Highly Stereoselective Boron Trifluoride-promoted 5-*endo* Cyclisation of Epoxy-allylic Stannanes

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A novel and highly stereoselective 5-*endo* cyclisation of epoxy-allylic stannanes **1** promoted by BF_3–Et_2O has been discovered. The same reaction occurs with lower regio- and stereo-selectivity *via* an allylic lithium as a result of transmetallation. The selective formation of *trans*-3-alkenylcyclopentanols is expected to be of importance in terpenoid syntheses.

The importance of stereoselective cyclopentane ring construction has led to the discovery of a number of complex synthetic routes. The 3-alkenylcyclopentanol framework is particularly important since it is both found in a number of terpenoids and also recognised as a key intermediate in the synthesis of a number of natural products.[1] Cyclisation of epoxy-allylic metal compounds to give 3-alkenylcyclopentanols occurs by way of epoxide ring opening, the stereoelectronic ease of cleavage of either of the two C–O bonds of the epoxide ring being an important factor in settling the regiochemistry. Based on this principle, it is generally believed that the 5-*endo* mode of cyclisation is disfavoured compared with the corresponding 4-*exo* one.

In the course of our study,[2] we have examined the cyclisation of epoxy-allylic stannanes **1**, which were supposed to give 4-*exo* and 5-*endo* cyclised products. The BF_3–OEt_2 promoted reactions were found, unexpectedly to afford exclusively the 5-*endo* cyclised products with excellent stereoselectivity. Herein we present these results and discuss this unprecedented excellent selectivity.

Results and Discussion

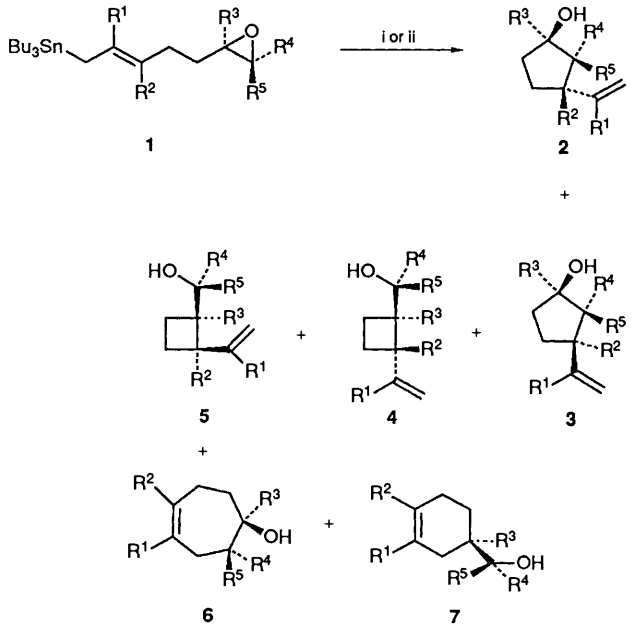
As an extension of our study on the Lewis acid-promoted cyclisation of epoxy-allylic stannanes,[2] the cyclisation of **1** was examined. Although $TiCl_4$ and TMSOTf had previously been found to be excellent promotors of this type of reaction, they were inefficient in the present reactions, resulting in the formation of acyclic chlorohydrins, epoxyalkenes and other by-products. By contrast, we obtained the 5-*endo* cyclised product **2** in 73–100% yield using 3 equiv. of BF_3–OEt_2 in CH_2Cl_2 at −78 °C. However, the presence of a methyl group at R^3 altered the cyclisation, making it non-selective and affording a complex product mixture of more than three isomers. These results are summarised in Table 1.

The compounds **2** obtained were epimerised to mixtures of **2** and **3** by oxidation with chromic acid followed by reduction with $LiAlH_4$. By comparison of its spectra with those of an authentic *cis* isomer **3a**,[3] **2a** was confirmed to be the *trans* isomer. The structures of five other products **2b–f** were deduced from lanthanide induced shift (LIS) experiments[4] using $Eu(fod)_3$. Our determination was based on shift experiments on the structurally defined **2a** and **3a** whose protons on the same side of hydroxy group exhibited larger downfield shift values than those on the opposite side. Since a similar relation was observed between **2b–f** and epimerised products **3b–f**, it was concluded that the products obtained, **2a–f**, had a *trans* configuration.

Table 1 BF_3–Et_2O-induced cyclisations of epoxy-allylic stannanes **1**

Entry	R^1	R^2	R^3	R^4	R^5	**2** Yield[a] (%)
a	H	H	H	H	H	73
b	H	H	H	Et	H	71[b]
c	H	H	H	H	Et	97[c]
d	Me	H	H	H	H	91
e	H	Me	H	H	H	75
f	H	Pr^i	H	H	H	100
g	H	H	Me	H	H	*d*

[a] Isolated yields. [b] A trace amount of **3b** was detected by ^{13}C NMR spectroscopy. [c] A trace amount of **7c** was detected. [d] A complex mixture of products was formed in 73% yield including more than three isomers.



Scheme 1 *Reagents:* i, BF_3–OEt_2 (3 equiv.), CH_2Cl_2, −78 °C; ii, BuLi (3 equiv.), THF, −78 °C

For comparison, the reaction of **1** was attempted *via* *trans*-metallation to the corresponding allylic lithiums by addition of butyllithium in THF (tetrahydrofuran).[2] Several isomeric cyclised products were obtained (Table 2). The terminally unsubstituted epoxides **1a** and **d–g** selectively gave the 7-*endo* cyclised products **6**. In contrast, the presence of a terminal ethyl

Table 2 Cyclisations of **1** *via* transmetallation to allylic lithiums

Entry	Yield[a] (%)	Regioselectivity[b] 2 + 3:4 + 5:6:7	Stereoselectivity[b] 2:3	4:5
a	73	4:—:96:—	0:1	—
b	88	30:55:—:15	1:2	85:15
c	83	—:70:15:15	—	93:7
d	90	17:—:83:—	1:8	—
e	72	6:6:88:—	1:3	(2:1)[c]
f	91	4:7:89:—	0:1	(1:1)[c]
g	75	6[c]:94:—	—	—

[a] Isolated yields as an isomeric mixture. [b] Determined by integral ratio in ^{1}H NMR spectroscopy. [c] Not assigned to a specific isomer.

group on the epoxide ring, **1b** and **c**, caused more competitive formation of a variety of isomers. Among these, the 4-*exo* cyclised products **4** and **5** predominated over the corresponding 5-*endo* cyclised products **2** and **3**.*

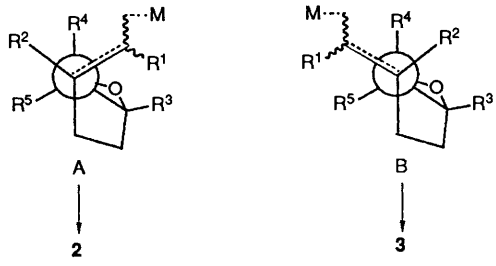
The 5-*endo* selectivity is rare in cyclisations *via* epoxide ring opening with very few exceptions. Stork and co-workers demonstrated that the 5-*endo* cyclisation of epoxy nitriles was unfavourable compared to 4-*exo* cyclisation when the epoxide ring was symmetrically substituted.[5] Alternatively, 5-*endo* cyclisation could occur, exceptionally, when the 4-*exo* attack in a similar system was subjected to steric hindrance.[6] However, no example of 5-*endo* selective cyclisation promoted by Lewis acid was demonstrated.

In the reaction using Lewis acid as a promoter, as described in the preliminary paper,[2] the regioselectivity is frequently controlled by the substitution pattern of the epoxide ring, the more stabilised cationic centre directing the mode of cyclisation. The observed regiospecificity of BF_3–Et_2O promoted cyclisation of **1** could not be interpreted by any of the above mentioned stereoelectronic, steric or substituent effects.

In the reaction *via* transmetallation to allylic lithium, the products at both the α- and γ-positions of allylic stannane were observed. The selective formation of the 7-*endo* cyclised products **6** for terminally unsubstituted substrates **1a** and **d**–**g** indicates that such a nucleophilic approach preferentially takes place onto the less bulky epoxide carbon. The regiochemical observation, 4-*exo* over 5-*endo*, in the reactions of **1b** and **c** should be regarded as a reflection of the stereoelectronic effect proposed by Stork *et al.*[5] These results show that the 5-*endo* mode of cyclisation is the least favoured process in this reaction.

Nevertheless, the BF_3–OEt_2 promoted reactions exclusively give the 5-*endo* cyclised products. To explain this abnormal regiochemistry, the hypothesis adopted in the preliminary paper seems to be acceptable.[2,7] If the initial electrophilic approach is to the centre of the bond in the allylic stannane and this stage can direct the reaction course, the cyclisation mode would be allowed because of its partial 6-*endo* character which is favoured stereoelectronically. By contrast, this makes the 4-*exo* alternative disfavoured by mixing of the 5-*endo* character.

The observed excellent stereoselectivity is also rare in epoxyallylic stannane or silane cyclisations. It is noteworthy that the stereochemistry is hardly influenced by any substituent examined and, in particular, that the presence of a bulky isopropyl group at C-3, compound **1f**, did not affect the selectivity. At present, we are unable to formulate any reasonable transition model to explain the stereochemistry



Scheme 2

(Scheme 2) although it is probable that an entropically favourable reaction course governs the stereochemistry.

Although no data are available to rationalise the highly regio- and stereo-selective cyclisation process, nevertheless the process has considerable synthetic potential. The results provide a convenient synthesis of *trans*-3-alkenylcyclopentanols.

Experimental

For general experimental details see ref. 2. Throughout this section *J* values are given in Hz.

Epoxyallylic Stannanes **1**.—These compounds were prepared by reported methods.[2]

Tributyl(6,7-epoxyhept-2-enyl)stannane **1a** *E*:*Z* = 78:22; δ_H(400 MHz; $CDCl_3$) 0.85 (6 H, m), 0.89 (9 H, t, *J* 7.4), 1.30 (6 H, m), 1.47 (1 H, m), 1.56 (2 H, m), 1.69 (2 H, m), 2.13 (2 H, m), 2.48 (1 H, m), 2.75 (1 H, m), 2.93 (1 H, m), 5.07 (0.22 H, dt, *J* 10.8 and 6.6), 5.23 (0.78 H, dt, *J* 14.9 and 6.6) and 5.58 (1 H, m); δ_C(100.4 MHz; $CDCl_3$) 9.2 (t), 9.4 (t), 13.7 (q), 14.2 (t), 23.4 (t), 27.4 (t), 29.0 (t), 29.14 (t), 19.17 (t), 29.2 (t), 32.7 (t), 33.2 (t), 47.2 (t), 52.0 (d), 122.7 (d), 124.2 (d), 129.3 (d) and 130.2 (d); ν_{max}(film)/cm^{-1} 2960, 2930, 2850, 1640, 1457, 1373, 1070 and 960 (Found: C, 57.05; H, 9.55. $C_{19}H_{38}OSn$ requires C, 56.88; H, 9.55).

trans-*Tributyl(6,7-epoxynon-2-enyl)stannane* **1b** *E*:*Z* = 78:22; δ_H(400 MHz; $CDCl_3$) 0.85 (6 H, m), 0.89 (9 H, t, *J* 7.4), 0.99 (3 H, t, *J* 7.4), 1.29 (6 H, m), 1.36–1.64 (10 H, m), 1.66–1.78 (2 H, m), 2.11 (2 H, m), 2.67 (2 H, m), 5.07 (0.22 H, dt, *J* 10.8 and 6.6), 5.22 (0.78 H, dt, *J* 14.9 and 6.6) and 5.58 (1 H, m); δ_C(100.4 MHz; $CDCl_3$) 9.2 (t), 9.4 (t), 10.0 (q), 13.8 (q), 14.2 (t), 23.5 (t), 25.3 (t), 27.4 (t), 29.1 (t), 29.18 (t), 29.21 (t), 29.3 (t), 32.3 (t), 32.8 (t), 58.3 (d), 60.1 (d), 122.8 (d), 124.3 (d), 129.2 (d) and 130.1 (d); ν_{max}(film)/cm^{-1} 2960, 2930, 2850, 1640, 1458, 1375, 1070 and 960 (Found: C, 59.15; H, 9.35. $C_{21}H_{42}OSn$ requires C, 58.76; H, 9.86).

cis-*Tributyl(6,7-epoxynon-2-enyl)stannane* **1c** *E*:*Z* = 77:23; δ_H(400 MHz; $CDCl_3$) 0.85 (6 H, m), 0.89 (9 H, t, *J* 7.4), 1.04 (2.3 H, t, *J* 7.4), 1.05 (0.7 H, t, *J* 7.4), 1.29 (6 H, m), 1.43–1.61 (10 H, m), 1.69 (2 H, m), 2.14 (2 H, m), 2.91 (2 H, m), 5.08 (0.23 H, dt, *J* 10.8 and 6.6), 5.23 (0.77 H, dt, *J* 14.9 and 6.6) and 5.59 (1 H, m); δ_C(100.4 MHz; $CDCl_3$) 9.2 (t), 9.4 (t), 10.7 (q), 13.7 (q), 14.2 (t), 21.2 (t), 24.0 (t), 27.4 (t), 28.0 (t), 28.5 (t), 29.1 (t), 29.18 (t), 29.21 (t), 29.8 (t), 57.0 (d), 58.4 (d), 122.8 (d), 124.3 (d), 129.3 (d) and 130.2 (d); ν_{max}(film)/cm^{-1} 2960, 2930, 2850, 1640, 1458, 1372, 1070 and 960 (Found: C, 59.0; H, 9.8. $C_{21}H_{42}OSn$ requires C, 58.76; H, 9.86).

Tributyl(6,7-epoxy-2-methylhept-2-enyl)stannane **1d** *E*:*Z* = 55:45; δ_H(400 MHz; $CDCl_3$) 0.83 (6 H, m), 0.89 (6 H, m), 1.30 (6 H, m), 1.41–1.65 (8 H, m), 1.60 (3 H, s), 1.66 (3 H, s), 1.69–1.82 (2 H, m), 2.11 (2 H, m), 2.76 (1 H, m), 2.93 (1 H, m), 4.84 (0.45 H, t, *J* 7.0) and 4.99 (0.55 H, t, *J* 7.0); δ_C(100.4 MHz; $CDCl_3$) 9.5 (t), 9.7 (t), 13.7 (d), 15.4 (t), 18.5 (q), 22.1 (t), 24.75 (t), 24.82 (t), 26.0 (t), 27.4 (t), 29.0 (t), 29.16 (t), 29.19 (t), 29.3 (t), 32.8 (t), 33.2 (t), 47.2 (t), 52.2 (d), 118.5 (d), 118.8 (d), 136.1 (s) and 136.2 (s); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1648, 1458, 1374, 1070, 960, 860 and 833 (Found: C, 57.7; H, 9.6. $C_{20}H_{40}OSn$ requires C, 57.85; H, 9.71).

* The configurations of **4** and **5** were deduced by ^{1}H NMR spectroscopy. The substitution pattern of the cyclobutane rings in major isomers was determined to be *trans* **4** based on the chemical shifts of two methine ring protons. Due to the shielding by the C–C σ bond of the substituents at the β-position to them showed upfield shifts relative to those of minor isomers.

Tributyl(6,7-epoxy-3-methylhept-2-enyl)stannane **1e** *E*:*Z* = 75:25; δ_H(400 MHz; $CDCl_3$) 0.83 (6 H, m), 0.89 (9 H, t, *J* 7.3), 1.29 (6 H, sextet, *J* 7.3), 1.40–1.55 (6 H, m), 1.58 (3 H, s), 1.55–1.75 (4 H, m), 2.13 (2 H, m), 2.49 (1 H, m), 2.75 (1 H, m), 2.91 (1 H, m), 5.33 (0.25 H, t, *J* 9.1) and 5.37 (0.75 H, t, *J* 9.1); δ_C(100.4 MHz; $CDCl_3$) 9.4 (t), 10.7 (t), 13.7 (d), 15.6 (q), 23.1 (q), 27.3 (t), 29.2 (t), 30.8 (t), 31.5 (t), 35.9 (t), 47.2 (t), 52.3 (d), 123.7 (d), 124.3 (d) and 128.0 (s); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1648, 1450, 1370, 1116, 1068, 958 and 860 (Found: C, 57.75; H, 9.65. $C_{20}H_{40}OSn$ requires C, 57.85; H, 9.71).

Tributyl(6,7-epoxy-3-isopropylhept-2-enyl)stannane **1f** *E*:*Z* = 3:97; δ_H(400 MHz; $CDCl_3$) 0.83 (6 H, m), 0.89 (9 H, t, *J* 7.2), 0.98 (6 H, d, *J* 6.7), 1.29 (6 H, sextet, *J* 7.2), 1.40–1.55 (6 H, m), 1.60 (2 H, m), 1.68 (2 H, dd, *J* 9.0 and 3.1), 2.12 (2 H, m), 2.20 (1 H, m), 2.49 (1 H, m), 2.77 (1 H, t, *J* 4.5), 2.98 (1 H, m), 5.22 (0.03 H, t, *J* 9.2) and 5.35 (0.97 H, t, *J* 9.2); δ_C(100.4 MHz; $CDCl_3$) 9.4 (t), 10.5 (t), 13.7 (q), 22.38 (q), 22.43 (q), 25.3 (t), 27.4 (t), 29.2 (t), 31.9 (q), 34.3 (d), 47.2 (t), 52.4 (d), 121.1 (d), 121.9 (d) and 138.4 (s); ν_{max}(film)/cm^{-1} 2960, 2920, 2860, 1635, 1456, 1370, 1068, 1000, 958, 925, 860 and 835 (Found: C, 59.45; H, 9.85. $C_{22}H_{44}OSn$ requires C, 59.61; H, 10.00).

Tributyl(6,7-epoxy-6-methylhept-2-enyl)stannane **1g** *E*:*Z* = 77:23; δ_H(400 MHz; $CDCl_3$) 0.84 (6 H, m), 0.89 (9 H, t, *J* 7.3), 1.24–1.37 (10 H, m), 1.37–1.59 (6 H, m), 1.59–1.77 (2 H, m), 2.57 (0.77 H, d, *J* 4.8), 2.62 (0.77 H, d, *J* 4.8), 2.64 (0.23 H, d, *J* 4.8), 5.03 (0.23 H, dt, *J* 14.8 and 6.9), 5.19 (0.77 H, dt, *J* 10.4 and 6.9) and 5.56 (1 H, m); δ_C(100.4 MHz; $CDCl_3$) 9.2 (t), 9.4 (t), 13.7 (q), 14.2 (t), 21.0 (t), 27.4 (t), 28.5 (t), 29.0 (t), 29.16 (t), 29.20 (t), 29.3 (t), 36.7 (t), 37.2 (t), 54.0 (t), 56.9 (s), 123.0 (d), 124.5 (d), 129.0 (d) and 129.8 (d); ν_{max}(film)/cm^{-1} 1960, 1930, 2860, 1640, 1452, 1373, 1070, 970 and 860 (Found: C, 58.05; H, 9.65. $C_{20}H_{40}OSn$ requires C, 57.85; H, 9.71).

A General Procedure for the Boron Trifluoride-induced Cyclisation of **1**.—To a solution of **1** (1.0 mmol) in dry dichloromethane (20 cm^3) at −78 °C was added slowly boron trifluoride (3.0 mmol). The mixture was stirred (30 min) at the same temperature under nitrogen and saturated aqueous $NaHCO_3$ (10 cm^3) was added; the mixture was then allowed to warm to room temperature. The organic layer was separated, washed with 10% aqueous NH_3 and brine, dried ($MgSO_4$) and concentrated. The residue was flash chromatographed on silica gel [eluting with hexane–ether] to give cyclised product **2**.

3-*Vinylcyclopentanol* **2a** δ_H(400 MHz; $CDCl_3$) 1.36 (1 H, m), 1.49 (1 H, s), 1.56 (1 H, ddd, *J* 13.7, 10.1 and 5.5), 1.59 (1 H, m), 1.81 (1 H, dd, *J* 5.5 and 2.7), 2.01 (2 H, m), 2.81 (1 H, sextet, *J* 8.2), 4.40 (1 H, tt, *J* 5.5 and 2.7), 4.91 (1 H, br d, *J* 10.2), 5.01 (1 H, br d, *J* 17.1) and 5.78 (1 H, ddd, *J* 17.1, 10.2 and 7.4); δ_C(100.4 MHz; $CDCl_3$) 30.6 (t), 35.2 (t), 41.5 (d), 42.5 (d), 73.6 (d), 112.8 (t) and 142.7 (d); ν_{max}(film)/cm^{-1} 3310, 3080, 2960, 2880, 1635, 1453, 1296, 1114, 963 and 910 (Found: M^+, 112.0890. $C_7H_{12}O$ requires *M*, 112.0888).

2-*Ethyl*-3-*vinylcyclopentanol* **2b** δ_H(400 MHz; $CDCl_3$) 0.93 (3 H, t, *J* 7.4), 1.25 (1 H, dt, *J* 13.8 and 7.4), 1.35 (1 H, dt, *J* 13.8 and 7.4), 1.48 (1 H, m), 1.50 (1 H, br s), 1.54 (1 H, m), 1.67 (1 H, ddd, *J* 12.9, 7.4 and 5.5), 1.93 (1 H, m), 2.11 (1 H, m), 2.83 (1 H, quintet, *J* 7.2), 3.99 (1 H, dt, *J* 7.1 and 5.1), 4.98 (1 H, br d, *J* 10.3), 5.00 (1 H, br d, *J* 17.0) and 5.74 (1 H, ddd, *J* 17.0, 10.3 and 8.7); δ_C(100.4 MHz; $CDCl_3$) 12.6 (q), 21.2 (t), 28.1 (t), 33.2 (t), 44.7 (d), 54.0 (d), 77.6 (d), 114.4 (t) and 139.6 (d); ν_{max}(film)/cm^{-1} 3340, 3080, 2960, 2880, 1637, 1460, 1070, 995 and 908 (Found: M^+, 140.1188. $C_9H_{16}O$ requires *M*, 140.1199).

2-*Ethyl*-3-*vinylcyclopentanol* **2c** δ_H(400 MHz; $CDCl_3$) 0.97 (3 H, t, *J* 7.3), 1.30 (2 H, m), 1.40 (2 H, m), 1.65 (2 H, m), 1.95 (1 H, m), 2.05 (1 H, m), 2.33 (1 H, quintet, *J* 9.0), 4.28 (1 H, td, *J* 4.4 and 1.2), 4.94 (1 H, br d, *J* 10.0), 4.99 (1 H, br d, *J* 17.0) and 5.66 (1 H, ddd, *J* 17.0, 10.0 and 8.6); δ_C(100.4 MHz; $CDCl_3$) 12.8 (q), 20.0 (t), 29.8 (t), 33.7 (t), 47.2 (d), 53.3 (d), 73.7 (d), 114.0 (t) and 142.8 (d); ν_{max}(film)/cm^{-1} 3380, 3075, 2960, 2870, 1637, 1458, 1140, 1005, 988, 957 and 904 (Found: M^+, 140.1193. $C_9H_{16}O$ requires *M*, 140.1199).

3-*Isopropenylcyclopentanol* **2d** δ_H(400 MHz; $CDCl_3$) 1.46 (1 H, m), 1.64 (3 H, m), 1.73 (3 H, s), 1.80 (1 H, m), 1.97 (1 H, m), 2.05 (1 H, m), 2.79 (1 H, quintet, *J* 8.8), 4.43 (1 H, tt, *J* 5.9 and 2.6), 4.69 (1 H, s) and 4.71 (1 H, s); δ_C(100.4 MHz; $CDCl_3$) 21.2 (q), 29.2 (t), 35.3 (t), 41.0 (t), 44.2 (d), 73.5 (d), 108.4 (t) and 148.3 (s); ν_{max}(film)/cm^{-1} 3350, 3090, 2960, 2870, 1640, 1435, 1372, 1335, 1172, 1013 and 884 (Found: M^+, 126.1054. $C_8H_{14}O$ requires *M*, 126.1044).

3-*Methyl*-3-*vinylcyclopentanol* **2e** δ_H(400 MHz; $CDCl_3$) 1.20 (3 H, s), 1.43 (1 H, dd, *J* 13.5 and 4.9), 1.46 (1 H, m), 1.64 (2 H, m), 2.00 (1 H, ddd, *J* 15.6, 9.6 and 6.7), 2.06 (1 H, dd, *J* 13.5 and 7.0), 4.39 (1 H, tt, *J* 6.1 and 3.8), 4.88 (1 H, d, *J* 10.6), 4.92 (1 H, d, *J* 17.5) and 5.82 (1 H, dd, *J* 17.5 and 10.6); δ_C(67.8 MHz; $CDCl_3$) 27.4 (q), 34.9 (t), 37.3 (t), 44.5 (s), 48.4 (t), 73.8 (d), 109.6 (t) and 147.9 (d); ν_{max}(film)/cm^{-1} 3360, 3090, 2960, 2870, 1640, 1445, 1345, 1050, 997 and 905 (Found: M^+, 126.1042. $C_8H_{14}O$ requires *M*, 126.1044).

3-*Isopropyl*-3-*vinylcyclopentanol* **2f** δ_H(400 MHz; $CDCl_3$) 0.83 (6 H, d, *J* 6.7), 1.37 (1 H, dd, *J* 13.2 and 6.6), 1.44 (1 H, br s), 1.54 (1 H, m), 1.63 (1 H, m), 1.68 (1 H, m), 1.70 (1 H, m), 1.92 (1 H, ddt, *J* 13.0, 9.7 and 7.5), 2.21 (1 H, dd, *J* 13.2 and 6.6), 4.32 (1 H, qd, *J* 6.6 and 3.8), 4.92 (1 H, d, *J* 17.4), 5.06 (1 H, d, *J* 10.8) and 5.70 (1 H, dd, *J* 17.4 and 10.8); δ_C(100.4 MHz; $CDCl_3$) 18.3 (q), 18.6 (q), 33.7 (t), 34.3 (t), 38.4 (d), 45.2 (t), 52.3 (s), 73.1 (d), 113.0 (t) and 142.4 (d); ν_{max}(film)/cm^{-1} 3350, 3090, 2970, 2880, 1633, 1465, 1442, 1412, 1382, 1366, 1340, 1060, 1000 and 905 (Found: M^+, 154.1363. $C_{10}H_{18}O$ requires *M*, 154.1357).

A General Procedure for the Epimerisation of **2**.—To a solution of chromic acid prepared from sodium dichromate dihydrate (52 mg, 0.18 mmol) and conc. sulphuric acid (70 mg, 0.68 mmol) in water (0.25 cm^3) was added compound **2** (0.5 mmol) in ether (0.2 cm^3). The mixture was stirred for 4 h after which the organic layer was separated, dried ($MgSO_4$) and concentrated. Without further purification, the obtained crude product was dissolved in dry ether (1 cm^3) and added slowly to a suspension of $LiAlH_4$ (19 mg, 0.5 mmol) in dry ether (1 cm^3). After 1 h, diluted hydrochloric acid was added and the organic layer was separated. The layer was dried ($MgSO_4$) and concentrated to give a diastereoisomeric mixture of **2** and **3** in quantitative yield.

3a discernible from mixture with **2a**; δ_H(400 MHz; $CDCl_3$) 1.38 (1 H, ddd, *J* 13.7, 8.7 and 5.0), 1.45 (1 H, br s), 1.65 (2 H, m), 1.81 (1 H, m), 2.19 (2 H, m), 2.49 (1 H, sextet, *J* 8.2), 4.51 (1 H, tdd, *J* 5.9, 5.1 and 3.7), 4.90 (1 H, br d, *J* 9.9), 5.00 (1 H, br d, *J* 17.1) and 5.87 (1 H, ddd, *J* 17.1, 9.9 and 7.4); δ_C(100.4 MHz; $CDCl_3$) 30.4 (t), 35.6 (t), 42.3 (d), 42.6 (t), 73.7 (d), 112.6 (t) and 143.2 (d).

3b discernible from mixture with **2c**; δ_H(400 MHz; $CDCl_3$) 0.97 (3 H, t, *J* 7.4), 1.25 (1 H, br s), 1.25–1.55 (3 H, m), 1.62 (2 H, m), 1.76 (1 H, m), 1.88 (1 H, m), 2.08 (1 H, quintet, *J* 8.1), 3.94 (1 H, dt, *J* 5.6 and 5.0), 4.92 (1 H, br d, *J* 10.0), 4.98 (1 H, br d, *J* 18.4) and 5.78 (1 H, ddd, *J* 18.4, 10.0 and 8.1); δ_C(67.8 MHz; $CDCl_3$) 12.1 (q), 25.1 (t), 30.1 (t), 34.4 (t), 49.1 (d), 55.8 (d), 78.4 (d), 113.4 (t) and 143.0 (d).

3c discernible from mixture with **2b**; δ_H(400 MHz; $CDCl_3$) 0.96 (3 H, t, *J* 7.4), 1.20–1.65 (4 H, m), 1.73 (1 H, m), 1.76 (1 H, m), 1.88 (2 H, m), 2.64 (1 H, qd, *J* 8.2 and 3.4), 4.22 (1 H, br t, *J* 3.6), 4.91 (1 H, br d, *J* 9.7), 4.94 (1 H, br d, *J* 17.2) and 5.93 (1 H, dt, *J* 17.2 and 9.7); δ_C(67.8 MHz; $CDCl_3$) 13.0 (q), 18.9 (t), 29.7 (t), 34.2 (t), 45.0 (d), 51.1 (d), 74.9 (d), 113.4 (t) and 142.5 (d).

3d discernible from mixture with **2d**; δ_H(400 MHz; $CDCl_3$) 1.26 (1 H, br s), 1.46 (1 H, m), 1.55–1.75 (3 H, m), 1.75 (3 H, s), 2.02 (1 H, m), 2.18 (1 H, dt, *J* 13.1 and 6.9), 2.46 (1 H, quintet, *J* 8.5), 4.35 (1 H, qd, *J* 6.2 and 3.4), 4.70 (1 H, br s) and 4.75 (1 H,

br s); δ_C(125.65 MHz; $CDCl_3$) 20.9 (q), 28.9 (t), 35.5 (t), 40.8 (t), 45.5 (d), 73.6 (d), 108.6 (t) and 148.3 (s).

3e discernible from mixture with **2e**; δ_H(400 MHz; $CDCl_3$) 1.06 (3 H, s), 1.29 (1 H, m), 1.53 (1 H, br s), 1.65 (2 H, m), 1.81 (1 H, dd, *J* 13.7 and 6.6), 1.88 (1 H, dt, *J* 12.8 and 8.1), 2.08 (1 H, m), 4.41 (1 H, tt, *J* 7.4 and 4.7), 4.92 (1 H, d, *J* 10.6), 5.01 (1 H, d, *J* 17.4) and 6.01 (1 H, dd, *J* 17.4 and 10.6); δ_C(125.65 MHz; $CDCl_3$) 26.6 (q), 35.1 (t), 37.2 (t), 44.3 (s), 49.0 (t), 74.1 (d), 109.8 (t) and 148.8 (d).

3f discernible from mixture with **2f**; δ_H(400 MHz; $CDCl_3$) 0.81 (3 H, d, *J* 6.7), 0.84 (3 H, d, *J* 6.7), 1.41 (1 H, dt, *J* 13.8 and 9.1), 1.50 (1 H, quintet, *J* 6.8), 1.59 (2 H, m), 1.74 (1 H, dd, *J* 13.8 and 6.8), 1.85 (1 H, br s), 1.90 (1 H, m), 2.06 (1 H, m), 4.38 (1 H, tdd, *J* 7.0, 4.6 and 2.7), 5.12 (1 H, d, *J* 17.5), 5.17 (1 H, d, *J* 11.0) and 5.92 (1 H, dd, *J* 17.5 and 11.0); δ_C(125.65 MHz; $CDCl_3$) 18.2 (q), 18.5 (q), 33.9 (t), 35.3 (t), 38.1 (d), 45.3 (t), 51.9 (s), 74.3 (d), 113.7 (t) and 144.3 (d).

The Butyllithium-promoted Cyclisation of **1**.—This reaction was carried out by the same method described in the previous paper.[2] Known cycloheptenols **6a**, **d** and **e** were identified with the authentic samples spectroscopically.[8,9]

6f discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.96 (6 H, d, *J* 6.9), 1.23–1.36 (2 H, m), 1.47 (1 H, br s), 1.84–1.98 (4 H, m), 2.10–2.25 (3 H, m), 3.78 (1 H, tt, *J* 5.5 and 3.9) and 5.52 (1 H, t, *J* 6.5); δ_C(125.65 MHz; $CDCl_3$) 21.1 (q), 21.2 (q), 22.4 (t), 24.3 (t), 35.70 (t), 35.73 (t), 36.9 (d), 74.6 (d), 122.5 (d) and 150.7 (s).

6g discernible from mixture; δ_H(400 MHz; $CDCl_3$) 1.26 (3 H, s), 1.37 (1 H, br s), 1.68 (4 H, m), 1.96 (2 H, m), 2.28 (2 H, m) and 5.74 (2 H, t, *J* 3.6); δ_C(125.65 MHz; $CDCl_3$) 23.4 (t), 30.1 (t), 40.6 (t), 73.7 (s) and 131.6 (d).

4b discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.94 (3 H, t, *J* 7.4), 1.20–2.07 (7 H, m), 2.16 (1 H, quintet, *J* 7.9), 2.69 (1 H, m), 3.46 (1 H, m), 4.91 (1 H, br d, *J* 10.3), 4.97 (1 H, br d, *J* 17.4) and 5.87 (1 H, ddd, *J* 17.3, 10.3 and 8.4); δ_C(125.65 MHz; $CDCl_3$) 9.9 (q), 20.4 (t), 24.3 (t), 27.5 (t), 41.2 (d), 47.0 (d), 76.0 (d), 113.0 (t) and 142.2 (d).

5b discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.94 (3 H, t, *J* 7.4), 1.20–2.10 (7 H, m), 2.46 (1 H, quintet, *J* 7.6), 3.03 (1 H, m), 3.59 (1 H, m), 5.05 (1 H, br d, *J* 17.6), 5.07 (1 H, br d, *J* 10.5) and 6.13 (1 H, ddd, *J* 17.6, 10.5 and 7.7); δ_C(125.65 MHz; $CDCl_3$) 9.9 (q), 21.1 (t), 23.9 (t), 27.7 (t), 40.9 (d), 44.0 (d), 73.7 (d), 114.7 (t) and 139.6 (d).

7b discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.98 (3 H, t, *J* 7.2), 1.2–2.15 (10 H, m), 3.34 (1 H, m) and 5.69 (2 H, br d); δ_C(125.65 MHz; $CDCl_3$) 10.0 (q), 24.1 (t), 25.3 (t), 27.0 (t), 28.1 (t), 39.2 (d), 76.8 (d), 126.3 (d) and 127.2 (d).

4c discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.93 (3 H, t, *J* 7.4), 1.18–1.52 (3 H, m), 1.59–1.84 (3 H, m), 1.98 (1 H, q, *J* 8.7), 2.17 (1 H, quintet, *J* 8.2), 2.77 (1 H, quintet, *J* 8.2), 3.48 (1 H, m), 4.92 (1 H, br d, *J* 10.5), 5.03 (1 H, br d, *J* 17.5) and 5.96 (1 H, ddd, *J* 17.5, 10.5 and 7.4); δ_C(125.65 MHz; $CDCl_3$) 9.9 (q), 21.0 (t), 24.2 (t), 27.6 (t), 42.4 (d), 47.4 (d), 77.7 (d), 112.9 (t) and 143.3 (d).

5c discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.94 (3 H, t, *J* 7.4), 1.10–2.20 (7 H, m), 2.47 (1 H, quintet, *J* 8.2), 3.06 (1 H, m), 3.61 (1 H, m), 5.13 (1 H, br d, *J* 9.9), 5.15 (1 H, br d, *J* 17.8) and 6.26 (1 H, ddd, *J* 17.8, 9.9 and 8.6); δ_C(125.65 MHz; $CDCl_3$) 9.8 (q), 21.9 (t), 23.1 (t), 26.7 (t), 40.6 (d), 44.8 (d), 73.9 (d), 115.3 (t) and 139.9 (d).

(2-*Isopropenylcyclobutyl*)*methanol* **4c** + **5c** 93:7 (Found: M^+, 140.1204. $C_9H_{16}O$ requires *M*, 140.1199).

6c discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.92 (3 H, t, *J* 7.2), 1.23–2.37 (10 H, m), 3.96 (1 H, m), 5.70 (1 H, dt, *J* 10.5 and 5.2) and 5.79 (1 H, dt, *J* 10.5 and 5.2); δ_C(125.65 MHz; $CDCl_3$) 12.1 (q), 22.7 (t), 23.0 (t), 26.8 (t), 32.8 (t), 44.0 (d), 74.8 (d), 130.3 (d) and 131.9 (d).

7c discernible from mixture; δ_H(400 MHz; $CDCl_3$) 0.98 (3 H, t, *J* 7.4), 1.23–2.37 (10 H, m), 3.42 (1 H, m) and 5.60 (2 H, br d); δ_C(125.65 MHz; $CDCl_3$) 10.3 (q), 25.4 (t), 25.6 (t), 26.1 (t), 27.1 (t), 39.0 (d), 77.1 (d), 126.5 (d) and 126.9 (d).

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