2 H, m, olefinic H); *m/z* 176 ($M^+ - H_2O$, 11%), 161 (14), 133 (40), 91 (34), 59 (27), 44 (35) and 40 (100).

Decahydro-4-(1-hydroxy-1-methylethyl)naphthalene-1,2-diol **25**. To a stirred solution of the olefinic alcohol **24** (202 mg, 1.04 mmol) in anhydrous THF (4 cm^3) were added successively *N*-methylmorpholine *N*-oxide (309 mg, 2.2 mmol), *tert*-butyl alcohol (4 cm^3), water (0.5 cm^3), and osmium tetraoxide (27 mg, 0.1 mmol). After being stirred for 1.3 h at room temperature, the reaction mixture was quenched by addition of aq. sodium hydrogen sulfate. The product was extracted with ethyl acetate to give the *triol* **25** (213 mg, 90%); ν_{max}/cm^{-1} 3400, 1445, 1370 and 1240; δ(60 MHz) 0.7–3.0 (16 H, m), 1.17 (3 H, s), 1.22 (3 H, s), 3.14 (1 H, dd, *J* 9, 3, 1-H) and 4.0 (1 H, m, 2-H); *m/z* 210 ($M^+ - H_2O$, 4%), 152 (43), 134 (38), 111 (26), 108 (28), 98 (19), 96 (19), 95 (29), 93 (21), 81 (31), 70 (69) and 59 (100) (Found: M^+, 228.1718. $C_{13}H_{24}O_3$ requires M, 228.1725).

(1S,2R,4R,4aR,8aR)-*Decahydro-4-(1-hydroxy-1-methylethyl)-1,2-bis-(4-methoxybenzoyloxy)naphthalene* **26**. To a stirred solution of the triol **25** (91 mg, 0.4 mmol) in anhydrous pyridine (4 cm^3) at 0 °C were added 4-(dimethylamino)pyridine (10 mg, 0.08 mmol) and *p*-methoxybenzoyl chloride (320 mg, 2 mmol). After the mixture had been stirred at 60 °C for 1 h, water was added. The product was extracted with ether. MPLC purification gave the *bismethoxybenzoate* **26** (142 mg, 71%) (Found: C, 69.9; H, 7.4. $C_{29}H_{36}O_7$ requires C, 70.1; H, 7.3%); λ_{max}(EtOH)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 32 400); λ_{max}(EtOH)/nm 266 ($\Delta\varepsilon$ −16.0) and 246 ($\Delta\varepsilon$ +7.8); ν_{max}/cm^{-1} 1720, 1610, 1510, 1285, 1255 and 1170; δ(300 MHz) 0.8–2.2 (14 H, m), 1.20 (3 H, s, Me), 1.23 (3 H, s, Me), 3.81 (3 H, s, OMe), 3.89 (3 H, s, OMe), 4.91 (1 H, dd, *J* 10.6, 2.7, 1-H), 5.60 (1 H, br s, $w_{\frac{1}{2}}$ 7, 2-H), 6.81 (2 H, d, *J* 8.9, ArH), 6.97 (2 H, d, *J* 8.9, ArH), 7.85 (2 H, d, *J* 8.9, ArH) and 8.03 (2 H, d, *J* 8.9, ArH); *m/z* 496 (M^+, 1.5%), 326 (91), 286 (22), 174 (48), 136 (100), 135 (100), 107 (33), 92 (24) and 77 (34).

4β-*Acetyl*-3,4,4aβ,7,8,8aα-*hexahydronaphthalene*-1,6(2H,5H)-*dione 6-Ethylene Ketal* **28**.—To sodium hydride (50%; 11 mg, 0.23 mmol) was added anhydrous methanol (1 cm^3) under nitrogen at 0 °C followed by a solution of the trimethylsilyldecalone **5c** (32 mg, 0.1 mmol) in methanol (1 cm^3). The resulting solution was stirred at room temperature for 10.5 h. The reaction was quenched by the addition of aq. ammonium chloride and the product was extracted with ether and then with ethyl acetate. Removal of the solvents left an oil (28 mg), which was purified by MPLC to give the *diketone* **28** (16 mg, 64%), m.p. 80–80.5 °C (Found: C, 66.9; H, 8.1. $C_{14}H_{20}O_4$ requires C, 66.6; H, 8.0%); ν_{max}/cm^{-1} 1720, 1360, 1145 and 1110; δ(60 MHz) 1.2–3.0 (13 H, m), 2.16 (3 H, s, COMe) and 3.88 (4 H, s, OCH_2CO_2O) (Found: M^+, 252.1372. $C_{14}H_{20}O_4$ requires M, 252.1362).

4β-*Acetyl*-3,4,4aβ,7,8,8aα-*hexahydronaphthalene*-1,6(2H,5H)-*dione 1,6-Ethylene Diketal* **29**.—A mixture of the diketone **28** (186 mg, 0.74 mmol), ethylene glycol (49 mm^3, 0.89 mmol) and PTSA (14 mg, 0.07 mmol) in anhydrous benzene (3 cm^3) was heated under reflux for 1 h under nitrogen. After

cooling to room temperature, the reaction mixture was quenched by the addition of aq. sodium hydrogen carbonate. The aqueous layer was extracted with ether and the solvents were evaporated off under reduced pressure. MPLC purification of the residue afforded the *diketal* **29** (159 mg, 73%), m.p. 111–111.5 °C (Found: C, 64.9; H, 8.3. $C_{16}H_{24}O_5$ requires C, 64.8; H, 8.2%); ν_{max}/cm^{-1} 1710, 1320, 1115, 1040 and 930; δ(300 MHz) 1.15–2.0 (12 H, m), 2.12 (3 H, s, COMe), 2.19 (1 H, td, *J* 11.5, 3.7, 4-H) and 3.9 (8 H, br s, OCH_2CH_2O).

3,4,4aβ,7,8,8aα-*Hexahydro*-4β-*isopropenylnaphthalene*-1,6-(2H,5H)-*dione* 1,6-*Ethylene Diketal* **30**.—To a stirred suspension of methyltriphenylphosphonium bromide (1.82 g, 5 mmol) in anhydrous THF cooled in an ice-bath was added BuLi (1.45 mol dm^{-3} solution in hexane; 4 mmol) under nitrogen. The resulting suspension was heated under reflux and a solution of the ketal **29** (42 mg, 0.14 mmol) in THF (1 cm^3) was added. After being heated for 31 h, the reaction mixture was quenched by addition of water. Extraction with ether, followed by MPLC purification, afforded the *isopropenyl acetal* **30** (34 mg, 81%), m.p. 104.5–105 °C (Found: C, 69.3; H, 9.1. $C_{17}H_{26}O_4$ requires C, 69.3; H, 8.9%); ν_{max}/cm^{-1} 3070, 1645 and 1115; δ(60 MHz) 0.7–2.0 (13 H, m), 1.62 (3 H, s, olefinic Me), 3.87 (4 H, s, OCH_2CH_2O), 3.9 (4 H, s, OCH_2CH_2O) and 4.67 (2 H, s, *exo*-methylene).

3,4,4aβ,7,8,8aα-*Hexahydro*-4β-*isopropylnaphthalene*-1,6(2H,5H)-*dione* **31**.—A solution of the isopropenyl ketal **30** (46 mg, 0.16 mmol) in ethanol (5 cm^3) was hydrogenated over palladium charcoal (10 mg; 10%) at room temperature. After the mixture had been stirred for 19 h, further palladium charcoal (10 mg) was added and the suspension was stirred for a further 4 h under hydrogen. Removal of the catalyst by filtration, followed by evaporation of the solvent, left an oil, which was dissolved in a solution of PTSA monohydrate (5 mg) in THF (1.5 cm^3)–water (0.5 cm^3). The resulting solution was then heated under reflux for 4 h. Extraction with ether, followed by MPLC purification, provided the diketone **31** (19 mg, 66% in two steps), m.p. 69–70 °C (lit.,[16c] 71–71.5 °C); ν_{max}/cm^{-1} 1720, 1365, 1325, 1230 and 1080; δ(60 MHz) 0.72 (3 H, d, *J* 6.5, Me), 0.97 (3 H, d, *J* 6.5, Me) and 1.9–2.9 (14 H, m).

ε-*Cadinene*, (4aβ,8aα)-*Decahydro*-4β-*isopropyl*-1,6-*dimethylenenaphthalene* **32**.—To a stirred suspension of methyltriphenylphosphonium bromide (1.09 g, 3 mmol) in anhydrous THF (3 cm^3) was added BuLi (1.45 mol dm^{-3} solution; 1.72 cm^3, 2.5 mmol) at room temperature under nitrogen. After this mixture had been stirred for 10 min, a solution of the diketone **31** (19 mg, 0.1 mmol) in THF (0.5 cm^3) was added and the mixture was stirred for 30 min. The reaction was quenched by addition of water and the product was extracted with pentane. Evaporation of the solvent, followed by MPLC purification of the residue, gave ε-cadinene **32** (14 mg, 75%); ν_{max}/cm^{-1} 3070, 2930, 2870, 1645 and 890; δ(60 MHz) 0.72 (3 H, d, *J* 6.5, Me), 0.93 (3 H, d, *J* 6.5, Me), 1.0–2.7 (14 H, m) and 4.7–4.4 (4 H, m, *exo*-methylene); *m*/*z* 204 (M$^+$, 15%), 176 (55), 161 (100), 133 (68), 119 (42), 105 (59), 93 (61), 91 (81), 81 (66), 79 (65) and 41 (69).

8α-*Acetyl*-3,4,4aβ,5,6,7,8,8aα-*octahydro*-5-*methylenenaphthalen*-2(1H)-*one* 2-*Ethylene Ketal* **33**.—To a stirred suspension of methyltriphenylphosphonium bromide (340 mg, 0.79 mmol) in anhydrous THF (4 cm^3) cooled in an ice-bath was added BuLi (1.57 mol dm^{-3} solution in hexane; 0.55 cm^3, 0.87 mmol) under nitrogen. After the mixture had been stirred for 15 min, a solution of the diketone **28** (198 mg, 0.79 mmol) in THF (5 cm^3) was added and the mixture was stirred for 5 h. The reaction was quenched by addition of water. Extraction with ether, followed by MPLC purification, afforded the *methylene ketone* **33** (89 mg, 45%), m.p. 83–84 °C (Found: C, 71.8; H, 8.8. $C_{15}H_{22}O_3$ requires C, 72.0; H, 8.9%); ν_{max}/cm^{-1} 3075, 1705, 1645, 1360, 1115, 1075 and 895; δ(60 MHz) 1.0–2.7 (13 H, m), 2.07 (3 H, s, COMe), 3.87 (4 H, s, OCH_2CH_2O), 4.61 (1 H, s, *exo*-methylene) and 4.69 (1 H, s, *exo*-methylene); *m*/*z* 250 (M$^+$, 100%), 207 (31), 167 (84), 149 (30), 87 (76) and 86 (61).

3,4,4aβ,5,6,7,8,8aα-*Octahydro*-8α-(1-*hydroxyethyl*)-5-*methylenenaphthalen*-2(1H)-*one* **34**.—To a stirred, ice-cooled suspension of LAH (12 mg, 0.31 mmol) in anhydrous ether (2 cm^3) was added a solution of the ketone **33** (78 mg, 0.31 mmol) in ether (2 cm^3) under nitrogen. After being stirred for 15 min, the reaction mixture was quenched by the addition of water. Filtration, followed by evaporation of the ether, left an oil, which was purified by MPLC to afford 3,4,4aβ,5,6,7,8,8aα-*octahydro*-8α-(1-*hydroxyethyl*)-5-*methylenenaphthalen*-2(1H)-*one ethylene ketal* (79 mg, quant) (Found: C, 71.2; H, 9.8. $C_{15}H_{24}O_3$ requires C, 71.4; H, 9.6%); ν_{max}/cm^{-1} 3620, 3460, 3075, 1645, 1445, 1140, 1050 and 890; δ(60 MHz) 0.8–2.7 (13 H, m), 1.15 (3 H, d, *J* 6.5, Me), 3.93 (4 H, s, OCH_2CH_2O), 3.8–4.3 (1 H, m, C*H*OH), 4.57 (1 H, s, *exo*-methylene) and 4.65 (1 H, s, *exo*-methylene).

A solution of the alcohol (75 mg, 0.3 mmol) and PTSA monohydrate (30 mg) in acetone (2 cm^3)–water (0.2 cm^3) was heated under reflux for 1.5 h. After addition of water, extraction with ether, followed by MPLC purification, gave the *hydroxy ketone* **34** (44 mg, 71%), m.p. 96.5–97.5 °C (Found: C, 74.9; H, 9.9. $C_{13}H_{20}O_2$ requires C, 75; H, 9.7%); ν_{max}/cm^{-1} 3620, 3440, 3075, 1710, 1645, 1260, 1095 and 890; δ(60 MHz) 1.0–3.0 (13 H, m), 1.17 (3 H, d, *J* 6.5, Me), 3.8–4.3 (1 H, m, C*H*OH), 4.58 (1 H, s, *exo*-methylene), and 4.72 (1 H, s, *exo*-methylene).

1-[(4aβ,8aα)-*Decahydro*-7-*hydroxy*-7-*methyl*-4-*methylene*-1-*naphthyl*]*ethanone* **35**.—To a solution of the hydroxy ketone **34** (44 mg, 0.21 mmol) in ice-cooled anhydrous ether (3 cm^3) was added a solution of MeLi (1.6 mol dm^{-3} solution in ether; 0.4 cm^3, 0.63 mmol) under nitrogen. After the mixture had been stirred for 1 h in an ice-bath, an additional solution of MeLi (0.4 cm^3) was added and the mixture was stirred for 1 h at ice-bath temperature and then room temperature for 1.5 h. The reaction was quenched by addition of aq. ammonium chloride. Extraction with ether, followed by MPLC purification, gave (4aβ,8aα)-*decahydro*-8α-(1-*hydroxyethyl*)-2-*methyl*-5-*methylenenaphthalen*-2-*ol* (24 mg, 51%, a mixture of two diastereoisomers); ν_{max}/cm^{-1} 3600, 3420, 3075, 1645, 1375, 1320, 1240, 1020 and 890; δ(60 MHz) 0.7– 2.6 (13 H, m), 1.16 (3 H, d, *J* 6, Me), 1.20 (3 H, s, Me), 3.8–4.3 (1 H, m, C*H*OH), 4.52 (1 H, s, *exo*-methylene) and 4.6 (1 H, s, *exo*-methylene).

To a stirred, ice-cooled solution of the diol (24 mg, 0.11 mmol) in acetone (1.5 cm^3) was added Jones' reagent dropwise until red colour persisted. Excess of Cr^{VI} was destroyed by the addition of propan-2-ol. Addition of water and extraction with ether, followed by MPLC purification, gave the hydroxy ketone **35** (15.5 mg, 63%, a mixture of two diastereoisomers); ν_{max}/cm^{-1} 3600, 3400, 3075, 1715, 1645, 1440, 1240, 1165 and 900; δ(60 MHz) 0.8–2.7 (13 H, m), 1.23 (3 H, s, Me), 2.12 (3 H, s, COMe), 4.58 (1 H, s, *exo*-methylene) and 4.68 (1 H, s, *exo*-methylene).

Khusitone, 1-(1,2,3,4,4aβ,5,6,8aα-*Octahydro*-7-*methyl*-4-*methylene*-1α-*naphthyl*)*ethanone* **36**.—To a stirred solution of the hydroxy ketone **35** (11 mg, 0.05 mmol) in pyridine (1 cm^3) was added phosphorus trichloride oxide (23 mm^3, 0.25 mmol) at 0 °C. After being stirred for 2.5 h at room temperature, the resulting solution was poured into ice–water. Extraction with ether, followed by MPLC purification, gave khusitone **36** (1.6 mg) along with an inseparable mixture of 1-(1,2,3,4,4aβ,5,8,8aα-octahydro-7-methyl-4-methylene-1-naphthyl)ethanone **37** and 1-[(4aβ,8aα)-decahydro-4,7-dimethylene-

1-naphthyl]ethanone **38** (3.5 mg) (51% total). Khusitone **36** had ν_{max}/cm^{-1} 3075, 1710, 1645, 1355, 1235 and 890; δ(90 MHz) 1.0–2.6 (11 H, m), 1.64 (3 H, s, olefinic Me), 2.12 (3 H, s, COMe), 4.63 (1 H, s, *exo*-methylene), 4.74 (1 H, s, *exo*-methylene) and 5.05 (1 H, br s, 8-H); *m/z* 204 (M^+, 22%), 161 (100), 119 (22), 105 (42), 91 (24), 81 (26) and 43 (47).

A mixture of isomers **37** and **38** had ν_{max}/cm^{-1} 3075, 1710, 1645, 1360, 1240, 1170 and 900; δ(90 MHz) 1.0–2.6 (10–11 H, m), 1.61 (br s, olefinic Me), 2.15 (3 H, s, COMe), 4.63 (s, *exo*-methylene), 4.76 (s, *exo*-methylene) and 5.43 (m, 8-H) (*exo*-methylene H : 6-H 3 : 1).

Methyl (4aβ,8aα)-7-*Ethylenedioxydecahydro*-4-*oxonaphthalene*-1α-*carboxylate* **39**.—To sodium hydride (50%; 50 mg, 1 mmol), washed three times with hexane at 0 °C, was added anhydrous methanol (2 cm^3) under nitrogen. After addition of a solution of the decalone **5d** (115 mg, 0.34 mmol) in methanol (3 cm^3), the resulting solution was heated at 40 °C for 4.4 h. The reaction was quenched by addition of aq. ammonium chloride. The water layer was acidified by dil. HCl and extracted with ethyl acetate. Evaporation of the solvents gave an oil, which was treated with diazomethane. MPLC purification afforded the decalone **39** (48 mg, 53%) along with other isomers (30%). The decalone **39** had m.p. (107.5–108.5 °C; ν_{max}/cm^{-1} 1740, 1715, 1195, 1150 and 1090; δ(300 MHz) 1.4–2.3 (11 H, m), 2.4 (1 H, td, *J* 12, 5.8, 4aβ-H), 2.58 (1 H, ddd, *J* 12.4, 10.6, 3.5, 1β-H), 3.72 (3 H, s, OMe) and 3.93 (4 H, s, OCH_2CH_2O); *m/z* 268 (M^+, 29%), 183 (73), 100 (24), 86 (100) and 55 (35).

Methyl (4aβ,8aα)-7-*Ethylenedioxydecahydro*-4-*methylenenaphthalene*-1α-*carboxylate* **40**.—To a stirred suspension of methyltriphenylphosphonium bromide (613 mg, 1.7 mmol) in anhydrous THF (6 cm^3) at 0 °C was added BuLi (1.57 mol dm^{-3} solution in hexane; 0.94 cm^3, 1.5 mmol) under nitrogen. After the mixture had been stirred for 15 min, a solution of the decalone **39** (307 mg, 1.14 mmol) in THF (7 cm^3) was added to the suspension and the mixture was stirred for a further 30 min. Aq. ammonium chloride was added to quench the reaction. Extraction with ether, followed by column chromatography on silica gel, gave the *olefinic ester* **40** (284 mg, 94%), m.p. 51.5–52.5 °C; ν_{max}/cm^{-1} 3075, 1735, 1645, 1260, 1160, 1080 and 900; δ(300 MHz) 1.2–2.5 (12 H, m), 2.27 (1 H, br t, *J* 9.7, 4aβ-H), 3.67 (3 H, s, OMe), 3.93 (4 H, s, OCH_2CH_2O), 4.64 (1 H, s, *exo*-methylene) and 4.73 (1 H, s, *exo*-methylene); *m/z* 266 (M^+, 100%), 207 (46), 183 (96), 100 (76), 99 (71), 87 (56), 86 (67) and 55 (43) (Found: M^+, 266.1506. $C_{15}H_{22}O_4$ requires M, 266.1517).

(4aβ,8aα)-7-*Ethylenedioxydecahydro*-4-*methylenenaphthalene*-1α-*carbaldehyde* **41**.—To a stirred suspension of LAH (97 mg, 2.54 mmol) in anhydrous THF (10 cm^3) at 0 °C was added a solution of the ester **40** (676 mg, 2.54 mmol) in THF (10 cm^3) under nitrogen. After being stirred for 25 min, the reaction mixture was quenched by the addition of water. Aluminium hydroxide was removed by filtration and the filtrate was passed through a short column of silica gel. Evaporation of the solvents left (4aβ,8aα)-*decahydro*-8α-*hydroxymethyl*-5-*methylenenaphthalen*-2(3H)-*one ethylene ketal* (650 mg, quant); ν_{max}/cm^{-1} 3620, 3440, 3075, 1640, 1445, 1240, 1110, 1090, 1020 and 890; δ(60 MHz) 0.7–2.6 (14 H, m), 3.56 (2 H, br d, *J* 2, CH_2OH), 3.90 (4 H, s, OCH_2CH_2O), 4.56 (1 H, s, *exo*-methylene) and 4.65 (1 H, s, *exo*-methylene); *m/z* 238 (M^+, 14%), 155 (34), 99 (100), 86 (26) and 55 (12) (Found: M^+, 238.1568. $C_{14}H_{22}O_3$ requires M, 238.1569).

To a stirred solution of oxalyl dichloride (1.2 cm^3, 13.6 mmol) in anhydrous dichloromethane (10 cm^3) at −80 °C was added dimethyl sulfoxide (DMSO) (0.31 cm^3, 27.2 mmol) under nitrogen. After the mixture had been stirred for 20 min, a solution of the above alcohol (645 mg, 2.72 mmol) in dichloromethane (25 cm^3) was added and the mixture was stirred for 30 min. Triethylamine (4.77 cm^3, 34 mmol) was added to the solution at −42 °C. The resulting slurry was stirred for 1 h and water was added to the mixture at −24 °C. Extraction with ether, followed by filtration through a short column of silica gel, gave the *aldehyde* **41** (650 mg, quant), m.p. 84–92 °C (Found: C, 71.0; H, 8.7. $C_{14}H_{20}O_3$ requires C, 71.2; H, 8.5%); ν_{max}/cm^{-1} 3075, 2700, 1730, 1645, 1440, 1240, 1130, 1095, 1050 and 890; δ(300 MHz) 1.2–2.5 (13 H, m), 3.93 (4 H, s, OCH_2CH_2O), 4.67 (1 H, s, *exo*-methylene), 4.77 (1 H, s, *exo*-methylene) and 9.49 (1 H, d, *J* 4, CHO); *m/z* 236 (M^+, 23%), 208 (52), 153 (100), 100 (48), 91 (67), 87 (83) and 55 (87).

3,4,4aβ,5,6,7,8,8aα-*Octahydro*-5-*methylene*-8α-*vinylnaphthalen*-2(1H)-*one Ethylene Ketal* **42**.—To a stirred, ice-cooled suspension of methyltriphenylphosphonium bromide (1.38 g, 3.9 mmol) in anhydrous THF (10 cm^3) was added BuLi (1.57 mol dm^{-3} solution in hexane; 2.1 cm^3, 3.3 mmol) under nitrogen. After this mixture had been stirred 15 min, a solution of the aldehyde **41** (604 mg, 2.6 mmol) in THF (10 cm^3) was added and the mixture was stirred for another 10 min. The product was extracted with ether, which was evaporated off through a Vigreaux column under atmospheric pressure. The *decalin* **42** thus obtained was used for the subsequent reaction without purification and had ν_{max}/cm^{-1} 3075, 1645, 1445, 1365, 1135, 1120, 1070, 915 and 895; δ(60 MHz) 0.9–2.7 (13 H, m), 3.88 (4 H, s, OCH_2CH_2O), 4.55 (1 H, br s, *exo*-methylene), 4.63 (1 H, br s, *exo*-methylene) and 4.7–5.75 (3 H, m, vinyl); *m/z* 234 (M^+, 13%), 178 (14), 151 (13), 99 (100), 86 (22) and 55 (13) (Found: M^+, 234.1611. $C_{15}H_{22}O_2$ requires M, 234.1619).

3,4,4aβ,5,6,7,8,8aα-*Octahydro*-5-*methylene*-8α-*vinylnaphthalen*-2(1H)-*one* **43**.—A solution of the ketal **42** and PPTS (50 mg) in acetone (2 cm^3)–water (0.2 cm^3) was heated under reflux and stirred at that temperature for 2 h, after which additional PPTS (30 mg) and water (0.3 cm^3) were added. After reflux for a further 2 h, further PPTS (300 mg), acetone (5 cm^3) and water (1 cm^3) were again added and the mixture was heated for 18 h. After cooling to room temperature, the aqueous layer was extracted with ether. MPLC purification afforded the *decalone* **43** (310 mg, 80% from the olefinic ester **40**), m.p. 40–41 °C (Found: C, 81.9; H, 9.2. $C_{13}H_{18}O$ requires C, 82.1; H, 9.5%); ν_{max}/cm^{-1} 3075, 1720, 1645, 1300, 1200, 1000, 920 and 900; δ(60 MHz) 0.8–2.8 (13 H, m) and 4.5–5.8 (5 H, m, *exo*-methylene and vinyl); *m/z* 190 (M^+, 53), 162 (41), 136 (50), 94 (51), 93 (58), 80 (61), 79 (100), 55 (47) and 41 (42).

Khusilal, 3,4,4aβ,5,6,7,8,8aα-*Octahydro*-5-*methylene*-8α-*vinylnaphthalene*-2-*carbaldehyde* **44**.—To a stirred solution of dichloromethane (38 mm^3, 0.6 mmol) in anhydrous THF (1 cm^3) at −95 °C was added BuLi (1.57 mol dm^{-3} solution in hexane; 0.32 cm^3, 0.5 mmol) under nitrogen. After the mixture had been stirred for 30 min, a solution of the ketone **43** (64 mg, 0.34 mmol) in THF (1.5 cm^3) was added. The reaction temperature was gradually raised to ambient during 2 h and then to reflux for 1.5 h. After cooling to room temperature, the solvents were evaporated off under reduced pressure. To the residue were added hexamethylphosphoric triamide (HMPA) (5 cm^3), lithium perchlorate (72 mg, 0.68 mmol), and calcium carbonate (84 mg, 0.84 mmol) and the resulting mixture was heated at 130 °C for 1 h. After the mixture had cooled to room temperature, water was added and the aqueous layer was extracted with ether. Evaporation of the solvent, followed by MPLC purification, gave khusilal **44** (14 mg, 21%) and the double-bond isomer **45** (17 mg, 25%). The synthetic khusilal **44** had ν_{max}/cm^{-1} 3075, 2700, 1690, 1645, 1180, 920 and 900; δ(60

MHz; CCl_4) 0.6–2.9 (11 H, m), 4.60 (1 H, s, *exo*-methylene), 4.70 (1 H, s, *exo*-methylene), 4.7–5.9 (3 H, m, vinyl), 6.58 (1 H, d, *J* 1.5, 1-H) and 9.28 (1 H, s, CHO); *m/z* 202 (M^+, 28%), 177 (21), 159 (31), 133 (34), 132 (61), 131 (36), 119 (39), 117 (45), 105 (46), 91 (100), 77 (59) and 41 (55).

1,4,4aβ,5,6,7,8,8aα-Octahydro-5-methylene-8α-vinylnaphthalene-2-carbaldehyde **45** had ν_{max}/cm^{-1} 3075, 2700, 1690, 1645, 1175, 915 and 895; δ(60 MHz) 0.8–2.9 (11 H, m), 4.63 (1 H, br s, *exo*-methylene), 4.78 (1 H, br s, *exo*-methylene), 4.8–5.8 (3 H, m, vinyl), 6.8 (1 H, br s, 3-H) and 9.33 (1 H, s, CHO); *m/z* 202 (M^+, 45%), 173 (53), 145 (56), 120 (50), 117 (46), 107 (52), 105 (58), 91 (100), 79 (66) and 43 (91).

8α-Formyloxy-3,4,4aβ,5,6,7,8,8aα-octahydro-5-methylnaphthalen-2(1H)-one 2-Ethylene Ketal **46**.—A solution of the aldehyde **41** (72 mg, 0.3 mmol) in ethyl acetate (5 cm^3) was hydrogenated over palladium on charcoal (10%; 20 mg) at room temperature. After the mixture had been stirred for 1.3 h, additional palladium on charcoal (20 mg) was added and the mixture was stirred for 5 h under hydrogen. Filtration of the catalyst, followed by evaporation of the solvent, left (4aβ,8aα)-7-ethylenedioxydecahydro-4-methylnaphthalene-1α-carbaldehyde (64 mg, 90%); ν_{max}/cm^{-1} 2700, 1725 and 1100; δ(60 MHz) 0.8–2.9 (14 H, m), 0.9 (3 H, d, *J* 6.5, Me), 3.90 (4 H, s, OCH_2CH_2O) and 9.3–9.6 (1 H, m, CHO).

A solution of the aldehyde (64 mg, 0.27 mmol) and MCPBA (80%; 117 mg, 0.54 mmol) in dichloromethane (2 cm^3) was stirred at room temperature for 3 h. The resulting solution was poured into aq. sodium hydrogen carbonate and the product was extracted with ether. Evaporation of the solvents, followed by MPLC purification, gave the formate **46** (33 mg, 48%); ν_{max}/cm^{-1} 1725, 1180 and 1100; δ(100 MHz) 0.7–2.2 (13 H, m), 0.94 (3 H, d, *J* 7, Me), 3.90 (4 H, s, OCH_2CH_2O), 4.3–4.7 (1 H, m, $w_{\frac{1}{2}}$ 22, 8-H) and 8.02 (1 H, s, CHO).

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