Ring Expansion of Cyclopropylmethanols to Cyclobutanes—An Enantioselective Total Synthesis of (*R*)-(+)-Dodecan-5-olide, and (*S*)-(+)- and (*R*)-(−)-5-[(*Z*)-Dec-1-enyl]dihydrofuran-2(3*H*)-one

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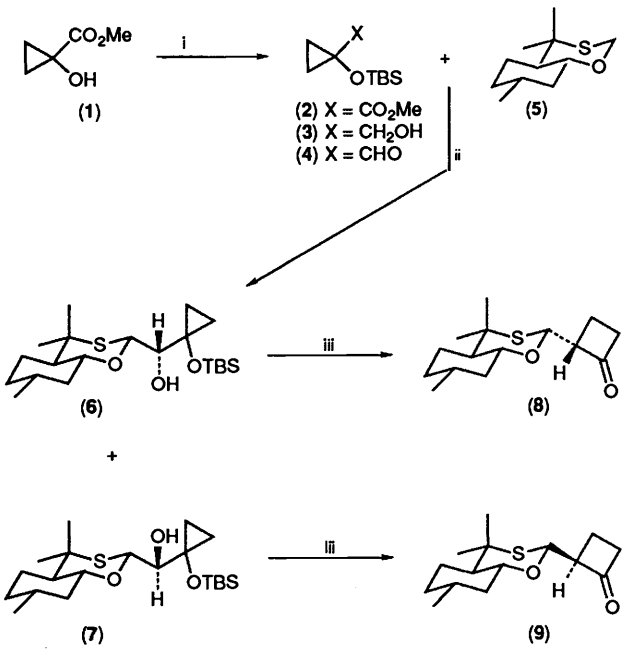
A novel and convenient route to chiral cyclobutanones (**8**) and (**9**) by ring expansion of the cyclopropylmethanols (**6**) and (**7**) was developed, leading to an enantioselective total synthesis of (*R*)-(+)-dodecan-5-olide (**25**), and (*S*)-(+)- and (*R*)-(−)-5-[(*Z*)-dec-1-enyl]dihydrofuran-2(3*H*)-one (**35**) and (**36**) (the pheromone of the Japanese beetle).

There has been increasing interest in the chemistry[1] of cyclobutane and cyclobutanone derivatives mainly because of their occurrence in the basic structure of some natural products[2] and their usefulness in the synthesis of a wide variety of compounds,[3] although there are very few studies[1,4] on the synthesis of optically active cyclobutane or cyclobutanone derivatives. We have therefore attempted to produce an efficient and flexible route to chiral cyclobutanone derivatives. We describe herein a novel and convenient route to chiral cyclobutanones, which leads to an enantioselective total synthesis of (*R*)-(+)-dodecan-5-olide (**25**), and (*S*)-(+)- and (*R*)-(−)-5-[(*Z*)-dec-1-enyl]dihydrofuran-2(3*H*)-one (**35**) and (**36**) (the pheromone of the Japanese beetle).

Our first goal in this context was a stereospecific ring expansion of the cyclopropylmethanols (**6**) and (**7**), giving the cyclobutanones (**8**) and (**9**), respectively (Scheme 1 and Table). The synthesis of the substrates (**6**) and (**7**) for this transformation was initiated by protection [t-butylchlorodimethylsilane (TBSCl), imidazole, 4-(dimethylamino)pyridine (DMAP)] of readily available methyl 1-hydroxycyclopropanecarboxylate (**1**)[5] to give compound (**2**) (89%), which on reduction [di-isobutylaluminium hydride (DIBAL)] yielded the alcohol (**3**) (78%). Swern oxidation of the alcohol (**3**) followed by condensation of the resulting aldehyde (**4**) with the anion of the oxathiane (**5**)[6] to give the *threo* and *erythro* compounds (**6**) and (**7**) (1:1) [73% overall yield from (**3**)] as a readily separable mixture. The ring expansion of the cyclopropane moiety of compounds (**6**) and (**7**) was carried out by mesylation [methanesulphonyl chloride (MsCl), Et_3N] followed by deprotection of the TBS group under various conditions. The results are summarised in the Table. From these results, it seemed possible that the mesyl esters of the cyclopropylmethanols (**6**) and (**7**) rearranged stereospecifically to give the corresponding cyclobutanones (**8**) and (**9**), respectively, in a concerted manner under the conditions of the deprotection of the t-butyldimethylsilyl group. However, under basic conditions [entry 3, substrate (**7**)] the initial product (**9**) was epimerised to give the thermodynamically favoured product (**8**). This was also supported by the fact that base [diazabicycloundecene (DBU)] treatment of the isolated cyclobutanone (**9**) afforded a mixture of isomers (**8**) and (**9**) (3:1, respectively). Thus, from a synthetic point of view, the cyclobutanone (**8**) could be prepared selectively by subjecting a mixture of compounds (**6**) and (**7**) directly to ring expansion, followed by base treatment of the crude product.

The flexibility of this chiral cyclobutanone (**8**) was effectively illustrated by the readily occurring synthesis of (*R*)-(+)-dodecan-5-olide (**25**) and (*S*)-(+)- and (R)-(−)-5-[(*Z*)-dec-1-enyl]dihydrofuran-2(3*H*)-one (**35**) and (**36**) as follows. Reduction ($NaBH_4$) of compound (**8**) gave a readily separable mixture of the cyclobutanols (**10**) and (**11**) (7:3) in 100% yield. Protection (TBSCl, imidazole, DMAP) of compound (**10**) afforded the silyl ether (**12**) (99%), which was then subjected to oxidative solvolysis [*N*-chlorosuccinimide (NCS), $AgNO_3$] to give the aldehyde (**14**) (85%). The tosyl ester (**18**), which was obtained in 75% overall yield by reduction ($NaBH_4$) of aldehyde (**14**) followed by tosylation [toluene-*p*-sulphonyl chloride (TsCl), pyridine] of the resulting alcohol (**16**), was coupled with heptylmagnesium bromide in the presence of a catalytic amount of dilithium tetrachlorocuprate (Li_2CuCl_4) to give compound (**20**) (99%). Deprotection (Bu_4NF) of the silyl ether (**20**) followed by Swern oxidation of the resulting alcohol (**22**) afforded the cyclobutanone (**24**), which was then subjected to Baeyer–Villiger oxidation (Bu^tOOH, 10% NaOH) to furnish (*R*)-(+)-dodecan-5-olide (**25**) [65% overall yield from (**20**)]. The product (**25**) thus obtained was identical with an authentic sample[7] in all aspects. By following the same chemical



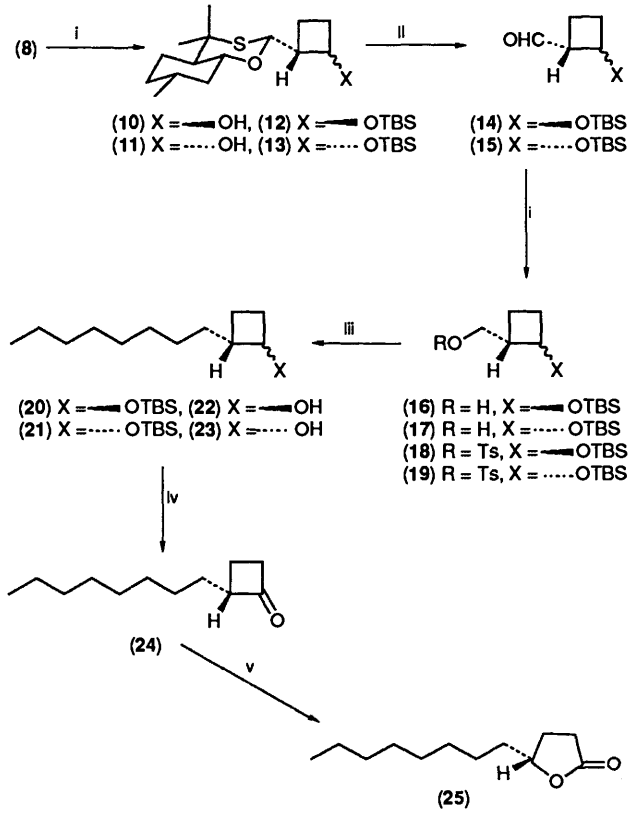
Scheme 1. *Reagents and conditions:* i, imidazole, DMAP (cat.), DMF, TBSCl; ii, (**3**), $(COCl)_2$, DMSO–CH_2Cl_2, −78 °C; then Et_3N, 0 °C [→(**4**)]; (**5**), BuLi, THF, −78 °C; then (**4**), THF, −78 °C; iii, MsCl, Et_3N, CH_2Cl_2, 0 °C.

Table. Rearrangement of cyclopropylmethanols (**6**) and (**7**) to cyclobutanones (**8**) and (**9**).

Entry	Reagents[a]	Substrates	Product ratio[b] [(**8**)]:[(**9**)]	Isolated yield[c] (%)
1	i, MsCl, Et_3N	(**6**)	3:1	88
	ii, 10% aq. HCl	(**7**)	1:8	92
2	i, MsCl, Et_3N	(**6**)	11:2	72
	ii, 50% aq. HF	(**7**)	1:8	71
3	i, MsCl, Et_3N	(**6**)	2:1	69
	ii, Bu_4NF	(**7**)	13:8	57

[a] All reactions were run under an inert atmosphere (argon) at room temperature (30 min for mesylation and 8 h for deprotection). [b] Determined by ^1H NMR analysis. The isomer [(**8**) and (**9**)] ratio was determined by ^1H NMR integration of the 2′-methine signals of the oxathiine rings which appeared at δ 5.31 (d, *J* 3.0 Hz) and 5.14 (d, *J* 5.0 Hz), respectively. These assignments were confirmed unambiguously by the transformation of compounds (**8**) and (**9**) into the title natural compounds. [c] All yields are based on purified product obtained on passage through a short column (SiO_2).

treatments described above, compound (**24**) was also prepared starting from the (*S*)-alcohol (**11**) through intermediates (**13**), (**15**), (**17**), (**19**), (**21**), and (**23**) (Scheme 2).



Scheme 2. *Reagents and conditions:* i, $NaBH_4$, MeOH–CH_2Cl_2, 0 °C; ii, NCS, $AgNO_3$, aq. MeCN–CH_2Cl_2, 0 °C; iii, $C_7H_{15}{}^nMgBr$, THF; then Li_2CuCl_4, THF, −78 °C; iv, $(COCl)_2$, DMSO, CH_2Cl_2, −78 °C; v, Bu^tOOH, aq. NaOH, THF, 0 °C.

The aldehyde (**14**) was then converted into the dibromo olefin (**26**) (75%) by Wittig reaction (CBr_4, Ph_3P).[8] Base (BuLi) treatment of dibromide (**26**) and alkylation of *in situ* generated lithium acetylide gave the alkyne (**28**) (85%). Semihydrogenation (H_2; Lindlar catalyst) of alkyne (**28**), followed by deprotection (Bu_4NF) of the resultant silyloxy alkene (**30**), afforded the alcohol (**32**) [69% overall yield from (**28**)], which on Swern oxidation yielded the cyclobutanone (**34**). Baeyer–Villiger oxidation (Bu^tOOH, 10% NaOH) of the ketone (**34**) furnished (*S*)-(+)-5-[(*Z*)-dec-1-enyl]dihydrofuran-2(3*H*)-one (**35**) [30% overall yield from (**32**)]. By following the same chemical treatments described above, compound (**35**) was also prepared from the tosyloxy aldehyde (**15**) through intermediates (**27**), (**29**), (**31**), (**33**), and (**34**) (Scheme 3). Inversion of chirality[9] was effectively achieved by successive treatment [KOH; then Ph_3P, diethyl azodicarboxylate (DEAD)] of compound (**35**) to yield (*R*)-(−)-5-[(*Z*)-dec-1-enyl]dihydrofuran-2(3*H*)-one (**36**) (76%), which was identical with an authentic sample[10] in all respects.

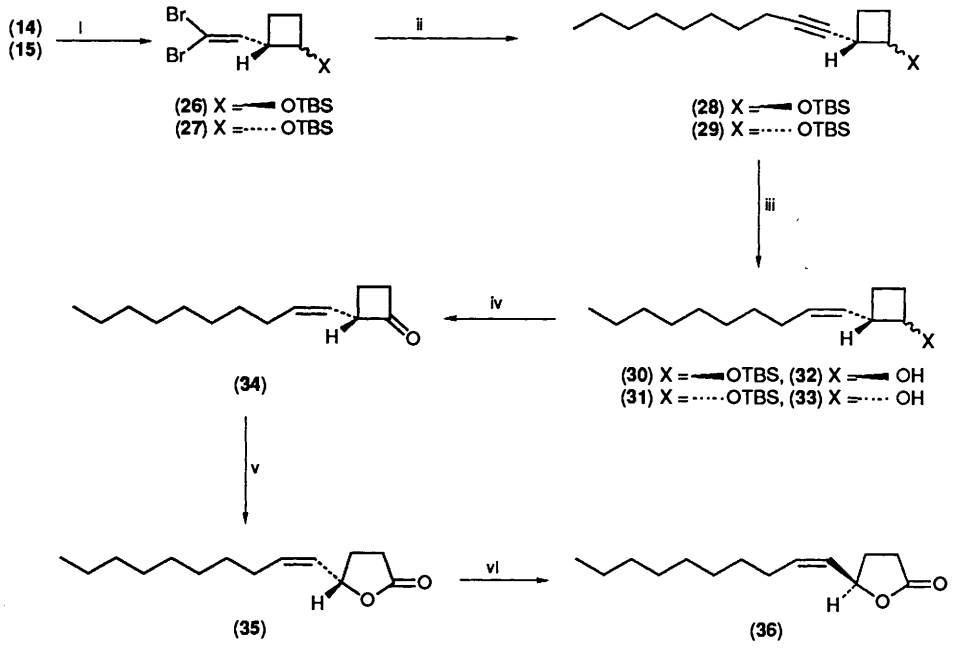
Experimental

General Methods.—M.p.s were determined on a Yanagimoto MP-22 apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260-10 spectrophotometer. NMR spectra were obtained on JEOL PS-100, JEOL FX-90, and JNM GX-500 spectrometers. Chemical shifts were recorded relative to internal $SiMe_4$. Mass spectra were taken on Hitachi M-52G and JEOL-TMS-01SG-2 spectrometers. Optical rotations were measured with a JASCO-DIP-340 polarimeter. All reactions were carried out under dry nitrogen. Column chromatography was carried out with silica gel (Wako gel C-200). The phrase 'residue upon work-up' refers to the residue obtained when the organic layer was separated, dried over anhydrous Na_2SO_4, and the solvent was evaporated off under reduced pressure. All new compounds described in this Experimental sections were homogeneous on TLC.

Methyl 1-(t-Butyldimethylsiloxy)cyclopropanecarboxylate (**2**).—To a stirred solution of the hydroxy ester (**1**) (4.4 g, 38 mmol), imidazole (4.1 g, 60 mmol), and a catalytic amount of DMAP in dimethylformamide (DMF) (50 ml) was added TBSCl (6.9 g, 46 mmol) at room temperature and the mixture was stirred for 12 h at the same temperature. The reaction mixture was then diluted with diethyl ether and washed successively with 10% HCl and saturated aq. NaCl. The residue upon work-up was distilled to give the *TBS ether* (**2**) (7.78 g, 89%) as an oil, b.p. 105–107 °C (17 mmHg) (Found: C, 57.15; H, 9.7. $C_{11}H_{22}O_3Si$ requires C, 57.35; H, 9.6%); $\nu_{max}(CHCl_3)$ 1 725 cm^{-1} (C=O); $\delta_H(CCl_4)$ 0.00 (6 H, s, $SiMe_2$), 0.40–1.20 (13 H, m, $SiCMe_3$ and CH_2CH_2), and 3.53 (3 H, s, OMe); *m/z* 173 ($M^+ - 57$).

1-(t-Butyldimethylsiloxy)cyclopropylmethanol (**3**).—To a stirred solution of the ester (**2**) (8.0 g, 35 mmol) in tetrahydrofuran (THF) (30 ml) at −40 °C was added a 1M solution of DIBAL in hexane (80 ml). After the mixture had been stirred for 24 h at the same temperature, it was quenched with saturated aq. NH_4Cl and extracted with diethyl ether. The extract was filtered through Celite. The residue upon work-up was distilled to give the *alcohol* (**3**) (5.5 g, 78%) as an oil, b.p. 83–85 °C (6 mmHg); (Found: C, 59.5; H, 11.05. $C_{10}H_{22}O_2Si$ requires C, 59.35; H, 10.95%); $\nu_{max}(CHCl_3)$ 3 600 cm^{-1}; $\delta_H(CCl_4)$ 0.00 (6 H, s, $SiMe_2$), 0.32–0.94 (13 H, m, $SiCMe_3$ and CH_2CH_2), 2.47–3.05 (1 H, br s, OH), and 3.40 (2 H, s, CH_2OH); *m/z* 145 ($M^+ - 57$).

(α′S,2R,4aR,7R,8aR)- and (α′R,2R,4aR,7R,8aR)-α-[1-(t-Butyldimethylsiloxy)cyclopropyl]-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4H-1,3-benzoxathiin-2-ylmethanol (**6**) *and* (**7**).—To a stirred solution of dimethyl sulphoxide (DMSO) (1.18 ml, 16.6 mmol) in methylene dichloride (40 ml) at −78 °C was added oxalyl chloride (1.45 ml, 16.6 mmol). After the mixture had been stirred for 10 min at −78 °C, a solution of the alcohol



Scheme 3. *Reagents and conditions:* i, CBr_4, PPh_3, CH_2Cl_2, −78 °C; ii, BuLi, THF–HMPA; iii, H_2, Lindlar cat., EtOAc; iv, $(COCl)_2$ DMSO–CH_2Cl_2, −78 °C; v, Bu'OOH, aq. NaOH, THF, 0 °C; vi, KOH, MeOH, 60 °C; then PPh_3, DEAD, benzene.

(**3**) (1.68 g, 8.3 mmol) in CH_2Cl_2 (10 ml) was added to the above solution and the mixture was stirred for 30 min at the same temperature. The reaction mixture was then treated with triethylamine (Et_3N) (4.9 ml, 35.2 mmol), allowed to warm to 0 °C, quenched with 10% aq. HCl, and extracted with diethyl ether. The residue upon work-up afforded the crude aldehyde (**4**) which was used for the next reaction without further purification because of its instability.

To a stirred solution of the 1,3-oxathiane (**5**) (1.8 g, 8.98 mmol) in THF (6 ml) at −78 °C was added dropwise a solution of butyl-lithium in hexane (1.56M; 5.6 ml, 8.74 mmol). The mixture was stirred for 3 min at −78 °C, warmed to 0 °C and then recooled to −78 °C. After being stirred for 10 min at −78 °C, the solution was treated with a solution of the crude aldehyde (**4**) obtained above in THF (5 ml) and the reaction mixture was stirred for 30 min at the same temperature, treated with saturated aq. NH_4Cl, and extracted with diethyl ether. The residue upon work-up was chromatographed with hexane–ethyl acetate (100:1 v/v) to give the oily *adducts* (**6**) (1.21 g, 36.5%) and (**7**) (1.21 g, 36.5%) from the first and second fraction, respectively.

Compound (**6**): $[\alpha]_D^{25}$ −7.17° (*c* 0.92, $CHCl_3$) (Found: C, 62.7; H, 10.15. $C_{21}H_{40}O_3SSi$ requires C, 62.8; H, 10.3%); ν_{max}(neat) 3 450 cm^{-1} (OH); δ_H($CDCl_3$) 0.08 and 0.10 (6 H, each s, $SiMe_2$), 0.55–0.80 (4 H, m, CH_2–CH_2), 0.85 (9 H, s, $SiCMe_3$), 0.90 (3 H, d, *J* 7 Hz, 7-Me), 1.25 and 1.41 (6 H, each s, 4-Me_2), 3.39 (1 H, dt, *J* 4 and 10 Hz, 8a-H), 3.50 (1 H, d, *J* 6 Hz, α-H), and 5.31 (1 H, d, *J* 6 Hz, 2-H); *m*/*z* 400 (M^+).

Compound (**7**): $[\alpha]_D^{25}$ −14.79° (*c* 1.122, $CHCl_3$) (Found: C, 62.5; H, 10.15%); ν_{max}(neat) 3 590 cm^{-1} (OH); δ_H($CDCl_3$) 0.07 and 0.09 (6 H, each s, $SiMe_2$), 0.50–0.75 (4 H, m, CH_2–CH_2), 0.85 (9 H, s, $SiCMe_3$), 0.90 (3 H, d, *J* 7 Hz, 7-Me), 1.25 and 1.41 (6 H, each s, 4-Me_2), 3.10 (1 H, d, *J* 7 Hz, C*H*OH), 3.45 (1 H, dt, *J* 4 and 10 Hz, 8a-H), and 5.21 (1 H, d, *J* 7 Hz, 2-H); *m*/*z* 400 (M^+).

(2R,2'R,4a'R,7'R,8a'R)- *and* (2S,2'R,4a'R,7'R,8a'R)-2-(4a',5',6',7',8',8'a-*Hexahydro*-4',4',7'-*trimethyl*-4'H-1',3'-*benzoxathiin*-2'-*yl*)*cyclobutanone* (**8**) *and* (**9**). *General Procedure for Ring Expansion of Compounds* (**6**) *and* (**7**).—To a stirred solution of the mixture of the alcohols (**6**) and (**7**) (1:1) 1.48 g, 3.69 mmol) and Et_3N (2.22 ml, 14.8 mmol) in CH_2Cl_2 (30 ml) at 0 °C was added MsCl (1.02 ml, 13.0 mmol). After being stirred for 30 min at 0 °C, the reaction mixture was treated with 10% aq. HCl (10 ml, 27.9 mmol), stirred for 8 h at room temperature, and then extracted with CH_2Cl_2. The extract was washed successively with water, saturated aq. $NaHCO_3$, and aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (50:1 v/v) to give the cyclobutanone (**8**) (455 mg, 46%) as prisms from the first fraction, and the cyclobutanone (**9**) (455 mg, 46%) as an oil from the second fraction.

Compound (**8**): m.p. 105–106 °C (from pentane); $[\alpha]_D^{22}$ −97.35° (*c* 1.136, $CHCl_3$) (Found: C, 66.95; H, 9.1. $C_{15}H_{24}O_2S$ requires C, 67.15; H, 9.0%); ν_{max}(neat) 1 780 cm^{-1} (C=O); δ_H($CDCl_3$) 0.92 (3 H, d, *J* 6 Hz, 7'-Me), 1.25 and 1.41 (6 H, each s, 4'-Me_2), 2.92–3.02 (2 H, m, CH_2CO), 3.38–3.46 (2 H, m, CHCO and 8'-H) and 5.31 (1 H, d, *J* 3 Hz, 2'-H); *m*/*z* 268 (M^+).

Compound (**9**): $[\alpha]_D^{24}$ +8.42° (*c* 2.54, $CHCl_3$) (Found: M^+, 268.1599. $C_{15}H_{24}O_2S$ requires *M*, 268.1497); ν_{max}(neat) 1 780 cm^{-1} (C=O); δ_H($CDCl_3$) 0.96 (3 H, d, *J* 6 Hz, 7'-Me), 1.25 and 1.41 (6 H, each s, 4'-Me_2), 2.85–3.10 (2 H, m, CH_2CO), 3.25–3.70 (2 H, m, CHCO and 8'-H), and 5.14 (1 H, d, *J* 5 Hz, 2'-H); *m*/*z* 268 (M^+).

Epimerisation of (2S)-(**9**) *into* (2R)-(**8**).—A solution of the cyclobutanone (**9**) (166 mg, 0.62 mmol) and DBU (5 drops) in THF (8 ml) was stirred for 1 h at 0 °C. The reaction mixture was then acidified with 10% HCl and extracted with diethyl ether. The extract was washed successively with saturated aq. $NaHCO_3$, water, and saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (50:1 v/v) to give the butanones (**8**) (120 mg, 72%) and (**9**) (40 mg, 24% recovery) from the first and second fraction, respectively.

(1R,2R,2'R,4a'R,7'R,8a'R)- *and* (1S,2R,2'R,4a'R,7'R,8a'R)-2-(4a',5',6',7',8',8a'-*Hexahydro*-4',4',7'-*trimethyl*-4'H-1',3'-*benzoxathiin*-2'-*yl*)*cyclobutanol* (**10**) *and* (**11**).—To a stirred solution of the cyclobutanone (**8**) (507 mg, 1.89 mmol) in

CH_2Cl_2 (6 ml)–MeOH (3 ml) at 0 °C was added portionwise $NaBH_4$ (70 mg, 1.85 mmol) and the mixture was stirred for a further 15 min at 0 °C, then treated with water and extracted with CH_2Cl_2. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (5:1 v/v) to give the cis-*alcohol* (**11**) (153 mg, 30%) as prisms and the trans-*alcohol* (**10**) (357 mg, 70%) as an oil from the first and second fraction, respectively.

Compound (**10**): $[\alpha]_D^{24}$ −35.46° (*c* 1.342, $CHCl_3$) (Found: C, 66.5; H, 9.65; S, 11.85. $C_{15}H_{26}O_2S$ requires C, 66.65; H, 9.7; S, 11.85%); ν_{max}(neat) 3 400 cm^{-1} (OH); δ_H($CDCl_3$) 0.92 (3 H, d, *J* 6 Hz, 7′-Me), 1.25 and 1.41 (6 H, each s, 4′-Me_2), 3.38 (1 H, dt, *J* 4 and 10 Hz, 8′-H), 4.00–4.28 (1 H, m, 1-H), and 4.95 (1 H, d, *J* 6 Hz, 2′-H); *m*/*z* 270 (M^+).

Compound (**11**): m.p. 50–51 °C (from pentane); $[\alpha]_D^{24}$ −24.60° (*c* 1.016, $CHCl_3$) (Found: C, 66.65; H, 9.65; S, 11.7%); ν_{max}(neat) 3 470 cm^{-1} (OH); δ_H($CDCl_3$) 0.92 (3 H, d, *J* 6 Hz, 7′-H), 1.25 and 1.41 (6 H, each s, 4′-Me_2), 3.50 (1 H, dt, *J* 4 and 10 Hz, 8′-H), 4.01–4.58 (1 H, m, 1-H), and 5.30 (1 H, d, *J* 5 Hz, 2′-H); *m*/*z* 270 (M^+).

(1′R,2R,2′R,4aR,7R,8aR)- *and* (1′R,2R,2′S,4aR,7R,8aR)-2-[2′-(*t-Butyldimethylsiloxy*)*cyclobutyl*']-4a, 5,6,7,8,8a-*hexahydro*-4,4,7-*trimethyl*-4H-1,3-*benzoxathine* (**12**) *and* (**13**).—To a stirred solution of the *trans*-alcohol (**10**) (410 mg, 1.52 mmol), imidazole (215 mg, 3.16 mmol), and a catalytic amount of DMAP in DMF (10 ml) at 0 °C was added TBSCl (367 mg, 244 mmol) and the mixture was stirred for 45 min at 0 °C, diluted with diethyl ether, and washed successively with water, 10% aq. HCl, saturated aq. $NaHCO_3$, and aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (50:1 v/v) to give the trans-*TBS ether* (**12**) (577 mg, 99%) as an oil. By following the same procedure, the *cis*-alcohol (**11**) (210 mg, 0.78 mmol) afforded the cis-*TBS ether* (**13**) (293 mg, 98%) as an oil.

Compound (**12**): $[\alpha]_D^{25}$ −54.76° (*c* 1.54, $CHCl_3$) (Found: C, 65.35; H, 10.65. $C_{21}H_{40}O_2SSi$ requires C, 65.55; H, 10.65%); δ_H($CDCl_3$) 0.05 (6 H, s, $SiMe_2$), 0.89 (9 H, s, $SiCMe_3$), 0.92 (3 H, d, *J* 6 Hz, 7-Me), 1.25 and 1.41 (6 H, each s, 4-Me_2), 3.34 (1 H, dt, *J* 4 and 10 Hz, 8-H), 4.20 (1 H, q, *J* 9 Hz, 2′-H), and 4.93 (1 H, d, *J* 4 Hz, 2-H); *m*/*z* 384 (M^+).

Compound (**13**): $[\alpha]_D^{23}$ −23.00° (*c* 6.904, $CHCl_3$) (Found: C, 65.4; H, 10.45%); δ_H($CDCl_3$) 0.05 (6 H, s, $SiMe_2$), 0.90 (9 H, s, $SiCMe_3$), 0.92 (3 H, d, *J* 6 Hz, 7-Me), 1.25 and 1.41 (6 H, each s, 4-Me_2), 2.38–2.68 (1 H, m, 1′-H), 3.40 (1 H, dt, *J* 4 and 10 Hz, 8a-H), 4.20 (1 H, q, *J* 7 Hz, 2′-H), and 5.15 (1 H, d, *J* 7 Hz, 2-H); *m*/*z* 384 (M^+).

(1R,2R)- *and* (1R,2S)-2-(*t-Butyldimethylsiloxy*)*cyclobutane-carboxaldehyde* (**14**) *and* (**15**).—To a stirred mixture of NCS (177 mg, 1.33 mmol) and $AgNO_3$ (263 mg, 1.55 mmol) in MeCN (9 ml)–water (1 ml) at 0 °C was added a solution of the *trans*-TBS ether (**12**) (70 mg, 0.442 mmol) in CH_2Cl_2 (1.5 ml)–MeCN (1.5 ml) and the mixture was stirred for 7 min at 0 °C, was then treated successively with saturated aq. Na_2SO_3 and aq. NaCl, and filtered through Celite. The filtrate was extracted with CH_2Cl_2 and the extract was washed with saturated aq. Na_2CO_3. The residue upon work-up was chromatographed with pentane–diethyl ether (100:1 v/v) to give the *aldehyde* (**14**) (80.5 mg, 85%) as an oil. By following the same procedure, the *cis*-TBS ether (**13**) (69 mg, 0.18 mmol) afforded the *aldehyde* (**15**) (32.7 mg, 85%) as an oil.

Compound (**14**): $[\alpha]_D^{24}$ −87.40° (*c* 0.54, $CHCl_3$) (Found: M^+ − 57, 157.0692. $C_7H_{13}O_2Si$ requires *m*/*z*, 157.0684); ν_{max}(neat) 1 720 cm^{-1} (C=O); δ_H($CDCl_3$) 0.02 (6 H, s, $SiMe_2$), 0.83 (9 H, s, $SiCMe_3$), 1.60–2.22 (4 H, m, CH_2CH_2), 3.10 (1 H, m, 1-H), 4.34 (1 H, q, *J* 7 Hz, 2-H), and 9.72 (1 H, d, *J* 3 Hz, CHO); *m*/*z* 157 (M^+ − 57).

Compound (**15**): $[\alpha]_D^{25}$ −31.60° (*c* 0.5, $CHCl_3$) (Found: M^+ − 57, 157.0677); ν_{max}(neat) 1 720 cm^{-1} (C=O); δ_H($CDCl_3$) 0.02 (6 H, s, $SiMe_2$), 0.83 (9 H, s, $SiCMe_3$), 1.48–2.45 (4 H, m, CH_2CH_2), 3.25 (1 H, m, 1-H), 4.59 (1 H, q, *J* 9 Hz, 2-H), and 9.93 (1 H, d, *J* 4 Hz, CHO); *m*/*z* 157 (M^+ − 57).

(1S,2R)- *and* (1S,2S)-2-(*t-Butyldimethylsiloxy*)*cyclobutyl-methanol* (**16**) *and* (**17**).—To a stirred solution of the aldehyde (**14**) (50.7 mg, 0.236 mmol) in MeOH (1 ml)–CH_2Cl_2 (2 ml) at 0 °C was added portionwise $NaBH_4$ (15 mg, 0.4 mmol) and the mixture was stirred for 15 min at the same temperature before being diluted with water and extracted with CH_2Cl_2. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (95:5 v/v) to give the *alcohol* (**16**) (44.7 mg, 87%) as an oil. By following the same procedure, the aldehyde (**15**) (83 mg, 0.39 mmol) afforded the *alcohol* (**17**) (65 mg, 78%) as an oil.

Compound (**16**): $[\alpha]_D^{24}$ −51.81° (*c* 0.88, $CHCl_3$) (Found: M^+ − 57, 159.0873. $C_7H_{15}O_2Si$ requires *m*/*z*, 159.0840); ν_{max}(meat) 3 350 cm^{-1} (OH); δ_H($CDCl_3$) 0.02 (6 H, s, $SiMe_2$), 0.86 (9 H, s, $SiCMe_3$), 1.39 (1 H, s, OH), 3.61 (2 H, d, *J* 6 Hz, CH_2OH), and 3.97 (1 H, q, *J* 7 Hz, 2-H); *m*/*z* 159 (M^+ − 57).

Compound (**17**): $[\alpha]_D^{25}$ +50.28° (*c* 1.4, $CHCl_3$) (Found: M^+ − 57, 159.0873); ν_{max}(neat) 3 555 cm^{-1} (OH); δ_H($CDCl_3$) 0.03 (6 H, s, $SiMe_2$), 0.86 (9 H, s, $SiCMe_3$), 3.68 (1 H, dd, *J* 5 and 11 Hz, CH*H*OH), 4.02 (1 H, dd, *J* 9 and 11 Hz, C*H*HOH), and 4.96 (1 H, q, *J* 7 Hz, 2-H); *m*/*z* 159 (M^+ − 57).

(1S,2R)- *and* (1S,2S)-2-(*t-Butyldimethylsiloxy*)*cyclobutyl-methyl Toluene*-p-*sulphonates* (**18**) *and* (**19**).—To a stirred solution of the alcohol (**16**) (39 mg, 0.18 mmol) in pyridine (2 ml) at 0 °C was added portionwise TsCl (52 mg, 0.27 mmol) and the mixture was stirred for 22 h at room temperature. The reaction mixture was diluted with diethyl ether and washed with 10% aq. HCl, saturated aq. $NaHCO_3$, and saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (98:2 v/v) to give the *tosyl ester* (**18**) (57.1 mg, 86%) as an oil. By following the same procedure, the alcohol (**17**) (39 mg, 0.18 mmol) afforded the *tosyl ester* (**19**) (63 mg, 93%) as an oil.

Compound (**18**): $[\alpha]_D^{28}$ −33.87° (*c* 0.98, $CHCl_3$) (Found: M^+ − 57, 313.0896. $C_{14}H_{21}O_3SSi$ requires *m*/*z*, 313.0929); δ_H($CDCl_3$) −0.05 (6 H, s, $SiMe_2$), 0.79 (9 H, s, $SiCMe_3$), 2.40 (3 H, s, Ar*Me*), 3.80–4.05 (3 H, m, 2-H and CH_2OTs), 7.29 (2 H, d, *J* 9 Hz, ArH), and 7.78 (2 H, d, *J* 9 Hz, ArH); *m*/*z* 313 (M^+ − 57).

Compound (**19**): $[\alpha]_D^{25}$ −10.28° (*c* 1.575, $CHCl_3$) (Found: M^+ − 171, 199.1536. $C_{11}H_{23}OSi$ requires *m*/*z*, 199.1517); δ_H($CDCl_3$) −0.06 (6 H, s, $SiMe_2$), 0.80 (9 H, s, $SiCMe_3$), 2.41 (3 H, s, Ar*Me*), 3.99–4.55 (3 H, m, 2-H and CH_2OTs), 7.31 (2 H, d, *J* 8 Hz, ArH), and 7.78 (2 H, d, *J* 8 Hz, ArH); *m*/*z* 199 (M^+ − 171).

(1R,2R)- *and* (1S,2R)-1-(*t-Butyldimethylsiloxy*)-2-*octylcyclobutane* (**20**) *and* (**21**).—To a stirred solution of the tosyl ester (**18**) (56 mg, 0.15 mmol) in THF (2 ml) at −78 °C were added a solution of heptylmagnesium bromide in THF (0.8M; 1 ml, 0.8 mmol) followed by a solution of dilithium tetrachlorocuprate in THF (0.1M; 0.02 ml, 0.002 mmol). After being stirred for 15 h at room temperature, the reaction mixture was treated with saturated aq. NH_4Cl and extracted with diethyl ether. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane to give the *alkylated compound* (**20**) (44.5 mg, 99%) as an oil. By following the same procedure, the tosyl ester (**19**) (63 mg, 0.17 mmol) afforded *compound* (**21**) (32 mg, 60%) as an oil.

Compound (**20**): $[\alpha]_D^{26}$ −42.58° (*c* 1.55, $CHCl_3$) (Found: M^+ − 57, 241.2012. $C_{14}H_{29}OSi$ requires *m*/*z*, 241.1986); δ_H($CDCl_3$) 0.02 (6 H, s, $SiMe_2$), 0.85 (3 H, t, *J* 6 Hz, CH_2Me),

0.86 (9 H, s, $SiCMe_3$), and 3.70 (1 H, q, *J* 7 Hz, 1-H); *m/z* 241 ($M^+ - 57$).

Compound (**21**): $[\alpha]_D^{27}$ −13.57° (*c* 1.09, $CHCl_3$) (Found: $M^+ - 57$, 241.2003); $\delta_H(CDCl_3)$ 0.00 (6 H, s, $SiMe_2$), 0.87 (3 H, t, *J* 6 Hz, CH_2Me), 0.87 (9 H, s, $SiCMe_3$), and 4.27 (1 H, q, *J* 7 Hz, 1-H); *m/z* 241 ($M^+ - 57$).

(1R,2R)- *and* (1S,2R)-2-*Octylcyclobutanol* (**22**) *and* (**23**).—To a stirred solution of the TBS ether (**20**) (45 mg, 0.15 mmol) in THF (2.5 ml) was added a solution of Bu^n_4NF in THF (1M; 0.3 ml, 0.3 mmol) and the mixture was stirred for 2 h at room temperature. The mixture was treated with water and extracted with CH_2Cl_2. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1 v/v) to give the *alcohol* (**22**) (26.4 mg, 95%) as an oil. By following the same procedure, the TBS ether (**21**) (14.7 mg, 0.05 mmol) afforded the *alcohol* (**23**) (8.8 mg, 97%) as an oil.

Compound (**22**): $[\alpha]_D^{24}$ −34.24° (*c* 1.32, $CHCl_3$) (Found: $M^+ - 18$, 166.1723. $C_{12}H_{22}$ requires *m/z*, 166.1720); ν_{max}(neat) 3 325 cm^{-1} (OH); $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 6 Hz, CH_2Me) and 3.73 (1 H, dt, *J* 6.5 and 14 Hz, 1-H); *m/z* 166 ($M^+ - 18$).

Compound (**23**): $[\alpha]_D^{29}$ −34.24° (*c* 0.87, $CHCl_3$) (Found: M^+, 184.1809. $C_{12}H_{24}O$ requires *M*, 184.1826); ν_{max}(neat) 3 350 cm^{-1} (OH); $\delta_H(CDCl_3)$ 0.85 (3 H, t, *J* 6 Hz, CH_2Me) and 4.33 (1 H, dt, *J* 6.8 and 13.5 Hz, 1-H); *m/z* 184 (M^+).

(R)-(+)-*Dodecanolide* (**25**).—To a stirred solution of DMSO (0.055 ml, 0.775 mmol) in CH_2Cl_2 (2 ml) at −78 °C was added oxalyl chloride (0.06 ml, 0.688 mmol). After the mixture had been stirred for 10 min at −78 °C, a solution of the alcohol (**22**) (25 mg, 0.136 mmol) in CH_2Cl_2 (2 ml) was added to the above solution and the mixture was stirred for 30 min at the same temperature. The reaction mixture was then treated with Et_3N (0.18 ml, 1.29 mmol), raised to 0 °C, quenched with 10% aq. HCl, and extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $NaHCO_3$, water, and saturated aq. NaCl. The residue upon work-up afforded the crude cyclobutanone (**24**), which was used for the next reaction without further purification.

To a stirred solution of 70% Bu^tOOH (0.035 ml, 0.272 mmol) and 10% aq. NaOH (0.082 ml, 0.204 mmol) in THF (0.5 ml) at 0 °C was added a solution of the crude cyclobutanone (**24**) in THF (1 ml) and the mixture was stirred for 40 min at 0 °C, treated with saturated aq. Na_2SO_3, and extracted with diethyl ether. The extract was washed with saturated aq. NaCl solution. The residue upon work-up was chromatographed with hexane–diethyl ether (94:6 v/v) to give the lactone (**25**) [18.5 mg, 69% from (**22**)] as an oil. By following the same procedure, the alcohol (**23**) (13 mg, 0.07 mmol) afforded the lactone (**25**) (10.2 mg, 73%), which was identical with the sample obtained from compound (**22**) in all aspects.

Compound (**25**): $[\alpha]_D^{27}$ +41.23° (*c* 1.00, MeOH) (Found: M^+, 198.1620. Calc. for $C_{12}H_{22}O_2$: *M*, 198.1619); ν_{max}(neat) 1 780 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 0.86 (3 H, t, *J* 5 Hz, CH_2Me), 1.00–2.00 (16 H, m), 2.00–2.55 (2 H, m, CH_2CO), and 4.23–4.60 (1 H, m, CHOC=O); *m/z* 198 (M^+). This was identical with an authentic sample[7] in all respects.

(1R,2R)- *and* (1S,2R)-1-(*t-Butyldimethylsiloxy*)-2-(2,2-*dibromoethenyl*)*cyclobutane* (**26**) *and* (**27**).—To a stirred solution of CBr_4 (440 mg, 1.33 mmol) in CH_2Cl_2 (1 ml) at 0 °C was added a solution of Ph_3P (695 mg, 2.65 mmol) in CH_2Cl_2 (1 ml) and the mixture was stirred for 1 h at 0 °C. To this reaction mixture, cooled to −78 °C, was added a solution of the aldehyde (**14**) (80.5 mg, 0.376 mmol) in CH_2Cl_2 (0.5 ml). The reaction mixture was stirred for 40 min and was then treated with Et_3N (0.47 ml, 3.13 mmol) at the same temperature. The mixture was diluted at 0 °C with hexane (100 ml) and filtered through Celite. The filtrate was evaporated to leave a residue, which was chromatographed with hexane–ethyl acetate (100:1 v/v) to give the *dibromo olefin* (**26**) (105 mg, 75%) as an oil. By following the same procedure, the aldehyde (**15**) (32.7 mg, 0.153 mmol) afforded the *dibromo olefin* (**27**) (45 mg, 80%) as an oil.

Compound (**26**): $[\alpha]_D^{25}$ −9.89° (*c* 0.91, $CHCl_3$) (Found: $M^+ - 57$, 310.9094. $C_8H_{13}Br_2OSi$ requires *m/z*, 310.9103); ν_{max}(neat) 1 600 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 0.01 (6 H, s, $SiMe_2$), 0.84 (9 H, s, $SiCMe_3$), 1.55–2.22 (4 H, m, CH_2CH_2), 2.95 (1 H, m, $CHCH{=}CBr_2$), 3.95 (1 H, q, *J* 7 Hz, 1-H), and 6.38 (1 H, d, *J* 9 Hz, $CH{=}CBr_2$); *m/z* 311 ($M^+ - 57$).

Compound (**27**): $[\alpha]_D^{25}$ −18.90° (*c* 1.206, $CHCl_3$) (Found: $M^+ - 57$, 310.9100); ν_{max}(neat) 1 608 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 0.02 (6 H, s, $SiMe_2$), 0.85 (9 H, s, $SiCMe_3$), 1.55–2.33 (4 H, m, CH_2CH_2), 3.20 (1 H, m, $CHCH{=}CBr_2$), 4.36 (1 H, q, *J* 7 Hz, 1-H), and 6.83 (1 H, d, *J* 9 Hz, $CH{=}CBr_2$); *m/z* 311 ($M^+ - 57$).

(1R,2S)-*and*(1S,2S)-1-(*t-Butyldimethylsiloxy*)-2-(*dec*-1-*ynyl*)-*cyclobutane* (**28**) *and* (**29**).—To a stirred solution of the dibromo olefin (**26**) (105 mg, 0.28 mmol) in THF (5 ml) at −78 °C was added a solution of BuLi in hexane (1.56M; 0.52 ml, 0.81 mmol). After the mixture had been stirred for 1 h at −78 °C, a solution of octyl bromide (0.13 g, 0.69 mmol) in hexamethylphosphoric triamide (HMPA) (0.9 ml) was added and the mixture was stirred for 30 min at room temperature, treated with water, and extracted with diethyl ether. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (100:1 v/v) to give the *acetylene* (**28**) (78 mg, 85%) as an oil. By following the same procedure, the dibromo olefin (**27**) (60 mg, 0.16 mmol) afforded the *acetylene* (**29**) (44 mg, 84%) as an oil.

Compound (**28**): $[\alpha]_D^{24}$ −65.75° (*c* 1.095, $CHCl_3$) (Found: $M^+ - 57$, 265.1986. $C_{16}H_{29}OSi$ requires *m/z*, 265.1986); $\delta_H(CDCl_3)$ 0.08 (6 H, s, $SiMe_2$), 0.86 (3 H, t, *J* 6 Hz, Me), 2.67 (1 H, m, 2-H), and 4.02 (1 H, q, *J* 7 Hz, 1-H); *m/z* 265 ($M^+ - 57$).

Compound (**29**): $[\alpha]_D^{24}$ −79.81° (*c* 1.06, $CHCl_3$) (Found: M^+, 322.2715. $C_{20}H_{38}OSi$ requires *M*, 322.2690); $\delta_H(CDCl_3)$ 0.05 and 0.07 (6 H, each s, $SiMe_2$), 0.89 (9 H, s, $SiCMe_3$), 0.90 (3 H, t, *J* 6 Hz, Me), 3.12 (1 H, m, 2-H), and 4.19 (1 H, q, *J* 7 Hz, 1-H); *m/z* 322 (M^+).

(1R,2S)- *and* (1S,2S)-1-(*t-Butyldimethylsiloxy*)-2-[(*Z*)-*dec*-1-*enyl*]*cyclobutane* (**30**) *and* (**31**).—A mixture of the acetylene (**28**) (78 mg, 0.24 mmol), Lindlar catalyst (15 mg), and ethyl acetate (3 ml) was stirred for 30 min at room temperature under H_2. The reaction mixture was then filtered through Celite and the filtrate was evaporated to give a residue, which was chromatographed with hexane to give the *olefin* (**30**) (78 mg, 99%) as an oil. By following the same procedure, the acetylene (**29**) (53 mg, 0.16 mmol) afforded the *olefin* (**31**) (50.5 mg, 95%) as an oil.

Compound (**30**): $[\alpha]_D^{23}$ +9.43° (*c* 1.23, $CHCl_3$) (Found: $M^+ - 57$, 267.2141. $C_{16}H_{31}OSi$ requires *m/z*, 267.2143); ν_{max}(neat) 1 650 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 0.02 (6 H, s, $SiMe_2$), 0.85 (9 H, s, $SiCMe_3$), 0.85 (3 H, t, *J* 6 Hz, Me), 2.93 (1 H, m, 2-H), 3.81 (1 H, q, *J* 7 Hz, 1-H), and 5.21–5.36 (2 H, m, CH=CH); *m/z* 267 ($M^+ - 57$).

Compound (**31**): $[\alpha]_D^{24}$ +6.61° (*c* 1.33, $CHCl_3$) (Found: $M^+ - 57$, 267.2157); ν_{max}(neat) 1 650 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 0.02 (6 H, s, $SiMe_2$), 0.89 (9 H, s, $SiCMe_3$), 0.90 (3 H, t, *J* 6 Hz, Me), 3.27 (1 H, m, 2-H), 4.31 (1 H, q, *J* 7 Hz, 1-H), and 5.25–5.98 (2 H, m, CH=CH); *m/z* 267 ($M^+ - 57$).

(1R,2S)- *and* (1S,2S)-2-[(*Z*)-*Dec*-1-*enyl*]*cyclobutanol* (**32**) *and* (**33**).—To a stirred solution of the TBS ether (**30**) (75 mg, 0.23 mmol) in THF (3 ml) was added a solution of Bu_4NF in THF (1M; 0.6 ml, 0.6 mmol) and the mixture was stirred for 1 h at room temperature, diluted with CH_2Cl_2, and washed

successively with water and saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (100:2 v/v) to give the *alcohol* (**32**) (34 mg, 70%) as an oil. By following the same procedure, the TBS ether (**31**) (51 mg, 0.154 mmol) afforded the *alcohol* (**33**) (22 mg, 68%) as an oil.

Compound (**32**): $[\alpha]_D^{26}$ −20.33° (*c* 1.2, $CHCl_3$) (Found: M^+ − 18, 192.1886. $C_{14}H_{24}$ requires *m/z*, 192.1877); ν_{max}(neat) 3 325 cm^{-1} (OH); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 6 Hz, Me), 2.91 (1 H, m, 2-H), 3.89 (1 H, q, *J* 7 Hz, 1-H), and 5.30–5.45 (2 H, m, CH=CH); *m/z* 192 (M^+ − 18).

Compound (**33**): $[\alpha]_D^{24}$ +106.66° (*c* 0.45, $CHCl_3$) (Found: M^+ − 18, 192.1889); ν_{max}(neat) 3 370 cm^{-1} (OH); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 6 Hz, Me), 2.91 (1 H, m, 2-H), 3.89 (1 H, q, *J* 7 Hz, 1-H), and 5.30–5.45 (2 H, m, CH=CH); *m/z* 192 (M^+ − 18).

(S)-5-[(Z)-*Dec*-1-*enyl*]*dihydrofuran*-2(3H)-*one* (**35**).—To a stirred solution of DMSO (0.014 ml, 0.196 mmol) in CH_2Cl_2 (1 ml) at −78 °C was added oxalyl chloride (0.016 ml, 0.178 mmol). After the mixture had been stirred for 10 min at −78 °C, a solution of the alcohol (**32**) (7.5 mg, 0.036 mmol) in CH_2Cl_2 (1 ml) was added and the mixture was stirred for 30 min at the same temperature, then treated with Et_3N (0.65 ml, 0.35 mmol), warmed to 0 °C, quenched with 10% aq. HCl, and extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $NaHCO_3$, water, and saturated aq. NaCl. Evaporation of the solvent afforded the crude cyclobutanone (**34**) which was used for the next reaction without further purification because of its instability.

To a stirred solution of 70% Bu^{t}OOH (0.01 ml, 0.078 mmol) and 10% aq. NaOH (0.01 ml, 0.042 mmol) in THF (0.2 ml) at 0 °C was added a solution of the crude butanone (**34**) obtained above in THF (1 ml) and the mixture was stirred for 30 min at the same temperature, then treated with saturated aq. Na_2SO_3, and extracted with diethyl ether. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–diethyl ether (20:1 v/v) to give the *furanone* (**35**) [2.4 mg, 30% from the alcohol (**32**)] as an oil. By following the same procedure, the alcohol (**33**) (16.6 mg, 0.07 mmol) afforded the *furanone* (**35**) (5.3 mg, 30%) which was identical with the furanone (**35**) obtained from the alcohol (**32**) in all respects.

Compound (**35**): $[\alpha]_D^{24}$ +69.99° (*c* 0.12, $CHCl_3$) (Found: M^+, 224.1759. $C_{14}H_{24}O_2$ requires *M*, 224.1775); ν_{max}(neat) 1 785 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 6 Hz, Me), 5.10 (1 H, m, 5-H), and 5.20–5.68 (2 H, m, CH=CH); *m/z* 224 (M^+).

(R)-5-[(Z)-*Dec*-1-*enyl*]*dihydrofuran*-2(3H)-*one* (**36**).—A mixture of the furanone (**35**) (5.0 mg, 0.022 mmol), KOH (12 mg, 0.214 mmol), and MeOH (1 ml) was stirred for 3 h at 60 °C. The residue upon evaporation of the solvent was dissolved in water (2 ml) and washed with CH_2Cl_2. The aqueous layer was acidified with AcOH to pH 4 and extracted with CH_2Cl_2. This extract was washed with saturated aq. NaCl. The residue upon work-up was used for the next reaction directly.

To a stirred solution of the residue obtained above and Ph_3P (28 mg, 0.107 mmol) in benzene (1.5 ml) was added DEAD (0.02 ml, 0.127 mmol) and the mixture was stirred for 13 h at room temperature. Evaporation of the solvent gave a residue, which was chromatographed with hexane–diethyl ether (20:1 v/v) to afford the furanone (**36**) (3.8 mg, 76%) as an oil, which was identical with the furanone (**35**) obtained above in all respects except for the optical behaviour, and which was also identical with an authentic sample in all respects, including ^{1}H NMR, IR, and optical rotation: $[\alpha]_D^{25}$ −70.82° (*c* 0.19, $CHCl_3$) (lit.,[10] −70.4°; lit.,[11,12] −70.0°; lit.,[13] −69.93°; lit.,[14] −69.7°).

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References

1 D. Bellus and B. Ernst, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 797.
2 T. K. Devon and A. I. Scott, 'Handbook of Naturally Occurring Compounds,' vol. II, 'Terpenes,' Academic, New York, 1972; A. F. Thomas and Y. Bessiere, 'The Synthesis of Monoterpenes, 1980–1986,' in 'The Total Synthesis of Natural Products,' ed. J. ApSimon, Wiley, New York, 1988, vol. 7, p. 275.
3 J. M. Conia and M. J. Robson, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 473; S. M. Ali, T. V. Lee, and S. M. Roberts, *Synthesis*, 1977, 155; W. T. Brady, *Tetrahedron*, 1981, **37**, 2949; C. S. Hwang and W. Reusch, *Heterocycles*, 1987, **25**, 589; J. Vidal and F. Huet, *J. Org. Chem.*, 1988, **53**, 611; T. Cohen and L. Brockunier, *Tetrahedron*, 1989, **45**, 2917. Some representatives related to the reactions of 2-vinylcyclobutanones are cited therein.
4 M. Nogradi, 'Stereoselective Synthesis,' VCH Verlagsgesellschaft, Winheim, 1987, p. 275; K. Hiroi, H. Nakamura, and T. Anzai, *J. Am. Chem. Soc.*, 1987, **109**, 1249; J. Salaun, B. Karkour, and J. Ollivier, *Tetrahedron*, 1989, **45**, 3151; Y. Hayashi and K. Narasaka, *Chem. Lett.*, 1989, 793; Y. Ichikawa, A. Narita, A. Shiozaki, Y. Hyashi, and K. Narasaka, *J. Chem. Soc., Chem. Commun.*, 1989, 1919; K. Hiroi, T. Anzai, T. Ogata, and M. Saito, *Tetrahedron Lett.*, 1990, **31**, 239.
5 M. H. O'Leary, W. J. DeGooyer, T. M. Dougherty, and V. Anderson, *Biochem. Biophys. Res. Commun.*, 1981, **100**, 1320.
6 J. E. Lynch and E. L. Eliel, *J. Am. Chem. Soc.*, 1984, **106**, 2943.
7 T. Sugai and K. Mori, *Agric. Biol. Chem.*, 1984, **48**, 2497; G. Solladie and F. Matloubi-Moghadam, *J. Org. Chem.*, 1982, **47**, 91.
8 E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 1972, 3769.
9 S. Takano, M. Yonaga, and K. Ogasawara, *Synthesis*, 1981, 265.
10 S. Senda and K. Mori, *Agric. Biol. Chem.*, 1983, **47**, 2595.
11 R. E. Doolittle, J. H. Tumlinson, A. T. Proveaux, and R. R. Heath, *J. Chem. Ecol.*, 1980, **6**, 473.
12 W. H. Pirkle and P. E. Adams, *J. Org. Chem.*, 1979, **44**, 2169.
13 M. M. Midland and N. H. Nguyen, *J. Org. Chem.*, 1981, **46**, 4107.
14 R. Baker and V. B. Rao, *J. Chem. Soc., Perkin Trans. 1*, 1982, 69.

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