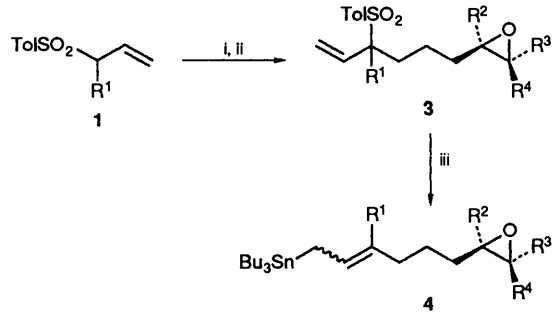
Facile Regio- and Stereo-chemical Control in Epoxy-allylic Stannane Cyclisations

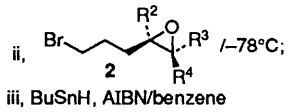
Makoto Yoshitake,[a] Makoto Yamamoto,[b,*] Shigeo Kohmoto[b] and Kazutoshi Yamada[b]
[a] *Graduate School of Science and Technology, Chiba University, 1–33 Yayoi-choi, Chiba-shi, 260 Japan*
[b] *Department of Materials Science, Faculty of Engineering, Chiba University, 1–33 Yayoi-cho, Chiba-shi, 260 Japan*

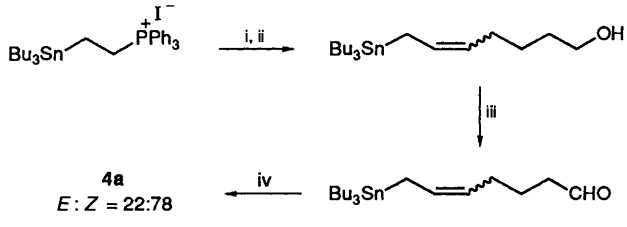
Lewis acid and butyllithium promoted cyclisations of epoxy-allylic stannanes have been studied. The regio-and stereo-chemistry of the cyclisations are described. The stereoelectronically favoured 5- and 6-membered ring formations have been explained by either the electronic nature of, or the steric hindrance induced by, the epoxide moiety of the substrates depending on whether the reaction was promoted by a Lewis acid or butyllithium, respectively. The different stereoselectivities observed are brought about by the mode of reaction. The contrasting results for the 5-membered ring formations are particularly remarkable.

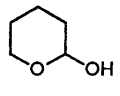
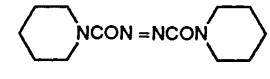
Although intramolecular cyclisations of epoxy-allylic silanes or stannanes are powerful methods for the construction of cyclic structures associated with natural product synthesis,[1] this methodology has been limited to Lewis acid promoted reactions. Thus, reactions promoted by fluoride ion or proceeding *via* transmetallation to more nucleophilic allylic metal species[2] have been unsuccessful in spite of their success in intramolecular reactions with carbonyl groups.[3] The lack of systematic regio- and stereo-chemical studies of nucleophilic reactions led us to reconsider this potent cyclisation strategy, especially in connection with Stork's pioneering work on the intramolecular reaction of various enolate anions with epoxides.[4]

We recently reported regio- and stereo-selective Lewis acid-induced cyclisation of epoxy-allylic stannanes.[1j] In that communication, we demonstrated the role of the substituent pattern of the epoxide ring in the regio- and stereo-chemical control of the cyclisations. Now we have discovered that the cyclisations also occurred with the addition of butyllithium in THF (tetrahydrofuran). In order to investigate the scope of these 5-*exo* and 6-*endo* epoxy-allylic stannane cyclisations further, from the regio- and stereo-chemical point of view, we examined the cyclisation of various substrates promoted by both Lewis acid and butyllithium. The observed regio- and stereo-selectivities are evaluated on the basis of differences in reaction conditions.



Scheme 1 *Reagents*: i, BuLi – HMPA/THF – Et_2O; ii,  /–78°C; iii, BuSnH, AIBN/benzene



Scheme 2 *Reagents*: i, BuLi /THF; ii,  ; iii,  , Bu^tOMgBr/THF; iv, $Me_3S^+(O)\ I^-$, NaH /DMSO

Results and Discussion

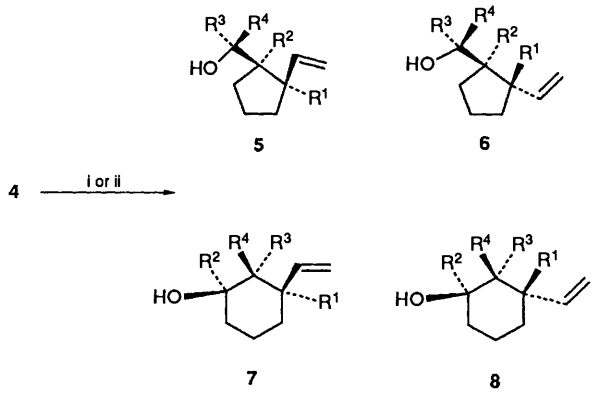
Preparation and Cyclisation of Epoxy-allylic Stannanes **4**.—Epoxy-allylic stannanes **4** were readily prepared in good yield as illustrated in Scheme 1. The low reaction temperature (−78 °C) in the first step was necessary for satisfactory yields since an undesirable epoxide ring opening occurred at higher temperature (−50 °C). The yield of the second step was dramatically improved at a higher dilution (0.4 mol dm^{-3}) than that generally used (1.2 mol dm^{-3}).[5] The isomeric mixture of **4a** with inverse isomer ratio to that above was prepared *via* a route using modified Proctor's procedure (Scheme 2).[1f]

The Lewis acid promoted ($TiCl_4$, 1 equiv.) reaction of **4** was carried out in CH_2Cl_2 at −78 °C, and then quenched with aq. $NaHCO_3$ after 30 min at this temperature. Treatment of the resulting mixture with aqueous ammonia to remove stannane residue followed by purification by flash column chromatography on silica gel afforded an isomeric mixture of cyclised products in excellent yield. The $TiCl_4$ promoted reaction resulted in the best selectivities among the several Lewis acids investigated ($TiCl_4$, Me_3SiOTf, BF_3–OEt_2 and $EtAlCl_2$). Decreasing of stereoselectivity was observed at elevated reaction temperature.[1j] The *E*/*Z* ratio of **4a** was not dependent on the reactivity and the selectivity.[1h]

The other type of reaction was performed in THF with the addition of BuLi (3 equiv.) at −78 °C to give an isomeric

Table 1 $TiCl_4$ and BuLi-promoted cyclisation reactions of **4**

Entry	R¹	R²	R³	R⁴	$TiCl_4$-promoted reaction: Yield (%)	Regioselectivity 5-*exo*:6-*endo*	Stereoselectivity 5-*exo* 5:6	Stereoselectivity 6-*endo* 7:8	BuLi-promoted reaction: Yield (%)	Regioselectivity 5-*exo*:6-*endo*	Stereoselectivity 5-*exo* 5:6	Stereoselectivity 6-*endo* 7:8
a	H	H	H	H	100	99<:—	74:26	—	76	99<:—	7:93	—
b	Me	H	H	H	93	99<:—	80:20	—	91	91: 9	26:74	99<:—
c	Pr^i	H	H	H	83	99<:—	91: 9	—	89	82:18	90:10	—:99<
d	H	Me	H	H	93	99<:—	72:28	—	76	—:99<	—	99<:—
e	Me	Me	H	H	88	99<:—	76:24	—	87	—:99<	—	99<:—
f	Pr^i	Me	H	H	95	99<:—	73:27	—	89	—:99<	—	—:99<
g	H	H	Me	Me	90	2:98	—:99<	99<:—	96	99<:—	9:91	—
h	Me	H	Me	Me	89	6:94	—:99<	87:13	96	99<:—	46:54	—
i	H	H	H	Et	97	99<:—	73:27	—	86	99<:—	7:93	—
j	H	H	Me	H	91	93: 7	27:73	99<:—	92	99<:—	9:91	—
k	H	H	Ph	H	100	3:97	—:99<	99<:—	96	70:30	—:99<	99<:—



Scheme 3 *Reagents:* i, $TiCl_4$ (1 equiv.)/CH_2Cl_2/−78 °C; ii, BuLi (3 equiv.)/THF/−78 °C

product mixture together with tetrabutylstannane in good yield. In this reaction, an excess of BuLi was necessary to complete the reaction. The transmetallation and the following cyclisation were fast enough to avoid the undesired intermolecular reaction with the remaining BuLi.

The isomeric mixture from the above two reactions was difficult to separate by flash chromatography on silica gel in the most cases, but its regio- and diastereo-isomeric ratios could be determined from the integral ratios of alkenic protons in the ^1H NMR spectra (Tables 1 and 2).

Configurations of the 5-membered ring products **5** and **6** were deduced from lanthanide induced shift (LIS) experiments.[6] Thus, the downfield shifts induced by addition of $[Eu(fod)_3]$ for the C-2 substituents of a cyclopentane ring were verified on their relative location from a europium atom chelated to an oxygen atom. The protons at the same side of a α-hydroxyalkyl group showed larger downfield shift values than those opposite. The shift values in the presence of 10 mol % of $Eu(fod)_3$ are summarised in Table 3.

For the 6-membered ring products **7** and **8**, proton–proton *J* couplings and nuclear Overhauser enhancement (NOE) experiments assisted the assignments. The former disclosed the conformational relation of the neighbouring cyclohexane ring protons, and from the magnitude of the latter the configurations at C-1 and C-3 were deduced. Thus, the structures of **7k** and **7l** were easily determined from the coupling constants and those of **7b–f** were deduced from NOE by irradiating 1-H or the methyl group. For example, the NOESY spectrum of **7d** showed the NOE relationship between 1-Me and 3-H, but no NOE between the 1-Me and the 3-vinyl protons. Consequently, the relation between the hydroxy group and the vinyl group could be assigned as *cis*.

Regioselectivity in the Cyclisations.—The results summarised in Table 1 show that the regiochemistry of a cyclisation is inherently distinctive with respect to the method of reaction. In addition, each regioselectivity is highly controlled by the substitution pattern of the epoxide ring. This regiochemical behaviour can be interpreted in terms of the following three factors: (1) the electronic nature of the epoxide carbons affected by the substituents; (2) steric hindrance; and (3) the stereoelectronic effect.

The Lewis acid promoted cyclisations could be interpreted *via* a borderline S_N2 mechanism,[7] since inversion of stereochemistry of the epoxides was confirmed from the cyclisation reactions of **4i**, **j** and **k**. The observed regioselectivities could be understood by the first and the third factors based on this push-pull mechanism. If epoxides were substituted unsymmetrically **4a–h** and **k**, bond formation would occur with the more stabilised cationic centre among those of the epoxide carbons generated by Lewis acid coordination. For substrates including electronically equally substituted epoxides **4i** and **j**, stereoelectronically favoured 5-*exo* cyclisation is superior to the corresponding 6-*endo*.

The reaction *via* transmetallation to allylic lithium, which proceeds *via* a typical S_N2 mechanism, is influenced by steric effects of the epoxide substitutions. Thus, the reaction at a quaternary epoxide carbon never occurs. However, the stereoelectronic factor seems to take precedence over the steric factor to direct the 5-*exo* cyclisations for **4a–c**, **i** and **j**. Lower selectivity for **4k** could be attributed to the electronic factor of the *trans* phenyl group.

The above regiochemical findings provide a facile and highly controlled construction of cyclopentane and cyclohexane skeletons from a single substrate in the epoxy-allylic stannane cyclisation strategy.

Stereoselectivity in Cyclisations.—Despite the importance of stereoselective cyclisations in natural product synthesis, there have been few examples of epoxy-allylic silanes or stannanes participating in such reactions. In order to investigate this stereochemical behaviour in detail, we chose substrates substituted with a methyl or isopropyl group at the allylic stannane formation **4b**, **c**, **e**, **f** and **h**, which would be expected to provide a probe for determination of stereoselectivity.

The dependence of the contrasting stereoselectivities on

Table 2 ^{1}H NMR (400 or 500 MHz) of compounds **5–8** (ppm from TMS and coupling constant Hz)

5a	1.31–1.88 (7 H, m), 2.20 (1 H, m), 2.69 (1 H, quintet, *J* 7.4), 3.48 (1 H, dd, *J* 11.1 and 6.5), 3.61 (1 H, dd, *J* 11.1 and 7.6), 5.02 (1 H, ddd, *J* 10.3, 2.1 and 0.8), 5.09 (1 H, ddd, *J* 17.3, 2.1 and 1.1), 5.88 (1 H, ddd, *J* 17.3, 10.3 and 9.2).
6a	1.31–1.88 (8 H, m), 2.15 (1 H, quintet, *J* 8.4), 3.54 (1 H, dd, *J* 10.5 and 6.2), 3.67 (1 H, dd, *J* 10.5 and 5.7), 4.95 (1 H, ddd, *J* 10.1, 1.9 and 0.5), 5.04 (1 H, ddd, *J* 17.0, 1.9 and 0.9), 5.79 (1 H, ddd, *J* 17.0, 10.1 and 8.3).
5b	1.16 (3 H, s), 1.35–1.55 (3 H, m), 1.59–1.75 (2 H, m), 1.80 (1 H, dt, *J* 8.8 and 7.1), 1.92 (1 H, m), 3.44 (1 H, dd, *J* 11.0 and 7.0), 3.62 (1 H, dd, *J* 11.0 and 3.6), 5.01 (1 H, dd, *J* 11.0 and 1.5), 5.02 (1 H, dd, *J* 17.4 and 1.5), 5.95 (1 H, dd, *J* 17.4 and 11.0).
6b	0.95 (3 H, s), 1.35–1.55 (3 H, m), 1.59–1.75 (2 H, m), 1.90 (1 H, dt, *J* 12.7 and 8.5), 1.95 (1 H, tt, *J* 8.5 and 6.8), 3.51 (1 H, dd, *J* 10.7 and 4.0), 3.66 (1 H, dd, *J* 10.7 and 4.0), 4.98 (1 H, dd, *J* 10.8 and 1.3), 5.03 (1 H, dd, *J* 17.4 and 1.3), 5.93 (1 H, dd, *J* 17.4 and 10.8).
7b	1.00 (3 H, s), 1.12–1.39 (3 H, m), 1.40–1.57 (2 H, m), 1.60–1.75 (3 H, m), 1.95 (1 H, m), 3.83 (1 H, tt, *J* 10.4 and 4.2), 4.90 (1 H, dd, *J* 10.7 and 1.2), 4.96 (1 H, dd, *J* 17.5 and 1.2), 5.83 (1 H, dd, *J* 17.5 and 10.7).
5c	0.85 (3 H, d, *J* 5.0), 0.87 (3 H, d, *J* 5.0), 1.33 (1 H, br s), 1.38 (1 H, m), 1.50–1.81 (5 H, m), 1.85 (1 H, m), 2.07 (1 H, dtd, *J* 8.4, 7.7 and 5.2), 3.43 (1 H, dd, *J* 10.7 and 8.4), 3.69 (1 H, dd, *J* 10.7 and 5.2), 4.99 (1 H, dd, *J* 17.6 and 1.4), 5.13 (1 H, dd, *J* 11.0 and 1.4), 5.77 (1 H, dd, *J* 17.6 and 11.0).
6c	0.79 (3 H, d, *J* 6.8), 0.89 (3 H, d, *J* 6.8), 1.30 (1 H, br s), 1.33 (1 H, m), 1.50–1.76 (5 H, m), 1.85 (1 H, m), 2.00 (1 H, m), 3.35 (1 H, dd, *J* 10.5 and 9.8), 3.81 (1 H, dd, *J* 10.5 and 4.4), 4.98 (1 H, dd, *J* 17.6 and 1.4), 5.13 (1 H, dd, *J* 11.0 and 1.4), 5.68 (1 H, dd, *J* 17.6 and 11.0).
8c	0.77 (3 H, d, *J* 6.9), 0.83 (3 H, d, *J* 6.9), 1.20–1.40 (3 H, m), 1.40–1.80 (6 H, m), 1.93 (1 H, m), 3.88 (1 H, m), 4.97 (1 H, dd, *J* 17.6 and 1.4), 5.09 (1 H, dd, *J* 11.0 and 1.4), 5.82 (1 H, dd, *J* 17.6 and 11.0).
5d	1.07 (3 H, s), 1.32–1.78 (6 H, m), 1.88 (1 H, m), 2.20 (1 H, q, *J* 8.7), 3.34 (1 H, d, *J* 11.1), 3.45 (1 H, d, *J* 11.1), 5.03 (1 H, ddd, *J* 10.2, 2.1 and 0.9), 5.07 (1 H, ddd, *J* 17.2, 2.1 and 1.2), 5.90 (1 H, dt, *J* 17.2, 10.2 and 8.3).
6d	0.85 (3 H, s), 1.32–1.78 (6 H, m), 1.82 (1 H, m), 2.29 (1 H, q, *J* 8.2), 3.41 (1 H, d, *J* 10.8), 3.47 (1 H, d, *J* 10.8), 5.00 (1 H, ddd, *J* 10.2, 2.6 and 0.7), 5.03 (1 H, ddd, *J* 17.2, 10.2 and 8.6), 5.78 (1 H, ddd, *J* 17.2, 10.2 and 8.6).
7d	1.15–1.50 (5 H, m), 1.25 (3 H, s), 1.63–1.79 (4 H, m), 2.09 (1 H, m), 4.92 (1 H, br d, *J* 10.4), 4.99 (1 H, br d, *J* 17.2), 5.77 (1 H, ddd, *J* 17.2, 10.4 and 6.4).
5e	0.97 (3 H, s), 1.01 (3 H, s), 1.25–1.80 (6 H, m), 1.87 (1 H, m), 3.32 (1 H, d, *J* 11.3), 3.44 (1 H, d, *J* 11.3), 5.01 (1 H, d, *J* 10.5), 5.01 (1 H, d, *J* 18.1), 6.00 (1 H, dd, *J* 18.1 and 10.5).
6e	0.97 (3 H, s), 1.03 (3 H, s), 1.25–1.80 (7 H, m), 1.93 (1 H, m), 3.44 (1 H, d, *J* 11.3), 3.61 (1 H, d, *J* 11.3), 4.99 (1 H, d, *J* 10.5), 4.99 (1 H, d, *J* 18.1), 6.05 (1 H, dd, *J* 18.1 and 10.5).
7e	0.97 (3 H, s), 1.17 (3 H, s), 1.10–1.35 (3 H, m), 1.42–1.92 (5 H, m), 2.21 (1 H, br s), 5.10 (1 H, d, *J* 10.9), 5.14 (1 H, d, *J* 17.7), 5.99 (1 H, dd, *J* 17.7 and 10.9).
5f	0.75 (3 H, d, *J* 6.9), 0.94 (3 H, d, *J* 6.9), 1.06 (3 H, s), 1.08–1.82 (7 H, m), 2.03 (1 H, m), 3.55 (1 H, d, *J* 11.0), 3.69 (1 H, d, *J* 11.0), 5.01 (1 H, dd, *J* 16.8 and 1.6), 5.18 (1 H, dd, *J* 11.0 and 1.7), 5.90 (1 H, dd, *J* 16.8 and 11.0).
6f	0.73 (3 H, d, *J* 6.9), 1.00 (3 H, d, *J* 6.9), 1.04 (3 H, s), 1.08–1.82 (7 H, m), 2.03 (1 H, m), 3.58 (1 H, d, *J* 10.7), 3.67 (1 H, d, *J* 10.8), 4.97 (1 H, dd, *J* 16.8 and 1.6), 5.18 (1 H, dd, *J* 11.0 and 1.7), 6.00 (1 H, dd, *J* 16.8 and 11.0).
8f	0.76 (3 H, d, *J* 6.9), 0.81 (3 H, d, *J* 6.9), 1.01 (1 H, tdd, *J* 13.5, 4.1 and 1.1), 1.17 (3 H, s), 1.19–1.36 (3 H, m), 1.54 (1 H, m), 1.62 (2 H, m), 1.92 (1 H, dt, *J* 14.0 and 2.5), 2.00 (1 H, br d, *J* 14.0), 2.36 (1 H, s), 5.12 (1 H, dd, *J* 18.2 and 1.4), 5.30 (1 H, dd, *J* 11.3 and 1.4), 5.81 (1 H, ddd, *J* 18.2, 11.3 and 1.1).
5g	1.16 (3 H, s), 1.31 (3 H, s), 1.53 (1 H, m), 1.60–1.83 (6 H, m), 1.89 (1 H, m), 2.77 (1 H, dt, *J* 10.5 and 6.0), 5.02 (1 H, dd, *J* 11.5 and 2.2), 5.12 (1 H, ddd, *J* 17.1, 2.2 and 0.7), 6.02 (1 H, dt, *J* 17.1 and 10.5).
6g	1.18 (3 H, s), 1.20 (3 H, s), 1.38–1.50 (2 H, m), 1.59 (2 H, m), 1.67 (1 H, br s), 1.78 (2 H, m), 1.83 (1 H, q, *J* 8.5), 2.45 (1 H, quintet, *J* 8.3), 4.93 (1 H, ddd, *J* 10.1, 1.8 and 0.5), 5.05 (1 H, ddd, *J* 1.8 and 0.7), 5.85 (1 H, ddd, *J* 17.1, 10.1 and 8.8).
7g	0.78 (3 H, s), 0.97 (3 H, s), 1.52–1.88 (8 H, m), 3.27 (1 H, dd, *J* 11.1 and 4.0), 4.93 (1 H, ddd, *J* 10.2, 1.9 and 0.5), 5.05 (1 H, ddd, *J* 17.0, 1.9 and 0.8), 5.75 (1 H, ddd, *J* 17.0, 10.2 and 8.4).
5h	1.15 (3 H, s), 1.28 (6 H, s), 1.45–1.80 (7 H, m), 1.83 (1 H, m), 5.06 (1 H, dd, *J* 10.7 and 1.6), 5.09 (1 H, dd, *J* 17.4 and 1.6), 6.26 (1 H, dd, *J* 17.4 and 10.7).
6h	1.15 (3 H, s), 1.20 (3 H, s), 1.23 (3 H, s), 1.45–1.80 (7 H, m), 1.83 (1 H, m), 4.94 (1 H, dd, *J* 17.4 and 1.5), 5.00 (1 H, dd, *J* 10.7 and 1.5), 5.94 (1 H, dd, *J* 17.4 and 10.7).
7h	0.85 (3 H, s), 0.93 (3 H, s), 1.01 (3 H, s), 1.14–1.78 (7 H, m), 3.69 (1 H, dd, *J* 10.9 and 4.3), 4.95 (1 H, dd, *J* 17.5 and 1.6), 5.00 (1 H, dd, *J* 11.0 and 1.6), 5.98 (1 H, dd, *J* 17.5 and 11.0).
8h	0.905 (3 H, s), 0.915 (3 H, s), 0.99 (3 H, s), 1.14–1.78 (7 H, m), 3.64 (1 H, dd, *J* 10.8 and 4.2), 4.99 (1 H, dd, *J* 17.5 and 1.6), 5.02 (1 H, dd, *J* 11.2 and 1.6), 6.19 (1 H, dd, *J* 17.5 and 11.2).
5i	0.96 (3 H, t, *J* 7.4), 1.24–1.49 (3 H, m), 1.49–1.71 (4 H, m), 1.71–1.90 (2 H, m), 1.93 (1 H, m), 2.80 (1 H, dtd, *J* 9.8, 6.7 and 2.8), 3.41 (1 H, ddd, *J* 9.8, 8.3 and 2.8), 5.04 (1 H, dd, *J* 10.0 and 1.9), 5.12 (1 H, dd, *J* 17.1 and 1.9), 5.90 (1 H, dt, *J* 17.1 and 10.0).
6i	0.95 (3 H, t, *J* 7.3), 1.24–1.49 (4 H, m), 1.50–1.70 (4 H, m), 1.76 (1 H, m), 1.83 (1 H, dtd, *J* 12.5, 7.4 and 5.1), 2.37 (1 H, quintet, *J* 8.5), 3.48 (1 H, td, *J* 7.9 and 3.1), 4.96 (1 H, dd, *J* 10.1 and 1.9), 5.12 (1 H, dd, *J* 17.1 and 1.9), 5.89 (1 H, ddd, *J* 17.1, 10.1 and 8.9).
5j	1.19 (3 H, d, *J* 6.3), 1.2–1.9 (8 H, m), 2.58 (1 H, m), 3.74 (1 H, quintet, *J* 4.4), 4.94 (1 H, dd, *J* 10.1 and 2.1), 5.02 (1 H, ddd, *J* 17.0, 2.1 and 0.9), 5.85 (1 H, ddd, *J* 17.0, 10.1 and 9.3).
6j	1.19 (3 H, d, *J* 6.3), 1.2–1.9 (8 H, m), 2.29 (1 H, quintet, *J* 8.6), 3.80 (1 H, quintet, *J* 4.4), 4.94 (1 H, dd, *J* 10.1 and 2.1), 5.02 (1 H, ddd, *J* 17.0, 2.1 and 0.9), 5.76 (1 H, ddd, *J* 17.0, 10.1 and 8.3).
7j	1.00 (3 H, d, *J* 6.5), 1.2–1.9 (8 H, m), 1.97 (1 H, m), 3.18 (1 H, dt, *J* 4.1 and 9.9), 4.96 (1 H, dd, *J* 9.9 and 2.2), 5.03 (1 H, ddd, *J* 16.9, 2.2 and 0.9), 5.60 (1 H, ddd, *J* 16.9, 9.9 and 8.8).
6k	1.42 (1 H, m), 1.59 (1 H, m), 1.71 (1 H, m), 1.84 (2 H, m), 1.94 (1 H, td, *J* 8.3 and 4.9), 4.68 (1 H, m), 4.83 (1 H, ddd, *J* 17.0, 1.9 and 1.0), 4.87 (1 H, ddd, *J* 10.2, 1.9 and 1.0), 5.61 (1 H, ddd, *J* 17.0, 10.2 and 8.3), 7.24 (1 H, m), 7.32 (4 H, m).
7k	1.31 (1 H, tdd, *J* 12.8, 10.8 and 3.6), 1.41 (1 H, dddd, *J* 13.5, 11.7, 10.7 and 3.3), 1.49 (1 H, dt, *J* 13.1 and 3.3), 1.53 (1 H, qt, *J* 13.1 and 3.3), 1.83 (1 H, dqd, *J* 12.9, 3.3 and 1.6), 1.90 (1 H, m), 2.13 (1 H, m), 2.25 (1 H, dd, *J* 11.1 and 9.8), 2.31 (1 H, tdd, *J* 11.5, 7.4 and 3.6), 3.70 (1 H, td, *J* 9.8 and 4.3), 4.72 (1 H, d, *J* 9.7), 4.75 (1 H, d, *J* 6.3), 5.45 (1 H, ddd, *J* 17.0, 10.5 and 7.2), 7.21 (3 H, m), 7.32 (2 H, m).

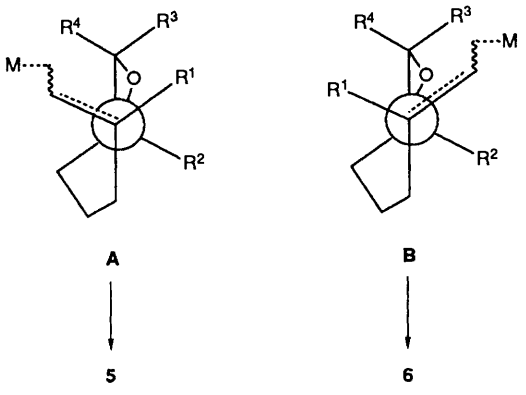
mode of reaction of 5-membered ring formation is remarkable, substituent effects seeming to play an important role. Thus the stereoselective outcome of Lewis acid promoted reactions was dependent on the size of the *trans* substituent and where it was bulky (R^3 = Me or Ph) reversal in stereoselection occurred (Table 1, g, h, j and k). In contrast, the size of the R^1 substituent scarcely affected the selectivity (R^1 = Me or Pr^i; Table 1, b, c, e, f and h). In butyllithium promoted reactions the stereoselective outcome for **4a** and **4i** was the reverse of that found in Lewis acid promoted reactions. Moreover the steric effect of the R^1 substituent (Me or Pr^i) was significant in these cases (Table 1, b, c and h).

Stork and co-workers have explained the stereoselectivity in epoxy nitrile, ketone and ester cyclisations under basic conditions in terms of the energy difference in the two possible transition states.[4] For the 5-membered ring formation in the butyllithium promoted reaction, this stereochemical explanation can be applied. Possible transition structures are described in Scheme 4. The transition state **B** seems to be more favourable than **A** owing to steric repulsion (R^1 = H). Since

Table 3 Downfield shift values (ppm) on ^{1}H NMR of **5** and **6** using 10 mol % of Eu(fod)$_3$

	5		6	
Compound	Vi[a]	R[b]	Vi[a]	R[b]
a	1.00	0.83	0.55	1.03
b	1.05	0.72	0.76	0.72
c	1.10	1.14	0.61	1.89
d	0.99	0.73	0.69	1.04
e	1.07	0.73	0.86	0.86
f	1.21	1.38	0.80	1.92
g	1.10	1.13	0.90	2.02
h	1.10	0.75	0.80	1.07
i	1.02	0.72	0.62	1.23
j	0.98	0.68	0.61	1.12
k	—	—	0.73	1.54

[a] α-Proton of vinyl group at C-2. [b] Proton, methyl protons or isopropyl methine proton at C-2.



Scheme 4

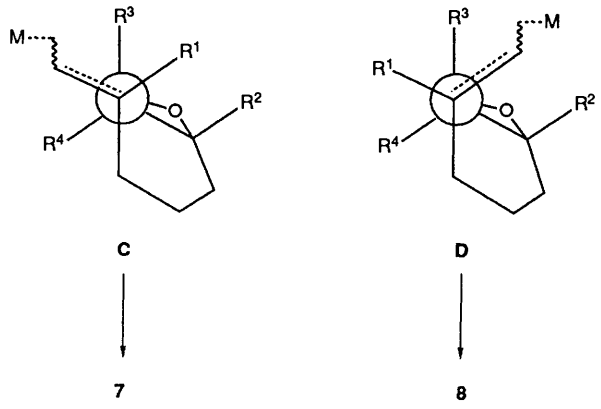
the presence of the R^1 substituent influences the energy difference, the observation decreasing (R^1 = Me) or reversal (R^1 = Pr^i) of stereoselectivity could also be well explained using this transition model.

Although the factors which control stereoselectivity in Lewis acid promoted reactions are poorly understood, a hypothesis adopted for interpretation of stereochemistry in intramolecular reactions of allylic silane[8] or stannane[9] with *N*-acyliminium ions helped us to consider the stereoselectivity. On the basis of the hypothesis that the initial approach of the electrophilic carbon is to the centre of the π-bond in the allylic stannane, the estimated stable π-complex intermediate resembles transition state **A** to bring about the *cis* selectivity **5** > **6**. If the stereochemistry is governed by the stability of such intermediates, the substituent effect of R^3 and the lack of such an effect for R^1 can be satisfactorily explained. We recognise that such an entropic predominance is important to evaluate a real transition energy difference in cyclisations. But, to our knowledge, no theoretical support nor strong experimental evidence are presently available to support the above hypothesis.

The 6-*endo* cyclisation of the substrates (R^1 = H, Me) was *cis* directed in both reaction methods. The *cis* selectivity was reversed by the presence of isopropyl group at R^1. These results suggest that this cyclisation process is controlled by a transition energy difference between transition state **C** and **D** (Scheme 5).

Conclusions

Various cyclisations of epoxy-allylic stannanes have been examined under Lewis acid and butyllithium promoted conditions. The regio- and stereo-selectivities were characteristically varied depending on the substitution pattern of the epoxide ring and the reaction conditions. The regiochemistry could be clearly rationalised based on the electronic, steric and stereoelectronic effects. Moderate stereoselectivity was observed. The contrasted stereo-selectivity in the 5-membered ring formation is not only remarkable but also mechanistically interesting.



Scheme 5

Experimental

General Details.—IR spectra were recorded with a JUSKO A-202 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on JEOL GX270, GSX400, GSX500 and VARIAN XL400 spectrometers with tetramethylsilane as an internal standard. *J* Values are given in Hz. Mass spectra were obtained with RNU-7M mass spectrometer at 70 eV. Flash chromatography was run with Fujigel BW-200. Dichloromethane and tetrahydrofuran (THF) were distilled over calcium hydride and lithium aluminium hydride, respectively and stored over molecular sieves 5 Å 1/16 under nitrogen before use. Unless otherwise noted, other solvents were used after simple distillation.

General Procedure for the Preparation of Epoxy-allylic Stannanes **4**.—To a solution of the allylic sulphone **1** (10 mmol) in ether and THF (1:1; 100 cm^3) at −20 °C was added butyllithium in hexane (1.6 mol dm^{-3}; 11 mmol) followed by HMPA (hexamethylphosphoramide) (3.5 cm^3, 20 mmol). After 20 min, the mixture was cooled to −78 °C and bromide **2** (11 mmol) was added. After 1 h at this temperature, acetic acid (0.5 cm^3) was added and the solution was allowed to warm to room temperature. Water (50 cm^3) and ether (50 cm^3) were added. The organic layer was separated, washed with saturated $NaHCO_3$ (50 cm^3), dried ($MgSO_4$) and concentrated. The residue was flash chromatographed on silica gel (eluting with hexane–ethyl acetate) to give a diastereo isomeric mixture of compounds **3**. Without further purification, the product, tributyltin hydride (5.4 cm^3, 20 mmol) and AIBN (azoisobutyronitrile) (20 mg) were dissolved in benzene (50 cm^3) and refluxed for 2 h. The mixture was concentrated and chromatographed on silica gel [eluting with hexane–ether–triethylamine (2%)] to give **4** as a mixture of *E*/*Z* isomers.

Tributyl(7,8-epoxyoct-2-enyl)stannane **4a** (62%) *E*:*Z* = 77:23; δ_H(500 MHz; $CDCl_3$) 0.83 (6 H, m), 0.88 (9 H, t, *J* 7.4), 1.28 (6 H, m), 1.36–1.58 (10 H, m), 1.68 (2 H, m), 1.96 (2 H, m), 2.44 (1 H, m), 2.72 (1 H, m), 2.88 (1 H, m), 5.04 (0.23 H, dt, *J* 10.8 and 6.7), 5.18 (0.77 H, dt, *J* 14.9 and 6.7) and 5.51 (1 H, m); δ_C(67.80 MHz; $CDCl_3$) 9.1(t), 9.3(t), 13.9(q), 14.08(q), 14.12(t), 22.6(t), 26.0(t), 26.4(t), 26.7(t), 27.3(t), 29.1(t), 31.6(t), 32.0(t), 32.3(t), 32.4(t), 47.1(t), 52.2(d), 123.5(d), 125.0(d), 128.8(d) and 129.8(d); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1645,

1455, 1370, 1067, 960, 860 and 830 (Found: C, 57.9; H, 9.75. $C_{20}H_{40}OSn$ requires C, 57.85; H, 9.71).

Tributyl(7,8-*epoxy*-3-*methyloct*-2-*enyl*)*stannane* **4b** (67%) *E*:*Z* = 72:28; δ_H(500 MHz; $CDCl_3$) 0.84 (6 H, m), 0.89 (9 H, t, *J* 7.4), 1.30 (6 H, m), 1.40–1.66 (10 H, m), 1.56 (3 H, s), 2.01 (2 H, m), 2.46 (1 H, m), 2.91 (1 H, m), 5.31 (0.28 H, t, *J* 9.1) and 5.32 (0.72 H, t, *J* 9.1); δ_C(125.65 MHz; $CDCl_3$) 9.4(t), 10.6(t), 13.7(q), 15.5(q), 23.0(t), 24.0(t), 24.6(t), 24.6(t), 27.4(t), 29.2(t), 31.1(t), 32.1(t), 32.5(t), 39.4(t), 47.1(t), 52.3(d), 123.4(d), 123.8(d), 128.7(d) and 129.1(d); ν_{max}(film)/cm^{-1} 2950, 2930, 2860, 1650, 1455, 1372, 1287, 1253, 1120, 1070 and 920 (Found: C, 58.35; H, 9.85. $C_{21}H_{42}OSn$ requires C, 58.76; H, 9.86).

Tributyl(7,8-*epoxy*-3-*isopropyloct*-2-*enyl*)*stannane* **4c** (54%) *E*:*Z* = 11:89; δ_H(500 MHz; $CDCl_3$) 0.83 (6 H, m), 0.89 (9 H, t, *J* 7.4), 0.98 (6 H, d, *J* 6.6), 1.30 (6 H, m), 1.40–1.77 (12 H, m), 1.97 (0.22 H, m), 2.02 (1.78 H, m), 2.20 (1 H, m), 2.47 (1 H, m), 2.74 (1 H, m), 2.92 (1 H, m), 5.22 (0.11 H, d, *J* 9.2) and 5.32 (0.89 H, d, *J* 9.2); δ_C(125.65 MHz; $CDCl_3$) 9.3(t), 10.5(t), 13.7(q), 22.4(q), 25.3(t), 27.4(t), 29.0(t), 29.1(t), 29.2(t), 29.3(t), 32.9(t), 34.1(d), 47.0(t), 52.2(d), 120.7(d), 121.7(d), 137.9(s) and 139.3(s); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1650, 1457, 1372, 1120, 1068 and 865 (Found: C, 60.45; H, 10.15. $C_{23}H_{46}OSn$ requires C, 60.41; H, 10.14).

Tributyl(7,8-*epoxy*-7-*methyloct*-2-*enyl*)*stannane* **4d** (72%) *E*:*Z* = 79:21; δ_H(400 MHz; $CDCl_3$) 0.84 (6 H, m), 0.89 (9 H, t, *J* 7.4), 1.30 (6 H, m), 1.30 (3 H, s), 1.38–1.56 (10 H, m), 1.59 (2 H, m), 1.98 (2 H, m), 2.57 (2 H, m), 5.04 (0.21 H, dt, *J* 10.4 and 7.0), 5.19 (0.79 H, dt, *J* 15.0 and 7.0) and 5.53 (1 H, m); δ_C(100.4 MHz; $CDCl_3$) 9.1(t), 9.3(t), 13.7(q), 14.1(t), 20.9(q), 25.4(t), 25.8(t), 27.3(t), 27.4(t), 29.1(t), 32.6(t), 36.3(t), 36.5(t), 53.9(t), 57.0(s), 123.6(d), 125.0(d), 128.8(d) and 129.7(d); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1640, 1455, 1372, 1070 and 960 (Found: C, 58.75; H, 9.95. $C_{21}H_{42}OSn$ requires C, 58.76; H, 9.86).

Tributyl(7,8-*epoxy*-3,7-*dimethyloct*-2-*enyl*)*stannane* **4e** (67%) *E*:*Z* = 68:32; δ_H(500 MHz; $CDCl_3$) 0.84 (6 H, m), 0.89 (9 H, t, *J* 7, 4), 1.30 (6 H, m), 1.30 (3 H, s), 1.40–1.75 (12 H, m), 1.56 (3 H, s), 1.97 (2 H, m), 2.58 (2 H, m), 5.30 (0.32 H, t, *J* 9.1) and 5.31 (0.68 H, t, *J* 9.1); δ_C(125.65 MHz; $CDCl_3$) 9.4(t), 10.5(t), 10.6(t), 13.7(q), 15.3(q), 15.5(q), 20.9(q), 23.0(t), 23.4(t), 23.9(t), 24.0(t), 27.4(t), 29.2(t), 31.3(t), 36.4(t), 36.8(t), 39.7(t), 53.9(t), 57.0(s), 123.3(d), 123.7(d), 128.7(s) and 129.0(s); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1650, 1455, 1372, 1115 and 1070 (Found: C, 59.6; H, 10.05. $C_{22}H_{44}OSn$ requires C, 59.61; H, 10.00).

Tributyl(7,8-*epoxy*-3-*isopropyl*-7-*methyloct*-2-*enyl*)*stannane* **4f** (52%) *E*:*Z* = 15:85; δ_H(500 MHz; $CDCl_3$) 0.83 (6 H, m), 0.89 (9 H, t, *J* 7.4), 0.97 (6 H, d, *J* 6.9), 1.30 (6 H, m), 1.32 (3 H, s), 1.40–1.60 (9 H, m), 1.61–1.75 (3 H, m), 1.92 (0.30 H, m), 1.97 (1.70 H, m), 2.19 (1 H, m), 2.57 (1 H, d, *J* 4.8), 2.61 (1 H, d, *J* 4.8), 5.22 (0.15 H, d, *J* 9.0) and 5.32 (0.85 H, d, *J* 9.0); δ_C(125.65 MHz; $CDCl_3$) 9.3(t), 10.5(t), 13.7(q), 22.40(q), 22.44(q), 24.6(t), 27.4(t), 29.1(t), 29.2(t), 29.3(t), 34.1(d), 37.2(t), 53.9(t), 56.9(s), 120.7(d), 121.7(d), 138.1(s) and 139.4(s); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1650, 1455, 1374, 1120, 1060 and 875 (Found: C, 61.2; H, 10.25. $C_{24}H_{48}OSn$ requires C, 61.15; H, 10.26).

Tributyl(7,8-*epoxy*-8-*methylnon*-2-*enyl*)*stannane* **4g** (69%) *E*:*Z* = 78:22; δ_H(500 MHz; $CDCl_3$) 0.84 (6 H, m), 0.89 (9 H, t, *J* 7.4), 1.26 (3 H, s), 1.29 (6 H, m), 1.31 (3 H, s), 1.40–1.62 (10 H, m), 1.70 (2 H, m), 2.02 (2 H, m), 2.71 (1 H, t, *J* 5.8), 5.06 (0.22 H, dt, *J* 10.4 and 7.0), 5.21 (0.78 H, dt, *J* 15.1 and 7.0) and 5.55 (1 H, m); δ_C(67.80 MHz; $CDCl_3$) 9.1(t), 9.3(t), 13.7(q), 14.1(t), 18.7(q), 24.9(q), 26.6(t), 26.8(t), 26.9(t), 27.0(t), 27.3(t), 27.7(t), 28.4(t), 28.7(t), 29.0(t), 29.1(t), 29.3(t), 32.5(t), 58.1(2), 64.4(d), 123.6(d), 125.0(d), 128.8(d) and 129.7(d); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1640, 1455, 1372, 1120, 1067, 960 and 870 (Found: C, 59.65; H, 10.05. $C_{22}H_{44}OSn$ requires C, 59.61; H, 10.00).

Tributyl(7,8-*epoxy*-3,8-*dimethylnon*-2-*enyl*)*stannane* **4h** (71%) *E*:*Z* = 65:35; δ_H(500 MHz; $CDCl_3$) 0.83 (6 H, m), 0.88 (9 H, t, *J* 7.4), 1.26 (3 H, s), 1.30 (6 H, m), 1.31 (3 H, s), 1.40–1.66 (10 H, m), 1.56 (3 H, s), 2.01 (2 H, m), 2.71 (1 H, m), 5.31 (0.35 H, t, *J* 9.1) and 5.33 (0.65 H, td, *J* 9.1 and 1.1); δ_C(125.65 MHz; $CDCl_3$) 9.4(t), 10.6(t), 13.7(q), 15.5(q), 18.7(q), 23.1(q), 24.6(t), 24.9(q), 25.3(t), 27.4(t), 28.6(t), 29.0(t), 29.1(t), 29.2(t), 29.3(t), 31.2(t), 39.6(t), 58.2(s), 64.5(d), 123.3(d), 123.7(d), 128.7(s) and 129.0(s); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1650, 1457, 1372, 1120, 1068 and 865 (Found: C, 60.25; H, 10.2. $C_{23}H_{46}OSn$ requires C, 60.41; H, 10.14).

Tributyl(7,8-*epoxydec*-2-*enyl*)*stannane* **4i** (73%) *E*:*Z* = 79:21; δ_H(500 MHz; $CDCl_3$) 0.83 (6 H, m), 0.89 (9 H, t, *J* 7.4), 1.29 (6 H, m), 1.29 (3 H, s), 1.40–1.60 (10 H, m), 1.69 (2 H, m), 2.01 (2 H, m), 2.62 (1 H, m), 2.73 (1 H, m), 5.03 (0.21 H, dt, *J* 10.8 and 6.9), 5.32 (0.79 H, dt, *J* 15.2 and 6.9) and 5.55 (1 H, m); δ_C(125.65 MHz; $CDCl_3$) 9.1(t), 9.3(t), 13.7(q), 14.1(t), 17.7(q), 26.1(t), 26.5(t), 26.7(t), 27.3(t), 29.05(t), 29.14(t), 31.5(t), 32.4(t), 54.5(d), 59.7(d), 123.6(d), 125.0(d), 128.8(d) and 129.7(d); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1650, 1455, 1372, 1120, 1067 and 875 (Found: C, 58.75; H, 9.9. $C_{21}H_{42}OSn$ requires C, 58.76; H, 9.86).

Tributyl(7,8-*epoxynon*-2-*enyl*)*stannane* **4j** (68%) *E*:*Z* = 81:19; δ_H(500 MHz; $CDCl_3$) 0.84 (6 H, m), 0.89 (9 H, t, *J* 7.4), 0.99 (3 H, t, *J* 7.6), 1.30 (6 H, m), 1.35–1.71 (14 H, m), 1.97 (2 H, m), 2.65 (2 H, m), 5.03 (0.19 H, dt, *J* 10.7 and 6.9), 5.20 (0.81 H, dt, *J* 15.1 and 6.9) and 5.52 (1 H, m); δ_C(125.65 MHz; $CDCl_3$) 9.1(t), 9.3(t), 9.9(q), 13.7(q), 14.1(t), 25.2(t), 25.5(t), 27.3(t), 27.4(t), 29.1(t), 29.2(t), 30.0(t), 32.0(t), 32.6(t), 58.6(d), 60.0(d), 123.9(d), 125.4(d), 128.4(d) and 129.3(d); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1650, 1455, 1372, 1120, 1067 and 875 (Found: C, 59.7; H, 10.1. $C_{22}H_{44}OSn$ requires C, 59.61; H, 10.00).

Tributyl(7,8-*epoxy*-8-*phenyloct*-2-*enyl*)*stannane* **4k** (75%) *E*:*Z* = 79:21; δ_H(500 MHz; $CDCl_3$) 0.84 (6 H, m), 0.89 (9 H, t, *J* 7.4), 1.30 (6 H, m), 1.37–1.63 (8 H, m), 1.65–1.74 (4 H, m), 2.05 (2 H, m), 2.94 (0.79 H, td, *J* 5.5 and 2.2), 2.96 (0.22 H, td, *J* 5.5 and 2.2), 3.59 (0.79 H, d, *J* 2.2), 3.61 (0.21 H, d, *J* 2.2), 5.06 (0.21 H, dt, *J* 10.5 and 6.6), 5.20 (0.79 H, dt, *J* 14.9 and 6.6), 5.55 (1 H, m) and 7.24–7.36 (5 H, m); δ_C(67.80 MHz; $CDCl_3$) 9.1(t), 9.3(t), 13.7(q), 14.2(t), 26.0(t), 26.4.(t), 26.7(t), 26.8(t), 27.3(t), 29.1(t), 29.2(t), 31.8(t), 32.1(t), 32.4(t), 58.6(d), 63.1(d), 123.4(d), 124.9(d), 125.5(d), 127.9(d), 128.4(d), 128.9(d), 129.9(d) and 138.0(d); ν_{max}(film)/cm^{-1} 2960, 2930, 2860, 1600, 1492, 1458, 1372, 1070, 960 and 880 (Found: C, 63.75; H, 9.1. $C_{26}H_{44}OSn$ requires C, 63.56; H, 9.03).

Preparation of Major Z-**4a**.—To a suspension of methyltriphenylphosphonium iodide (4.0 g, 10 mmol) in THF (80 cm^3) at 0 °C was added BuLi in hexane (1.6 mol dm^{-3}; 6.3 cm^3, 10 mmol). After being stirred at room temperature for 1 h, the reaction mixture was cooled to 0 °C (iodomethyl)tributylstannane (4.32 g, 10 mmol) was added, and the mixture stirred for 1 h at room temperature. To the cooled (−78 °C) mixture was added LDA (lithium diisopropylamide) (10 mmol) in THF (20 cm^3) freshly prepared from BuLi and diisopropylamine, after which the mixture was allowed to warm to room temperature. It was then recooled to −78 °C, treated with tetrahydropyran-2-ol (1.02 g, 10 mmol) and stirred at room temperature overnight. Saturated NH_4Cl (50 cm^3) was added and the organic layer was separated. The aqueous layer was extracted with ether (3 × 10 cm^3) and the combined extracts were washed with brine, dried ($MgSO_4$) and concentrated. The residue was flash chromatographed on silica gel [eluting with hexane–ether–triethylamine (2%)] to give 7-(tributylstannyl)-hept-5-enol (1.53 g) as an *E*/*Z* mixture (38%).

To a solution of propylmagnesium bromide (3.0 mmol) in THF (8 cm^3) was added *tert*-butyl alcohol (0.22 g, 3.0 mmol)

Table 4 ^{13}C NMR (125.65 MHz) of compounds **5–8** (ppm from TMS and multiplicity)

5a	23.7(t), 28.0(t), 31.6(t), 45.7(d), 45.9(d), 64.3(t), 114.7(t), 139.8(d).
6a	24.1(t), 29.0(t), 33.3(t), 48.04(d), 48.07(d), 66.3(t), 113.7(t), 143.0(d).
5b	22.1(t), 25.6(q), 28.4(t), 39.6(t), 46.4(s), 52.7(d), 64.6(t), 111.7(t), 143.9(d).
6b	17.1(q), 21.8(t), 27.5(t), 41.2(t), 46.3(s), 50.9(d), 64.4(t), 111.0(t), 149.0(d).
7b	20.2(t), 23.5(q), 35.6(t), 35.9(t), 37.7(s), 45.7(t), 67.7(d), 109.5(t), 150.0(d).
5c	17.2(q), 18.8(q), 21.9(t), 28.5(t), 29.8(t), 33.5(d), 48.1(d), 53.6(s), 64.6(t), 113.9(t), 141.9(d).
6c	18.7(q), 18.8(q), 21.0(t), 26.0(t), 32.2(d), 33.0(t), 47.6(d), 54.9(s), 62.7(t), 113.7(t), 141.5(d).
8c	16.7(q), 16.9(q), 29.7(t), 32.1(t), 32.3(d), 35.0(t), 41.9(t), 42.4(s), 67.3(d), 113.0(t), 143.7(d).
5d	22.5(t), 23.9(q), 31.0(t), 35.9(t), 46.9(s), 53.6(d), 68.1(t), 114.9(t), 139.6(d).
6d	18.4(q), 22.1(t), 30.7(t), 36.2(t), 46.7(s), 50.2(d), 71.1(t), 115.0(t), 140.3(d).
7d	23.2(t), 26.1(q), 31.7(t), 39.4(d), 40.1(t), 46.2(t), 40.1(t), 46.2(t), 71.1(s), 112.2(t), 143.5(d).
5e	19.0(q), 20.0(t), 22.1(q), 27.9(s), 34.4(t), 36.9(t), 48.9(s), 69.2(t), 111.7(t), 144.9(d).
6e	15.3(q), 17.5(t), 20.4(q), 26.9(s), 34.8(t), 37.5(t), 48.6(s), 65.9(t), 111.6(t), 146.3(d).
7e	18.3(t), 30.9(q), 32.3(q), 35.1(t), 36.6(s), 38.4(t), 50.4(t), 70.6(s), 112.2(t), 147.3(d).
5f	18.4(q), 19.0(q), 19.8(t), 20.1(q), 33.6(d), 34.1(t), 36.2(t), 50.3(s), 55.7(s), 69.9(t), 114.3(t), 139.7(d).
6f	17.5(t), 18.8(q), 19.0(q), 19.5(t), 19.7(q), 33.2(d), 34.7(t), 49.3(s), 54.8(s), 66.9(t), 114.0(t), 139.7(d).
8f	16.6(q), 16.8(q), 18.1(t), 30.9(t), 31.0(d), 38.5(t), 39.6(d), 42.1(s), 47.2(t), 70.6(s), 115.7(t), 143.0(d).
5g	21.7(t), 23.5(t), 29.5(q), 29.8(q), 32.9(t), 46.1(d), 55.6(d), 72.1(s), 114.6(t), 141.3(d).
6g	24.6(t), 26.8(q), 28.7(q), 28.8(t), 34.6(t), 46.1(d), 56.5(d), 73.6(s), 113.2(t), 145.2(d).
7g	12.9(q), 18.2(q), 23.9(t), 26.0(d), 30.6(t), 38.5(s), 51.0(d), 78.2(d), 115.3(t), 139.4(d).
5h	21.1(t), 26.7(q), 27.2(t), 30.1(q), 30.4(q), 43.7(t), 47.1(s), 58.8(d), 73.2(s), 111.5(t), 145.0(d).
6h	18.2(q), 20.8(t), 25.6(t), 29.8(q), 30.4(q), 43.2(t), 47.1(s), 60.6(d), 73.5(s), 110.3(t), 150.8(d).
7h	16.2(q), 19.8(q), 19.9(t), 21.6(q), 30.6(t), 32.6(t), 40.2(s), 42.4(s), 74.5(d), 111.8(t), 145.8(d).
8h	15.8(q), 19.8(t), 21.7(q), 22.1(q), 30.5(t), 34.0(t), 40.2(s), 42.7(s), 74.8(d), 112.5(t), 143.8(d).
5i	9.8(q), 23.4(t), 27.1(t), 28.6(t), 32.3(t), 45.5(d), 50.9(d), 74.2(d), 114.7(t), 140.4(d).
6i	9.8(q), 24.2(t), 28.3(t), 29.2(t), 34.0(t), 45.5(d), 51.5(d), 78.2(d), 113.7(t), 144.8(d).
5j	22.2(q), 23.2(t), 26.1(t), 32.5(t), 46.4(d), 51.7(d), 69.6(d), 111.4(t), 139.6(d).
6j	22.3(q), 24.2(t), 26.2(t), 33.8(t), 46.7(d), 52.5(d), 68.7(d), 113.7(t), 143.2(d).
7j	17.5(q), 23.9(t), 32.9(t), 35.4(t), 44.1(d), 48.5(d), 75.9(d), 114.2(t), 142.5(d).
6k	24.1(t), 26.1(t), 33.2(t), 46.5(d), 52.9(d), 74.7(d), 113.6(t), 126.2(d), 127.2(d), 128.1(d), 142.4(d), 144.4(s).
7k	23.7(t), 32.2(t), 33.9(t), 46.2(d), 58.3(d), 74.5(d), 114.1(t), 126.9(d), 128.6(d), 128.7(d), 141.1(s), 141.2(d).

Table 5 GC mass spectra of compounds **5–8** (relative intensity)

5a + 6a	108 (24, $M^+ - 18$), 95(77), 93(100), 79(68), 67(73), 41(83), 39(71).
5b	140 (1, M^+), 122(5), 109(100), 107(48), 93(36), 81(40), 79(45), 67(83), 55(45), 53(42), 41(71), 39(61).
6b	122 (4, $M^+ - 18$), 109(100), 107(40), 93(38), 81(50), 79(54), 67(93), 55(49), 53(45), 41(85), 39(61).
7b	122 (55, $M^+ - 18$), 107(72), 97(30), 93(44), 81(57), 79(67), 67(52), 55(58), 53(49), 41(100), 39(71).
5c + 6c	168 (1, M^+), 150(3), 137(31), 107(63), 95(66), 81(84), 79(100), 67(53), 55(51), 43(44), 41(90), 39(44).
8c	168 (7, M^+), 150(3), 135(5), 107(10), 97(13), 82(100), 69(28), 67(37), 55(58), 43(49), 41(89), 39(41).
5d + 6d	140 (1, M^+), 122(24), 109(39), 97(26), 93(29), 79(55), 71(52), 67(92), 55(71), 41(100), 39(81).
7d	122 (22, $M^+ - 18$), 97(65), 83(21), 71(29), 66(24), 58(25), 55(26), 43(100), 41(37), 39(33).
5e + 6e	136 (13, $M^+ - 18$), 123(35), 121(28), 107(38), 93(45), 81(63), 79(42), 68(100), 67(84), 55(43), 53(42), 41(82), 39(42).
7e	136 (15, $M^+ - 18$), 121(21), 111(20), 93(15), 81(28), 69(19), 55(18), 43(100), 41(50), 39(26).
5f + 6f	168 (1, $M^+ - 14$), 150(5), 125(16), 110(15), 97(24), 82(83), 81(44), 67(57), 55(67), 43(73), 41(100), 39(42).
8f	164 (6, $M^+ - 18$), 139(18), 121(43), 95(13), 81(63), 71(21), 55(17), 43(100), 41(47), 39(16).
5g	139 (5, $M^+ - 15$), 136(5), 121(4), 110(6), 96(21), 81(20), 67(63), 59(100), 43(54), 41(33), 39(19).
6g	139 (3, $M^+ - 15$), 136(3), 121(4), 96(24), 81(18), 67(43), 59(100), 43(52), 41(31), 39(18).
7g	136 (27, $M^+ - 18$), 126(6), 121(9), 111(26), 93(18), 83(43), 67(60), 59(46), 57(38), 57(38), 55(63), 43(76), 41(100), 39(58).
5h	168 (0.3, M^+), 154(2), 135(4), 110(11), 95(25), 81(28), 67(25), 59(100), 43(50), 41(34), 39(18).
6h	168 (0.3, M^+), 154(2), 135(1), 110(14), 95(20), 81(21), 67(24), 59(100), 43(49), 41(31), 39(16).
7h + 8h	168 (0.8, M^+), 150(5), 135(5), 125(14), 110(16), 97(23), 82(83), 81(43), 67(61), 55(67), 43(74), 41(100), 39(42).
5i	136 (15, $M^+ - 18$), 125(10), 121(5), 107(29), 97(24), 81(46), 67(100), 59(46), 43(17), 41(47), 39(27).
6i	136 (23, $M^+ - 18$), 125(8), 121(17), 107(83), 97(32), 81(33), 67(100), 59(58), 43(18), 41(63), 39(27).
5j + 6j	122 (5, $M^+ - 18$), 111(16), 93(29), 85(45), 67(47), 57(100), 43(36), 41(34), 39(31).
7j	122 (34, $M^+ - 18$), 107(34), 93(65), 79(45), 67(100), 45(98), 43(55), 41(71), 39(59).
6k + 7k	202 (3, M^+), 184(38), 169(3), 142(14), 129(33), 117(18), 115(25), 91(100), 83(17), 77(18), 67(20), 57(24), 55(22), 41(25), 39(21).

in THF (5 cm^3). After 10 min, the alcohol (1.01 g, 2.5 mmol) in THF (5 cm^3) was added followed by azodicarboxydipiperidide (0.76 g, 3.0 mmol) in THF (10 cm^3). After 1 h, brine (10 cm^3) was added and the organic layer was separated. The organic layer was washed with saturated $NaHCO_3$ (2 × 10 cm^3), dried ($MgSO_4$) and concentrated. The residue was flash chromatographed on silica gel [eluting with hexane–triethylamine (2%)] to give 7-(tributylstannyl)hept-5-enal (828 mg) as an *E*/*Z* mixture (83%).

To a mixture of sodium hydride (0.13 g, 2.8 mmol) and trimethylsulphoxonium iodide (0.62 g, 3.0 mmol) was added DMSO (20 cm^3). After evolution of hydrogen gas had ceased, the aldehyde (828 mg, 2.2 mmol) in DMSO (1 cm^3) was added. The mixture was stirred for 15 min at room temperature and then for 1 h at 50 °C; it was then cooled to room temperature. The resulting mixture was diluted with ether (60 cm^3) and the organic layer was separated, washed with water (15 cm^3) and brine (10 cm^3), dried ($MgSO_4$) and concentrated. The residue was flash chromatographed on silica gel [eluting with hexane–triethylamine (2%)] to give **1a** (548 mg) in the *E*/*Z* ratio of 22/78 (60%).

General Procedure for the Titanium Tetrachloride-induced Cyclisation of **4**.—To a solution of **4** (1.0 mmol) in dry dichloromethane (20 cm^3) at −78 °C was added slowly a solution of titanium tetrachloride in dichloromethane (0.2 mol

dm^{-3}; 5.0 cm^3, 1.0 mmol). The mixture was stirred for 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 an isomeric mixture of the cyclised products **5–8**.

General Procedure for the Butyllithium-promoted Cyclisation of **4**.—To a solution of **4** (1.0 mmol) in dry THF (20 cm^3) at −78 °C was added alowly a solution of butyllithium in hexane (1.6 mol dm^{-3}; 1.9 cm^3, 3.0 mmol). The mixture was stirred at the same temperature for 30 min and saturated aqueous NH_4Cl (10 cm^3) was added; the mixture was then allowed to warm to room temperature. Ether (20 cm^3) was added and the organic layer was separated. The aqueous layer was thrice extracted with ether. The combined organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The residue was flash chromatographed on silica gel [eluting with hexane–ether] to give an isomeric mixture of cyclised products **5–8**.

The results of cyclisation reactions and ^1H, ^{13}C NMR and GC mass spectral data of compounds **5–8** and are summarised in Table 2, 4 and 5, respectively.

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