PERKIN 1

Organozinc reagents in synthesis: the facile generation of 2-(trialkylsilyl)prop-2-enylzinc from 2-bromo-1-trimethylsilylprop-2-ene

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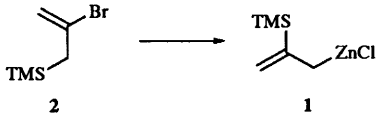
A range of electrophiles react with 2-(trimethylsilyl)prop-2-enylzinc chloride, which is prepared by sequentially treating 2-bromo-1-trimethylsilylprop-2-ene with Bu^tLi and then zinc chloride. The addition of transition metal catalysts can alter the reactivity of the organometallic compound from prop-2-enylation to prop-1-en-2-ylation.

The generation of carbon–carbon bonds by nucleophilic reaction of organometallic reagents with electrophiles is a well established method.[1] Organometallic reagents are sometimes difficult to use because they can (i) react as a base instead of as a nucleophile,[2] (ii) be difficult to make,[3] (iii) have poor chemo-,[4] regio-[5] or stereo-selectivity.[6] These problems have resulted in a constant investigation of organometallic reagents and their varying reactivities.

The formation of 2-(trialkylsilyl)prop-2-enylcuprates by the silylcupration of allene(prop-1,2-diene) and their use has been described by Fleming[7] and Overman.[8] The use of 2-(trimethylsilyl)prop-2-enylmagnesium bromide is also well documented.[9,10] Trost and co-workers have described many elegant uses for this reagent including the generation and trapping of trimethylenemethanepalladium complexes.[10]

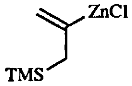
We now report in full, our findings[11,12] that 2- (trimethylsilyl)prop-2-enylzinc chloride **1**[13b] can be generated in one pot from 2-bromo-3-trimethylsilylprop-1-ene **2** and that the organozinc reagent **1** is a useful reagent that can be trapped with a range of electrophiles.



2 **1**

Scheme 1

This work complements that of Fleming and Overman but adds a further dimension since under certain catalysed conditions the organozinc reagent **1** can be trapped as its prop-1-en-2-yl isomer **3**.[12]

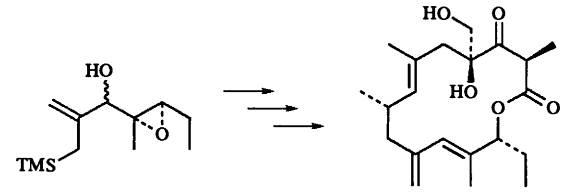


3

The development of organozinc chemistry has recently witnessed a revival, mainly due to the extensive work by Knochel. Knochel usually transmetallates the organozinc reagent to a more reactive species such as a copper organometallic which can react more efficiently with electrophiles.[13]

Results and discussion

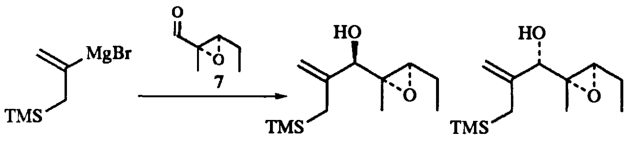
Our studies have been concerned with the construction of the allylic alcohol **4** and its use in the total synthesis of galbonolide B **5**[14] (Scheme 2).



4 **5**

Scheme 2

The alcohols **4a** and **4b** were formed in good yield when 3-(trimethylsilyl)prop-1-en-2-ylmagnesium bromide **6** was added to the homochiral epoxide **7** (Scheme 3). X-Ray analysis[15] of the nitrobenzoate ester of **4b** confirmed a 5 : 6 diastereoselection in favour of the *syn* product **4b**. It was interesting to note that no Payne rearrangement product[16] was observed during the preparation of **4**.



6 **4a** **4b**

Scheme 3

In order to optimise the diastereoisomeric ratio of **4** in favour of **4b** we investigated the use of other organometallic reagents. To our surprise, when 2-bromo-1-trimethylsilylprop-2-ene was treated with Bu^tLi followed by ethereal zinc chloride, an 'apparent' equilibration (or isomerisation) of the initially formed zinc species **3** to another reagent, presumed to be **1**, was observed.‡

The apparent equilibration (or isomerisation) of the prop-1-en-2-ylzinc **3** to the prop-2-enylzinc **1** is aided by raising the temperature, as demonstrated in Table 1. However, when the reagent is re-cooled to −70 °C, after storage at ambient temperature, there were no products from prop-1-en-2-yl attack on **7** to give **4**. Transmetallation of the prop-1-en-2-yllithium to give the prop-2-enylzinc reagent **1** could be slow at low

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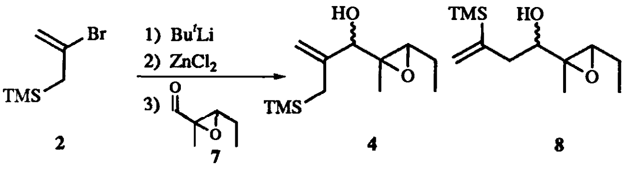
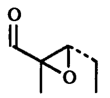
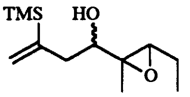
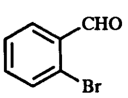
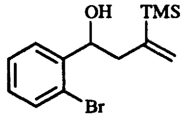
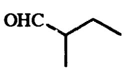
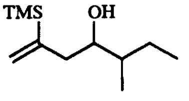
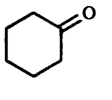
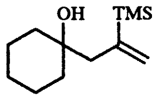
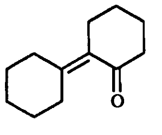
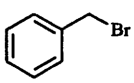
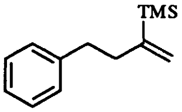
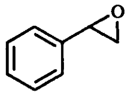
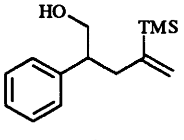
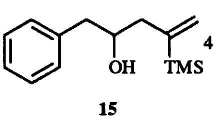
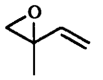
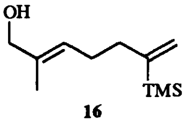
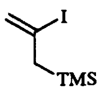
‡ It should be noted that the reaction of the Grignard reagent **6** resulted in a ≈2% contamination with the products of prop-2-enyl attack, **8**. A brief investigation of other metals indicated that the corresponding organoaluminium reagents formed by the reaction of 2-(1-trimethylsilylprop-2-enyl)lithium with diethylaluminium chloride also exhibited a similar 'equilibration' although reactions with this reagent were generally poor.

Table 1 The reaction of propenylzinc with the aldehyde **7**



Temp. (t/°C) for organozinc formation	Yields of isomers (%)			
	4a (*anti*)	**4b** (*syn*)	**8a**	**8b**
−70 to 0	0	0	48	17
−70 to 20 to −70	0	0	58	19
−70 to −50	25	13	7	5
−100	10	50	10	6

Table 2 Reaction of the prop-2-enylzinc reagent **1** with electrophiles

Electrophile	Products	Yield (%)
	 **8**	65 (3:1 ratio of diastereoisomers)
	 **9**	90
	 **10**	76 (1:1 *syn/anti*)
	 **11**  **12**	50, 20
	 **13**	86
	 **14**  **15**	49, 20
	 **16**	27
I$_2$	 **17**	73

temperature explaining why no prop-1-en-2-yl attack is observed when the anion stored at ambient temperature is re-cooled to −70 °C.

The prop-2-enylzinc reagent **1** was treated with a variety of other electrophiles including epoxides and alkyl halides. Our results are summarised in Table 2.

The prop-2-enylzinc reagent **1** added smoothly to a wide range of aldehydes resulting in the formation of the homoallylic alcohols **8**–**10**. With cyclohexanone, the reaction with **1** proceeded less well; the desired homoallylic alcohol **11** was isolated along with the unsaturated ketone **12** which arises from an aldol condensation of cyclohexanone with itself.

Clearly the organozinc reagent **1** can act as a base/Lewis acid system as well as being nucleophilic in character. This duality of Lewis acidity and nucleophilicity is apparent from Table 1 when the organozinc reagent **1** promotes rearrangement of styrene oxide to phenylacetaldehyde as well as acting as a nucleophile **14**–**15**. It is interesting to note that when iodine is added to the prop-2-enylzinc reagent **1** the product of formal prop-1-en-2-yl anion attack is isolated in 73% yield.§

We next investigated the reaction of **1** with a range of electrophiles in the presence of Lewis acids and selected transition-metal catalysts. Our results are summarised in Table 3.

The prop-2-enylzinc reagent **1** failed to react with cyclohexenone. Thus, we attempted a nickel acetylacetonate-assisted conjugate addition[17] to cyclohexenone and, to our surprise, the product of the reaction, **19**, resulted exclusively from prop-1-en-2-yl attack. The addition of a nickel catalyst apparently caused the organozinc **1** to react as if it were **3**. In contrast, when boron trifluoride was used as a Lewis acid in this reaction, the product of prop-2-enyl attack, **18**, was obtained as the sole product albeit in a low yield; this demonstrated a complete switch in the chemical reactivity of the organozinc species. Palladium-mediated coupling[18] of 1-iodo-4-isopropylbenzene with the organozinc reagent gave the prop-1-en-2-yl product **22** as the exclusive product. Treatment of cyclohexadiene oxide with the organozinc reagent under catalysed and uncatalysed reaction conditions led exclusively to the products of prop-2-enyl attack in all cases.

In our research towards the total synthesis of the galbonolides we required the synthesis of the alcohols **28** which contain the much bulkier *tert*-butyldiphenylsilyl group in place of the trimethylsilyl group of alcohol **4**. Fleming has found that reaction of *tert*-butyl(diphenyl)silyl cuprates with propa-1,2-diene followed by quenching with electrophiles gives formal prop-1-en-2-yl attack at low temperatures,[7b] whereas phenyl(dimethyl)silyl cuprates leads to prop-2-enyl attack. He has further suggested that these reactions may be reversible.[7] We were thus interested to see if switching to the more bulky, 2-bromo-1-(*tert*-butyldiphenylsilyl)prop-2-ene would affect the ratio of prop-1-en-2-yl to prop-2-enyl adduct of the organozinc reagent. The results are shown in Table 4.

At temperatures above 0 °C the major product **29** results from prop-2-enyl attack although a small amount of prop-1-en-2-yl attack is always observed. Re-cooling the organozinc reagent did not result in a reversion back to prop-1-en-2-yl attack. It was interesting to note that the products of prop-1-en-2-yl attack, **28**, can be formed exclusively if the transmetallation/reaction sequence is carried out at low temperature. This could be due to slower transmetallation or a shift in equilibrium.

Further work will determine the mechanism of this intriguing reaction and we are currently investigating this by NMR spectroscopy. Interesting comparisons can be made with the regiochemical variations observed in the silylcupration of allene[7] and the 1,2-silyl migration and destannylation observed

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§ Reaction of iodine with 2-dimethyl(phenyl)silylprop-2-enyl cuprate gave a similar result for which the following explanation was proposed by Fleming:[7a]

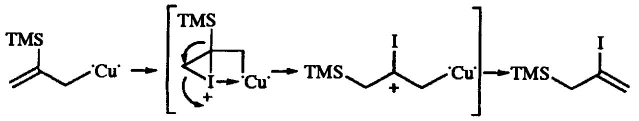
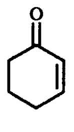
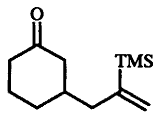
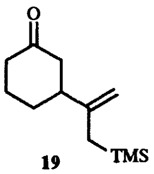
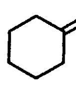
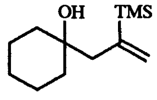
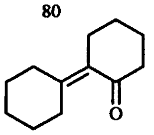
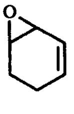
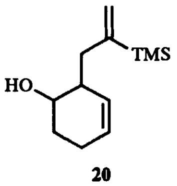
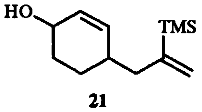
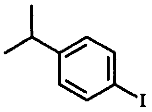
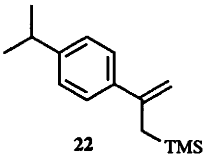
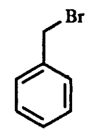
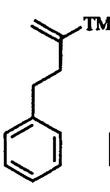
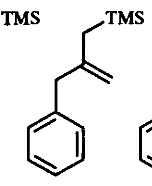
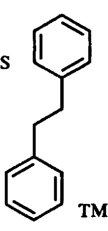
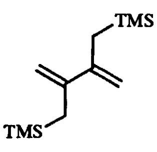
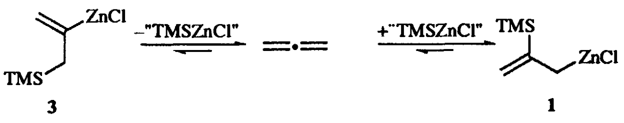


Table 3 Reaction of the zinc reagent **1** with electrophiles and a catalyst

Substrate + catalyst	Product(s) and % yields	
	 **18**	 **19**
None	0	0
$BF_3.Et_2O$	34	0
$Ni(acac)_2$	0	80
	 **11**	 **12**
None	50	20
$BF_3.Et_2O$	66	0
$Ni(acac)_2$	0	>95
	 **20**	 **21**
None	37	21
$Ni(acac)_2$	21	16
$Pd(PPh_3)_4$	27	14
	 **22**	
$Pd(PPh_3)_4$	88	
	 **23**  **24**	 **25**  **26**

in the Lewis acid-mediated reactions of 2-stannyl-3-trimethylsilylprop-2-ene with acid chlorides.[19]

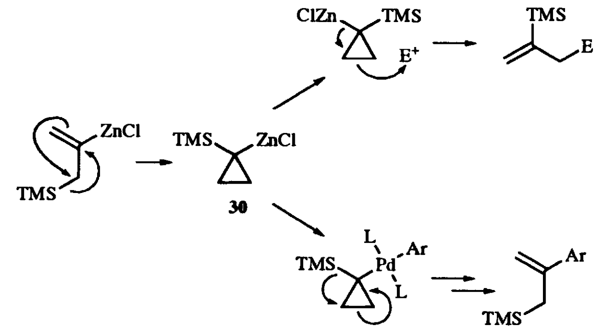
It may be that the rearrangement occurs *via* the intermediacy of the prop-1,2-diene followed by a silylzincation process to yield the prop-2-enylzinc **1** (Scheme 4).



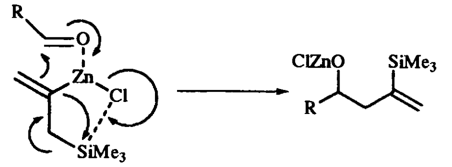
Scheme 4

Alternatively, a new cyclopropyl organozinc species **30** may form, and this can react by different mechanisms depending on the reaction (Scheme 5).

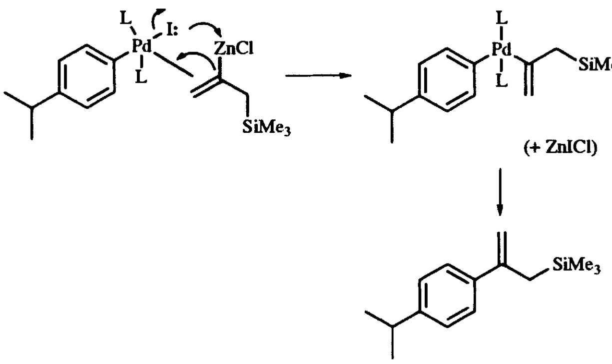
A further possibility arises if, prior to nucleophilic attack, coordination of the electrophile to zinc could occur. This may then allow an interaction of the chloride with silicon allowing a sequential alkylation/silicon shift (Scheme 6).



Scheme 5

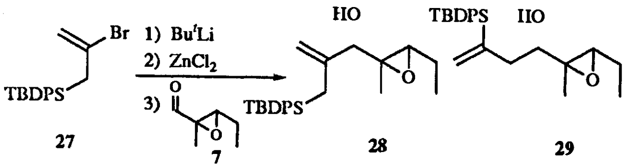


Scheme 6



Scheme 7

Table 4 The reaction of propenylzinc with the aldehyde **7**



Temp. (t/°C) for organozinc formation	Yields (%) of isomers			
	28a	**28b**	**29a**	**29b**
−70 to 20	<2	<2	38	16
−70 to 20 to −70	<2	<2	27	13
−70 to 0	2	3	37	9
−70	20	25	0	0

In the palladium-mediated coupling, prior coordination of the zinc species could occur. It is conceivable that iodide coordination with zinc would disfavour chloride association with silicon in the transition state and hence coupling at the prop-1-en-2-yl carbon of the organozinc reagent occurs (Scheme 7).

Whether the presence of iodide anion will affect product ratios remains to be seen.

Experimental

General methods

All reactions were conducted under an atmosphere of nitrogen. Reaction solvents were purified/dried by standard procedures; ether refers to diethyl ether. Vacuum liquid chromatography (VLC) was performed on silica gel 60 (Merck 7729, particle size less than 0.063 mm). Gas chromatographic (GC) analyses were performed on a Hewlett–Packard 5890A equipped with a 25 m Chrompack fused-silica capillary column, (coating CP-SIL 5CB, film thickness 0.12 µm, i.d. 0.25 mm) using helium as the carrier gas, and a FID detector. Gas chromatographic–mass spectra (GC–MS) were obtained on a Fisons Trio 1. Fast atom bombardment–mass spectra (FAB–MS) and probe mass spectra were obtained on a JEOL DX303. Exact mass measurements were made by high-resolution mass spectrometry (HRMS) using a VG Autospec Q instrument. All mps are uncorrected. Optical rotations $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1} and were measured on an Optical Activity AA-100 polarimeter. Elemental analyses were carried out on a Perkin-Elmer 240G. IR spectra were recorded on a Perkin-Elmer 298 or a Nicolet FT-IR 205 spectrophotometer. NMR spectra were obtained on either a JEOL GX400 FTNMR (^{1}H 400 MHz, ^{13}C 100 MHz, ^{19}F 376 MHz) or a JEOL GSX270 (^{1}H 270 MHz, ^{13}C 67.8 MHz, ^{19}F 254 MHz) spectrometer. Chemical shift δ values are referenced to tetramethylsilane. J Values are given in Hz.

2-*Bromo*-1-*trimethylsilylprop*-2-*ene* **2**.—This compound was used either as supplied by Fluka or prepared according to the procedure of Itoh.[9]

2,3-*Epoxy*-2-*methylpentan*-1-*al* **7**.—This compound was prepared according to literature procedure.[20]

4,5-Epoxy-4-methyl-2-(trimethylsilylmethyl)hept-1-en-3-ol 4

To a suspension of magnesium (0.62 g, 0.026 mol) and 1,2-dibromoethane (110 mm^3, 1.3 mmol) in THF (10 cm^3) was added compound **2** (4.44 cm^3, 26 mmol) dropwise over 30 min, the mixture being held at gentle reflux after initiation had occurred. Upon cooling of the mixture to 0 °C an opaque olive-coloured solution containing a gelatinous precipitate was obtained. The aldehyde (2.74 cm^3, 24 mmol) **7** in THF (5 cm^3) was added dropwise to the Grignard solution over 20 min and the reaction mixture allowed to warm to room temperature over 30 min. A solution of saturated aqueous ammonium chloride was added carefully with stirring to the mixture until no precipitate remained. The mixture was then filtered and the aqueous layer separated and extracted with ether. The combined organic layer and extracts were dried (MgSO$_4$), filtered through a silica plug and dried *in vacuo*. Chromatography with 20% ether–pentane yielded the two product diastereomers.

4a: R_F 0.33 (1.15 mg, 20%), clear colourless oil (Found: C, 62.6; H, 10.6. Calc. for $C_{12}H_{24}O_2Si$: C, 63.1; H, 10.6); ν_{max}(thin film)/cm^{-1} 3480br s (OH), 2970s (CH), 1640w (C=C), 1250s and 850s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 4.95 (1 H, s, C=C*H*H), 4.80 (1 H, s, C=CH*H*), 3.93 [1 H, s, C(*H*)OH], 3.09 (1 H, t, J 6.5, C*H*CH$_2$), 2.14 (1 H, br s, OH), 1.75–1.48 (4 H, m, 2 × CH$_2$), 1.25 (3 H, s, CH$_3$), 1.05 (3 H, t, J 7.5, CH$_2$C*H*$_3$) and 0.06 (9 H, s, TMS); δ_C(100 MHz; CDCl$_3$; Me$_4$Si) 145.77 (C), 110.56 (CH$_2$), 77.22 (CH), 62.24 (C), 61.03 (CH), 23.12 (CH$_2$), 21.59 (CH$_2$), 14.25 (CH$_3$), 10.53 (CH$_3$) and −1.16 (3 × CH$_3$); m/z (EI) 210 (M$^+$ − H$_2$O, 1%), 195 (M$^+$ − H$_2$O − Me, 1), 170 (18), 155 (22) and 73 (TMS$^+$, 100); m/z (HRMS) 228.1546 (Calc.: 228.1546).

4b: R_F 0.27 (1.121 g, 25%), clear colourless oil (Found: C, 62.8; H, 10.6. Calc. for $C_{12}H_{24}O_2Si$: C, 63.1; H, 10.6); ν_{max}(thin film)/cm^{-1} 3470br s (OH), 2975s (CH), 1640w, 1250s and 850s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 5.08 (1 H, s, C=CH*H*), 4.78 (1 H, s, C=C*H*H), 3.63 [1 H, d, J 4, C(*H*)OH], 2.94 (1 H, t, J 6.5, C*H*CH$_2$), 2.25 (1 H, d, J 4, OH), 1.69 (1 H, dpent, J 14 and 7, C*H*HCH$_3$), 1.65 (1 H, d, J 14, C*H*HTMS), 1.54 (1 H, dpent, J 14 and 7, CH*H*CH$_3$), 1.34 (1 H, d, J 14, CH*H*TMS), 1.20 (3 H, s, CH$_3$), 1.05 (3 H, t, J 7, CH$_2$C*H*$_3$) and 0.04 (9 H, s, TMS); δ_C(100 MHz; CDCl$_3$; Me$_4$Si) 144.85 (C), 109.03 (CH$_2$), 79.19 (CH), 63.86 (CH), 63.19 (C), 23.03 (CH$_2$), 21.47 (CH$_2$), 11.31 (CH$_3$), 10.42 (CH$_3$) and −1.25 (3 × CH$_3$); m/z (EI) 210 (M$^+$ − H$_2$O, 1%), 195 (M$^+$ − H$_2$O − Me, 2), 170 (8), 155 (33) and 73 (TMS$^+$, 100); m/z (HRMS) 228.1546 (Calc.: 228.1546).

2-Trimethylsilylprop-2-enylzinc reagent 1. A solution of compound **2** (2.05 cm^3, 12 mmol) in ether (7 cm^3) at −80 °C was treated with Bu^{t}Li (1.7 mol dm^{-3} in pentane solution; 14.1 cm^3, 24 mmol) over 10 min (exotherm to −52 °C), and stirred a further 5 min (re-cooled to −80 °C). To the pale yellow solution was added a solution of zinc dichloride (1.0 mol dm^{-3} in ether solution; 12.6 cm^3, 12.6 mmol) over 5 min. The mixture was then allowed to warm to room temperature and stirred for 2 h at that temperature. Further ether was commonly added to make solutions of convenient concentration. Measured aliquots were then added to various electrophiles.

Uncatalysed reactions

5,6-Epoxy-5-methyl-2-trimethylsilyloct-1-en-4-ol 8. A solution of compound **2** (4.74 cm^3, 27.8 mmol) in ether (20 cm^3) at −70 °C was treated with Bu^{t}Li (1.0 mol dm^{-3} in pentane solution; 55.5 cm^3, 55.5 mmol) over 20 min. The pale yellow solution was allowed to warm to 0 °C after which it was stirred for 1 h and then re-cooled to −70 °C. A solution of zinc chloride (1.0 mol dm^{-3} in ether solution; 27.8 cm^3, 27.8 mmol) was added over 5 min to the mixture which was then warmed to 0 °C and stirred for 1 h before being re-cooled to −70 °C. The resulting solution of vinylzinc chloride was added *via* a cannula over 1 h to a solution of the aldehyde **7** (2.11 g, 18.5 mmol) in ether (20 cm^3) at −70 °C. The cooling bath was removed and the mixture allowed to reach 0 °C when it was quenched with saturated aqueous ammonium chloride. The aqueous layer was separated and extracted with ether and the combined organic layer and extracts were dried (MgSO$_4$), filtered and concentrated under reduced pressure. Chromatography of the residue in 20% ether–hexane yielded two diastereoisomeric products.

8a: R_F 0.31 (2.01g, 48%), clear colourless oil (Found: C, 63.0; H, 10.6. Calc. for $C_{12}H_{24}O_2Si$: C, 63.1; H, 10.6); ν_{max}(thin film)/cm^{-1} 3470br s (OH), 2950s (CH), 1245s and 835s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 5.70 (1 H, br s, C=CH*H*), 5.46 (1 H, d, J 3, C=C*H*H), 3.60 [1 H, dd, J 10 and 2.5, C(*H*)OH], 2.94 (1 H, t, J 6.5, C*H*CH$_2$), 2.50 (1 H, dd, J 14 and 2.5, C=CC*H*H), 2.15 (1 H, dd, J 14 and 10, C=CCH*H*), 2.07 (1 H, s, OH), 1.63 (1 H, dpent, J 14 and 7, C*H*HCH$_3$), 1.52 (1 H, dpent, J 14 and 7, CH*H*CH$_3$), 1.28 (3 H, s, CH$_3$), 1.02 (3 H, t, J 7, CH$_2$C*H*$_3$) and 0.10 (9 H, s, TMS); δ_C(67.8 MHz; CDCl$_3$; Me$_4$Si) 148.75 (C), 127.35 (CH$_2$), 72.03 (CH), 62.61 (C), 61.40 (CH), 39.87 (CH$_2$), 21.47 (CH$_2$), 13.88 (CH$_3$), 10.47 (CH$_3$) and −1.33 (CH$_3$ × 3); m/z (GC–MS, EI) 155 (M$^+$ − TMS, 70%) and 73 (TMS$^+$, 100); m/z (CI) 246 (M + NH$_4^+$, 10), 229 (MH$^+$, 8), 211 (68), 171 (73), 155 (84) and 58 (100); m/z (HRMS) 228.1550 (Calc.: 228.1546).

8b: R_F 0.15 (0.715 g, 17%), clear colourless oil (Found: C, 62.8; H, 10.6. Calc. for $C_{12}H_{24}O_2Si$: C, 63.1; H, 10.6); ν_{max}(thin film)/cm^{-1} 3440br s (OH), 2955s (CH), 1245s and 833s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 5.69 (1 H, br s, C=C*H*H), 5.49 (1 H, d, J 2, C=CH*H*), 3.38 [1 H, dt, J 9.5 and 3.5, C(*H*)OH], 2.84 (1 H, t, J 6.5, C*H*CH$_2$), 2.45 (1 H, dd, J 14 and 3.5, C=CC*H*H), 2.28 (1 H, dd, J 14 and 9.5, C=CCH*H*), 1.84 (1 H, br s, OH), 1.62 (1 H, dpent, J 14 and 7, C*H*HCH$_3$), 1.51 (1 H, dpent, J 14 and 7, CH*H*CH$_3$), 1.29 (3 H, s, CH$_3$), 1.02 (3 H, t, J 7, CH$_2$C*H*$_3$) and 0.10 (9 H, s, TMS); δ_C(67.8 MHz; CDCl$_3$; Me$_4$Si) 148.30 (C), 127.81 (CH$_2$), 74.82 (CH), 63.40 (C), 62.94 (CH), 39.93 (CH$_2$), 21.40 (CH$_2$), 11.68 (CH$_3$), 10.46 (CH$_3$) and −1.33 (3 × CH$_3$); m/z (GC–MS, EI) 155 (M$^+$ − TMS, 80%), 73 (TMS$^+$, 100); m/z (CI) 246 (M + NH$_4^+$, 10), 229 (MH$^+$, 4), 211 (28), 195 (45), 171 (69), 155 (72) and 58 (100); m/z (HRMS) 228.1550 (Calc.: 228.1546).

1-(2-Bromophenyl)-3-trimethylsilylbut-3-en-1-ol 9. To a solution of 2-bromobenzaldehyde (117 mm^3, 1 mmol) in ether (2 cm^3) at room temperature was added a solution of the pre-formed allylzinc reagent **1** [2 mmol in ether (5.5 cm^3)] over 1 h.

After complete addition the mixture was treated with saturated aqueous ammonium chloride to quench the reaction and the aqueous layer extracted with ether. The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography in 20% ether–hexane (R_F 0.35) yielded a clear colourless oil (269 mg, 90%); ν_{max}(thin film)/cm^{-1} 3450br m (OH), 2960m (CH), 1570w, 1468m, 1440m, 1245s and 840s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.63 (1 H, dd, *J* 7 and 1, ArH), 7.52 (1 H, d, *J* 7, ArH), 7.35 (1 H, t, *J* 7, ArH), 7.13 (1 H, td, *J* 7 and 1, ArH), 5.81 (1 H, s, C=C*H*H), 5.62 (1 H, d, *J* 1, C=CH*H*), 5.09 [1 H, dd, *J* 9 and 1, C(*H*)OH], 4.75 (1 H, br s, OH), 2.85 [1 H, br d, *J* 12, C(H)OHC*H*H], 2.20 [1 H, dd, *J* 12 and 9, C(H)OHCH*H*] and 0.20 (9 H, s, TMS); δ_C(67.8 MHz; $CDCl_3$; Me_4Si) 149.20 (C), 143.13 (C), 132.53 (CH), 128.92 (CH_2), 128.66 (CH), 127.71 (CH), 127.35 (CH), 121.65 (C), 70.75 (CH), 45.34 (CH_2) and −1.29 (3 × CH_3); *m*/*z* (EI) (consistent with one bromine) 298/300 (M^+, 1/1%), 283/285 (M^+ − Me, 8/9), 257/259 (12/13), 185/187 (100/83) and 73 (TMS^+, 48); *m*/*z* (HRMS) 298.0390 (Calc.: 298.0389).

5-Methyl-2-trimethylsilylhept-1-en-4-ol 10. To a solution of 2-methylbutanal (86 mg, 1 mmol) in ether (2 cm^3) at 0 °C was added a solution of the pre-formed allylzinc reagent **1** [2 mmol in ether (8 cm^3)] over 5 min. After the mixture had been stirred for 1 h it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was separated and extracted with ether and the combined extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Chromatography in 20% ether–pentane (R_F 0.50) yielded a pale yellow oil (158 mg, 76%) as a 1 : 1 mix of diastereoisomers A and B (Found: C, 65.8; H, 12.1. Calc. for $C_{11}H_{24}OSi$: C, 65.9; H, 12.1); ν_{max}(thin film)/cm^{-1} 3480br m (OH), 2960s (CH), 1461w, 1250s and 839s; δ_H(400 MHz; $CDCl_3$; Me_4Si) 5.67 (1 H, m, C=CHH, A and B), 5.50 (1 H, d, *J* 3, C=CHH, A or B), 5.49 (1 H, d, *J* 3, A or B), 3.56 (1 H, ddd, *J* 10.0 and 3.5 and 3.5, A or B), 3.47 (1 H, ddd, *J* 10.5 and 5.5 and 2.5, A or B), 2.51–2.46 (1 H, m, CHHC=C, A or B), 2.45–2.40 (1 H, m, CHHC=C, A or B), 2.14 (1 H, dd, *J* 14 and 10, CHHC=C, A or B), 2.05 (1 H, dd, *J* 13.5 and 10.5, CHHC=C, A or B), 1.77–1.39 (3 H, m, A and B), 1.27–1.11 (1 H, m, A and B), 0.91 (6 H, m, CH_3CH and CH_3CH_2, A and B), 0.102 (9 H, s, TMS, A or B) and 0.103 (9 H, s, TMS, A or B); δ_C(100 MHz; $CDCl_3$; Me_4Si) (diastereoisomer 1): 150.02 (C), 127.93 (CH_2), 72.71 (CH), 40.90 (CH_2), 40.09 (CH), 25.06 (CH_2), 14.47 (CH_3), 11.63 (CH_3) and −1.28 (3 × CH_3); (diastereoisomer 2): 149.92 (C), 127.64 (CH_2), 72.28 (CH), 41.79 (CH_2), 39.85 (CH), 25.74 (CH_2), 13.71 (CH_3), 11.84 (CH_3) and −1.28 (3 × CH_3); *m*/*z* (EI) 185 (M^+ − Me, 7%), 159 (30), 99 (100), 75 (97), 73 (TMS^+, 75); *m*/*z* (CI) 218 (M + NH_4^+, 27) and 90 (100); *m*/*z* (HRMS) 200.1597 (Calc.: 200.1597).

1-(2-Trimethylsilylprop-2-enyl)cyclohexanol 11. To a solution of cyclohexanone (104 mm^3, 1 mmol) in ether (2 cm^3) at room temperature was added a solution of the pre-formed allylzinc reagent **1** [2 mmol in ether (8 cm^3)] over 5 min. After the mixture had been stirred for 30 min it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Chromatography of the residue in 10% ether–pentane (R_F 0.41) yielded the title compound as a clear colourless oil (106 mg, 50%) (Found: C, 67.8; H, 11.3. Calc. for $C_{12}H_{24}OSi$: C, 67.9; H, 11.4); ν_{max}(thin film)/cm^{-1} 3478br m (OH), 2930m (CH), 2855m (CH), 1447s, 1246m and 838s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.72 (1 H, d, *J* 2, C=CHH), 5.57 (1 H, d, *J* 2, C=CHH), 2.30 [2 H, s, C*H*$_2$C(TMS)=CH_2], 2.67–1.14 (11 H, m, Cy − H + OH) and 0.11 (9 H, s, TMS); δ_C(67.8 MHz; $CDCl_3$; Me_4Si) 148.79 (C), 129.91 (CH_2), 71.15 (C), 48.55 (CH_2), 37.98 (2 × CH_2), 25.80 (CH_2), 22.16 (2 × CH_2) and −0.62 (3 × CH_3); *m*/*z* (EI) (M^+ − H_2O, 194, 11%), (M^+ − H_2O − Me, 179, 22), 120 (36) and 73 (TMS, 100); *m*/*z* (HRMS) 212.1597. (Calc.: 212.1597).

Also obtained was 2-cyclohexylidenecyclohexanone **12**: (R_F 0.33) (18 mg, 20%); ν_{max}(thin film)/cm^{-1} 2930s (CH), 2860s (CH), 1682s (C=C), 1620m (C=C), 1448m, 1285m, 1212m and 1130m; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.40 (2 H, m), 2.31 (4 H, m), 2.10 (2 H, m), 1.78 (2 H, m), 1.64 (2 H, m) and 1.48 (6 H, m); δ_C(100 MHz; $CDCl_3$; Me_4Si) 207.02 (C), 147.14 (C), 131.43 (C), 44.13 (CH_2), 32.40 (CH_2), 31.40 (CH_2), 30.34 (CH_2), 29.31 (CH_2), 28.88 (CH_2), 27.25 (CH_2), 26.19 (CH_2) and 26.12 (CH_2); *m*/*z* (EI) 178 (M^+, 86%), 149 (100) and 79 (74); *m*/*z* (HRMS) 178.1358 (Calc.: 178.1359).

4-Phenyl-2-trimethylsilylbut-1-ene 13. To a solution of benzyl bromide (119 mm^3, 1 mmol) in ether (2 cm^3) at room temperature was added a solution of the pre-formed allylzinc reagent **1** [2 mmol in ether (8 cm^3)] in one portion. The reaction was stirred for 3 days and then further allylzinc reagent [2 mmol in ether (8 cm^3)] was added and the reaction stirred for a further 3 days. The reaction was quenched with saturated aqueous ammonium chloride and the aqueous layer was separated and extracted with ether. The combined extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Chromatography of the residue in pentane (R_F 0.49) yielded a clear colourless oil (175 mg, 86%) (Found: C, 76.3; H, 9.9. Calc. for $C_{13}H_{20}Si$: C, 76.4; H, 9.9); ν_{max}(thin film)/cm^{-1} 3030m (ArH), 2957s (CH), 1603w, 1495w, 1451w, 1249s and 835s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.33–7.11 (5 H, m, ArH), 5.61 (1 H, br s, C=C*H*H), 5.37 (1 H, d, *J* 1, C=CH*H*), 2.71 (2 H, m, ArC*H*$_2$), 2.41 (2 H, m, CH_2C=C) and 0.11 (9 H, s, TMS); δ_C(100 MHz; $CDCl_3$; Me_4Si) 151.77 (C), 142.48 (C), 128.30 (2 × CH), 128.36 (2 × CH), 125.75 (CH), 124.05 (CH_2), 37.69 (CH_2), 35.57 (CH_2) and −1.50 (3 × CH_3); *m*/*z* (EI) 204 (M^+, 5%), 189 (M^+ − Me, 55), 130 (47), 91 ($PhCH_2^+$, 37) and 73 (TMS^+, 100); *m*/*z* 204.1339 (Calc. for $C_{13}H_{20}Si$: 204.1334).

2-Phenyl-4-trimethylsilylpent-4-en-1-ol 14 and 1-phenyl-4-trimethylsilylpent-4-en-2-ol 15. To a solution of styrene oxide (114 mm^3, 1 mmol) in ether (2 cm^3) at 0 °C was added a solution of the pre-formed allylzinc reagent **1** [2 mmol in ether (8 cm^3)] over 10 min. The mixture was stirred overnight at room temperature after which it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography in 20% ether–pentane yielded two regioisomeric compounds **14** and **15**.

14: R_F 0.21 (115 mg, 49%), clear colourless oil (Found: C, 71.6; H, 9.5. Calc. for $C_{13}H_{19}OSi$: C, 71.7; H, 9.5); ν_{max}(thin film)/cm^{-1} 3380br m (OH), 3030w (ArH), 2955m (CH), 1249s, 839s and 700s; δ_H(400 MHz; $CDCl_3$; Me_4Si) 7.33–7.18 (5 H, m, PhH), 5.50 (1 H, dt, *J* 3 and 1, C=C*H*H), 5.34 (1 H, dt, *J* 3 and 1, C=CH*H*), 3.77 (1 H, dd, *J* 11 and 5.5, C*H*HOH), 3.68 (1 H, dd, *J* 11 and 7.5, CH*H*OH), 2.98 (1 H, dddd, *J* 7.5 and 7 and 7 and 5.5, PhC*H*), 2.53 (1 H, ddt, *J* 14 and 7 and 1, C*H*HC=CH_2), 2.47 (1 H, ddt, *J* 14 and 7 and 1, CH*H*C=CH_2), 1.49 (1 H, s, OH) and 0.08 (9 H, s, TMS); δ_C(100 MHz; $CDCl_3$; Me_4Si) 149.55 (C), 142.37 (C), 128.54 (2 × CH), 128.06 (2 × CH), 126.66 (CH), 126.31 (CH_2), 66.99 (CH_2), 47.15 (CH), 38.69 (CH_2) and −1.40 (3 × CH_3); *m*/*z* (EI) 203 (M^+ − CH_2OH), 201 (M^+ − H_2O − Me), 73 (TMS^+); *m*/*z* (CI), 252 (M + NH_4^+); *m*/*z* (HRMS) 234.1439 (Calc.: 234.1440).

15: R_F 0.32 (47 mg, 20%), clear colourless oil (Found: C, 71.6; H, 9.4. Calc. for $C_{13}H_{19}OSi$: C, 71.7; H, 9.5); ν_{max}(thin film)/cm^{-1} 3440br m (OH), 3035w (PhH), 2958m (CH), 1249s, 838s and 701s; δ_H(400 MHz; $CDCl_3$; Me_4Si) 7.33–7.20 (5 H, m, PhH), 5.69 (1 H, dt, *J* 3 and 1.5, C=C*H*H), 5.50 (1 H, d, *J* 3, C=CH*H*), 3.89 [1 H, dddd, *J* 9 and 7.5 and 5.5 and 4, C(*H*)OH], 2.79 (1 H, dd, *J* 14 and 5.5, PhC*H*H), 2.75 (1 H, dd, *J* 14 and 7.5, PhCH*H*), 2.44 [1 H, ddd, *J* 14 and 4 and 1.5, C(H)OHC*H*H], 2.25 [1 H, dd, *J* 14 and 9, C(H)OHCH*H*], 1.76 (1 H, s, OH) and 0.08 (9 H, s, TMS); δ_C(100 MHz; $CDCl_3$; Me_4Si) 149.28 (C), 138.62 (C), 129.36 (2 × CH), 128.44 (2 × CH), 127.76 (CH_2), 126.37 (CH), 70.81 (CH), 44.17 (CH_2), 43.50 (CH_2), −1.38

$(3 \times CH_3)$; m/z (EI) 216 ($M^+ - H_2O$, 7%), 201 ($M^+ - H_2O -$ Me, 12), 142 (38), 129 (51), 73 (TMS^+, 100); m/z (CI) 252 ($M + NH_4^+$, 70), 234 ($M + NH_4^+ - H_2O$, 7) and 217 ($MH^+ - H_2O$, 22); m/z (HRMS) 234.1439 (Calc.: 234.1440).

(*E*)-2-Methyl-6-trimethylsilylhepta-2,6-dien-1-ol 16. To a solution of 2-methyl-2-vinyloxirane (98 mm^3, 1 mmol) in ether (2 cm^3) at 0 °C was added a solution of the pre-formed allylzinc reagent **1** [2 mmol in ether (8 cm^3)] over 10 min. The mixture was stirred at 0 °C for 2 h after which it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue in 20% ether–pentane (R_F 0.23) yielded a clear colourless oil (92% by GC analysis), with 8% of a single unidentified impurity (59 mg, 27%); ν_{max}(thin film)/cm^{-1} 3350br s (OH), 2960s (CH), 1250s and 840s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.55 (1 H, br s, C=C*H*H), 5.40–5.26 (2 H, includes 1 H, d, *J* 2 at 5.34, 2C=CH), 4.11 (2 H, br s, C*H*$_2$OH), 2.21–2.10 (4 H, m, CH_2CH_2), 1.80 (3 H, s, CH_3) and 0.08 (9 H, s, TMS); δ_C(100 MHz; $CDCl_3$; Me_4Si) 151.76 (C), 134.43 (C), 128.05 (CH), 124.06 (CH_2), 61.48 (CH_2), 35.81 (CH_2), 27.11 (CH_2), 21.20 (CH_3) and −1.58 $(3 \times CH_3)$; m/z (EI) 180 ($M^+ - H_2O$, 6%), 165 ($M^+ - H_2O -$ Me, 3), 106 (15), 91 (22), 73 (TMS^+, 100); m/z (CI) 216 ($M + NH_4^+$, 1), 198 ($M + NH_4^+ - H_2O$, 4), 181 ($MH^+ - H_2O$, 50) and 90 (100).

2-Iodo-3-trimethylsilylprop-1-ene 17. To a solution of iodine (3.81 g, 15 mmol) in ether (50 cm^3) was added a solution of the pre-formed allylzinc reagent **1** (16.5 mmol in 55 cm^3 ether) over 10 min. The mixture was stirred for 20 min after which it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to yield a brown liquid (2.61 g, 73%); ν_{max}(thin film)/cm^{-1} 2963m (CH), 1609m (C=C), 1250s, 1189m, 1069m, 938m and 852s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.74 (1 H, s, C=C*H*H), 5.53 (1 H, s, C=CH*H*), 2.28 (2 H, s, C=CCH_2) and 0.13 (9 H, s, TMS); δ_C(100 MHz; $CDCl_3$; Me_4Si) 123.21 (CH_2), 105.60 (C), 37.76 (CH_2) and −1.41 $(3 \times CH_3)$; m/z (HRMS) 239.9825 (Calc. for $C_6H_{13}ISi$: 239.9830).

Catalysed reactions

3-(2-Trimethylsilylprop-2-enyl)cyclohexanone 18. To a solution of cyclohex-2-enone (580 mm^3, 6 mmol) and boron trifluoride–diethyl ether (812 mm^3, 6.6 mmol) in ether (20 cm^3) at −15 °C was added a solution of the pre-formed prop-2-enylzinc reagent **1** [6.6 mmol in ether (22 cm^3)] over 10 min. The mixture was stirred for 5 min after which it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined organic layer and extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue in 20% ether–hexane (R_F 0.29) yielded the title compound as a clear colourless oil (515 mg, 37%) (Found: C, 68.7; H, 10.5. Calc. for $C_{12}H_{22}OSi$: C, 68.5; H, 10.5); ν_{max}(thin film)/cm^{-1} 2960s (CH), 1715s (C=O), 1249s and 834s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.53 (1 H, d, *J* 1, =C*H*H), 5.40 (1 H, d, *J* 1, =CH*H*), 2.48–1.78 (9 H, m), 1.2–1.50 (1 H, m), 1.35–1.16 (1 H, m) and 0.08 (9 H, s, TMS); δ_C(100 MHz; $CDCl_3$; Me_4Si) 211.78 (C), 149.33 (C), 126.40 (CH_2), 48.11 (CH_2), 43.92 (CH_2), 41.44 (CH_2), 37.96 (CH), 31.16 (CH_2), 25.07 (CH_2) and −1.38 $(3 \times CH_3)$; m/z (EI) 210 (M^+, 1%), 195 ($M^+ -$ Me, 100), 167 ($M^+ -$ Me − CO, 21) and 73 (TMS, 70); m/z (CI) 228 ($M + NH_4^+$, 100%); m/z (HRMS) 210.1443 (Calc. for $C_{12}H_{22}OSi$: 210.1443).

3-(1-Trimethylsilylprop-2-en-2-yl)cyclohexanone 19. To a solution of cyclohex-2-enone (290 mm^3, 3 mmol) and nickel acetylacetonate (16 mg, 0.06 mmol) in ether (10 cm^3) at −15 °C was added a solution of the pre-formed prop-2-enylzinc reagent **1** [3.3 mmol in ether (11 cm^3)] over 10 min. After the mixture had been stirred for 5 min at −15 °C it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined organic layer and extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography in 20% ether–pentane (R_F 0.30) yielded the title compound as a clear colourless oil (504 mg, 80%) (Found: C, 68.2; H, 10.6. Calc. for $C_{12}H_{22}OSi$: C, 68.5; H, 10.5); ν_{max}(thin film)/cm^{-1} 2960s (CH), 1715s (C=O), 1632m (C=C), 1250s and 850s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 4.64 (1 H, s, C=C*H*H), 4.62 (1 H, s, C=CH*H*), 2.51–1.90 (7 H, m), 1.70–1.45 (4 H, m) and 0.00 (9 H, s, TMS); δ_C(67.8 MHz; $CDCl_3$; Me_4Si) 211.59 (C), 149.71 (C), 106.39 (CH_2), 47.06 (CH_2), 45.64 (CH), 41.19 (CH_2), 30.40 (CH_2), 25.60 (CH_2), 25.09 (CH_2) and −1.43 $(3 \times CH_3)$; m/z (EI) 210 (M^+, 12%), 195 ($M^+ -$ Me, 100), 167 ($M^+ -$ Me − CO, 93) and 73 (TMS^+, 96); m/z (HRMS) 210.1443 (Calc. for $C_{12}H_{22}OSi$: 210.1443).

1-(2-Trimethylsilylprop-2-enyl)cyclohexanol 11. To a solution of cyclohexanone (310 mm^3, 3 mmol) and boron trifluoride–diethyl ether (406 mm^3, 3.3 mmol) in ether (10 cm^3) at −15 °C was added a solution of the pre-formed allylzinc reagent **1** [3.3 mmol in ether (11 cm^3)] over 10 min. After the mixture had been stirred for 1.5 h it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined organic layer and extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography in 10% ether–pentane (R_F 0.41) yielded the title compound as a clear colourless oil (417 mg, 66%) (Found: C, 67.8; H, 11.3. Calc. for $C_{12}H_{24}OSi$: C, 67.9; H, 11.4.); ν_{max}(thin film)/cm^{-1} 3478br m (OH), 2930m (CH), 2855m (CH), 1447s, 1246m and 838s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.72 (1 H, d, *J* 2, C=C*H*H), 5.57 (1 H, d, *J* 2, C=CH*H*), 2.30 [2 H, s, C*H*$_2$C(TMS)=CH$_2$], 2.67–1.14 (11 H, m, Cy − H + OH) and 0.11 (9 H, s, TMS); δ_C(67.8 MHz; $CDCl_3$; Me_4Si) 148.79 (C), 129.91 (CH_2), 71.15 (C), 48.55 (CH_2), 37.98 $(2 \times CH_2)$, 25.80 (CH_2), 22.16 $(2 \times CH_2)$ and −0.62 $(3 \times CH_3)$; m/z (EI) 194 ($M^+ - H_2O$, 11%), 179 ($M^+ - H_2O -$ Me, 22), 120 (36) and 73 (TMS, 100); m/z 212.1597 (Calc.: 212.1597).

2-Cyclohexylidenecyclohexanone 12. To a solution of cyclohexanone (310 mm^3, 3 mmol) and nickel acetylacetonate (16 mg, 0.06 mmol) in ether (10 cm^3) at −15 °C was added a solution of the pre-formed allylzinc reagent **1** [3.3 mmol in ether (11 cm^3)] over 10 min. After the mixture had been stirred for 0.5 h at −15 °C and then 18 h at room temperature, it was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined organic layer and extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue in 10% ether–pentane (R_F 0.33) yielded the title compound as a clear colourless oil (267 mg, 100%); ν_{max}(thin film)/cm^{-1} 2930s (CH), 2860s (CH), 1682s (C=C), 1620m (C=C), 1448m, 1285m, 1212m and 1130m; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.40 (2 H, m), 2.31 (4 H, m), 2.10 (2 H, m), 1.78 (2 H, m), 1.64 (2 H, m) and 1.48 (6 H, m); δ_C(100 MHz; $CDCl_3$; Me_4Si) 207.02 (C), 147.14 (C), 131.43 (C), 44.13 (CH_2), 32.40 (CH_2), 31.40 (CH_2), 30.34 (CH_2), 29.31 (CH_2), 28.88 (CH_2), 27.25 (CH_2), 26.19 (CH_2) and 26.12 (CH_2); m/z (EI) 178 (M^+) and 149; m/z (HRMS) 178.1358 (Calc.: 178.1359).

2-(2-Trimethylsilylprop-2-enyl)cyclohex-3-enol 20 and 4-(2-trimethylsilylprop-2-enyl)cyclohex-2-enol 21. To a solution of 3,4-epoxycyclohexene (480 mg, 5 mmol) in ether (15 cm^3) at −15 °C was added a solution of the pre-formed allylzinc **1** [5.5 mmol in ether (18.5 cm^3)] over 10 min. After 5 min the mixture was treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was extracted with ether and the combined organic layer and extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography in 30% ether–pentane followed by chromatography in 20% ethyl acetate–hexane yielded the regioisomeric title compounds as clear colourless oils.

20: (389 mg, 37%), R_F 0.32 (in 30% ether–hexane) (Found: C, 68.1; H, 10.5. Calc. for $C_{12}H_{22}OSi$: C, 68.5; H, 10.5); ν_{max}(thin film)/cm^{-1}; 3350br s (OH), 3025m (C=CH), 2958s (CH), 1437m, 1410m, 1251s, 1046m, 930m, 837s, 760m and 692m; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 5.66 (1 H, dt, *J* 3 and 1.5, C=C*H*H), 5.66–5.58 (1 H, m, HC=C*H*), 5.51–5.45 (1 H, m, *H*C=CH), 5.45 (1 H, dt, *J* 3 and 1, C=CH*H*), 3.59 [1 H, ddd, *J* 10 and 7 and 3, C(*H*)OH], 2.51 (1 H, ddt, *J* 14 and 6 and 1, C*H*HC=C), 2.30–1.98 (4 H, m), 1.97–1.80 (1 H, m), 1.65 [1 H, dddd, *J* 12.5 and 9.5 and 8.5 and 6, H*H*CC(H)OH] and 0.12 (9 H, s, TMS); δ_C(100 MHz; CDCl$_3$; Me$_4$Si) 151.03 (C), 128.42 (CH), 126.28 (CH), 126.14 (CH$_2$), 71.95 (CH), 42.53 (CH), 40.90 (CH$_2$), 29.56 (CH$_2$), 23.64 (CH$_2$) and −1.30 (3 × CH$_3$); *m*/*z* (EI) 195 (M$^+$ − Me, 3%), 119 (35), 96 (100), 73 (TMS$^+$, 95), 45 (52); *m*/*z* (CI) 228 (M + NH$_4$$^+$, 13), 211 (MH$^+$, 10), 193 (45), 121 (85) and 90 (100); *m*/*z* (HRMS) 210.1443 (Calc. for $C_{12}H_{22}OSi$: 210.1443).

21: (193 mg, 18%), R_F 0.20 (in 30% ether–hexane) 3.5:1 ratio of diastereoisomers, by GC analysis (Found: C, 68.2; H, 10.4. Calc. for $C_{12}H_{22}OSi$: C, 68.5; H, 10.5); ν_{max}(thin film)/cm^{-1} 3345br s (OH), 3025m (=CH$_2$), 2940s (CH), 1408m, 1248m and 860m; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 5.80–5.70 (2 H, m, C*H*=CH), 5.58 (1 H, d, *J* 1, =C*H*H), 5.42 (1 H, d, *J* 1, =CH*H*), 4.24–4.11 [1 H, m, C*H*(OH)], 2.31–1.99 (3 H, m, HCCH$_2$C=C), 1.90–1.10 (5 H, m) and 0.08 (9 H, s, TMS); δ_C(100 MHz; CDCl$_3$; Me$_4$Si) 149.92 (C), 135.23 (CH), 128.74 (CH), 125.91 (CH$_2$), 66.82 (CH), 42.37 (CH$_2$), 34.06 (CH), 30.17 (CH$_2$), 24.06 (CH$_2$) and −1.37 (3 × CH$_3$); *m*/*z* (EI) 192 (M$^+$ − H$_2$O, 16%), 177 (M$^+$ − H$_2$O − Me, 6), 118 (22), 79 (66) and 73 (TMS$^+$, 100); *m*/*z* (CI) 228 (M + NH$_4$$^+$, 7), 211 (MH$^+$, 17), 210 (83), 193 (100) and 90 (99); *m*/*z* 210.1443 (Calc. for $C_{12}H_{22}OSi$: 210.1443).

2-(4-Isopropylphenyl)-1-trimethylsilylprop-2-ene 22. To 4-iodoisopropylbenzene (984 mg, 4 mmol) and tetrakistriphenylphosphinepalladium (116 mg, 0.1 mmol) in ether (5 cm^3) at −15 °C was added a solution of the pre-formed allylzinc reagent **1** [4.4 mmol in ether (15 cm^3)] over 10 min. The mixture was stirred for 10 min after which it was treated with saturated aqueous ammonium chloride to quench the reaction. The layers were separated and the aqueous layer extracted with ether. The combined organic layer and extracts were washed with brine, dried (MgSO$_4$) and concentrated. Chromatography of the residue with hexane (R_F 0.39) yielded a clear colourless oil (817 mg, 88%), and recovered starting material (46 mg, 5%) (Found: C, 77.2; H, 10.3. Calc. for $C_{15}H_{24}Si$: C, 77.5; H, 10.4); ν_{max}(thin film)/cm^{-1} 3085w (ArH), 2963m (CH), 1616m (C=C), 1249s, 855s and 839s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 7.32 (2 H, d, *J* 7, ArH), 7.14 (2 H, d, *J* 7, ArH), 5.11 (1 H, s, =C*H*H), 4.81 (1 H, s, =CH*H*), 2.88 (1 H, hept, *J* 7, C*H*Me$_2$), 1.99 (2 H, s, C*H*$_2$TMS), 1.24 [6 H, d, *J* 7, CH(C*H*$_3$)$_2$] and 0.10 [9 H, s, Si(CH$_3$)$_3$]; δ_C(100 MHz; CDCl$_3$; Me$_4$Si) 147.87 (C), 146.34 (C), 140.15 (C), 126.19 (2 × CH), 126.05 (2 × CH), 109.27 (CH$_2$), 33.72 (CH), 26.02 (CH$_2$), 23.97 (2 × CH$_3$) and −1.37 (3 × CH$_3$); *m*/*z* (EI) 232 (M$^+$, 8%), 217 (M$^+$ − Me, 9), 189 (M$^+$ − Pr, 51) and 73 (TMS$^+$, 100); *m*/*z* 232.1648(24) (Calc. for $C_{15}H_{24}Si$: 232.1647).

2,3-Bis(trimethylsilylmethyl)buta-1,3-diene 26. To benzyl bromide (594 mm^3, 5 mmol) and tetrakistriphenylphosphinepalladium (173 mg, 0.15 mmol) in ether (15 cm^3) at −15 °C was added a solution of the pre-formed prop-2-enylzinc reagent **1** [5.5 mmol in ether (18.5 cm^3)] over 10 min. The mixture was stirred for 15 min after which it was treated with saturated aqueous ammonium chloride to quench the reaction. The layers were separated and the aqueous layer was extracted with ether. The combined organic layer and extracts were washed with brine, dried (MgSO$_4$) and concentrated. Chromatography of the residue with pentane yielded three components.

26: (315 mg, 51%, based on allylzinc), R_F 0.62 (Found: C, 63.6; H, 11.6. Calc. for $C_{12}H_{26}Si_2$: C, 63.6; H, 11.6); ν_{max}(thin film)/cm^{-1} 3098w (=CH$_2$), 2955, 2900s (CH), 1588m (C=C), 1414m, 1249s, 1162m, 840s and 697s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 4.92 [2 H, s, (C=C*H*H)$_2$], 4.73 [2 H, s, (C=CH*H*)$_2$], 1.75 [4 H, s, (C*H*$_2$TMS)$_2$] and 0.00 [18 H, s, Si(CH$_3$)$_3$]; δ_C(67.8 MHz; CDCl$_3$; Me$_4$Si) 145.81 (2 × C), 110.98 (2 × CH$_2$), 24.08 (2 × CH$_2$) and −1.07 (6 × CH$_3$); *m*/*z* (EI) 226 (M$^+$, 20%), 211 (M$^+$ − Me, 11), 123 (32) and 73 (TMS, 100); *m*/*z* (HRMS) 226.1572 (Calc. for $C_{12}H_{26}Si_2$: 226.1573).

24: (134 mg, 13%), R_F 0.48; ν_{max}(thin film)/cm^{-1} 3065w (ArH), 3030w (=CH), 2958 and 2900s (CH), 1633m (C=C), 1248s, 850s and 699s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 7.40–7.18 (5 H, m, ArH), 4.69 (1 H, s, =CHH), 4.62 (1 H, s, =CHH), 3.32 (2 H, s, ArC*H*$_2$), 1.55 (2 H, s, C*H*$_2$TMS) and 0.10 [9 H, s, Si(CH$_3$)$_3$]; δ_C(67.8 MHz; CDCl$_3$; Me$_4$Si) 146.75 (C), 139.85 (C), 129.10 (2 × CH), 128.22 (2 × CH), 126.01 (CH), 109.44 (CH$_2$), 45.04 (CH$_2$), 26.11 (CH$_2$) and −1.25 (3 × CH$_3$); *m*/*z* (EI) 204 (M$^+$, 20%) and 73 (TMS, 100); *m*/*z* (HRMS) 204.1339 (Calc. for $C_{13}H_{20}Si$: 204.1334).

Benzyl bromide (446 mg, 75%).

2-Benzyl-3-trimethylsilylpropene 24, 1,2-diphenylethane 25 and 2,3-bis(trimethylsilylmethyl)buta-1,3-diene 26. To benzyl bromide (238 mm^3, 2 mmol) and nickel acetylacetonate (14 mg, 0.05 mmol) in ether (5 cm^3) at −15 °C was added a solution of the pre-formed prop-2-enylzinc reagent **1** [2.2 mmol in ether (7.7 cm^3)] over 10 min. The mixture was stirred for 36 h at room temperature after which it was treated with saturated aqueous ammonium chloride to quench the reaction. The layers were separated and the aqueous layer was extracted with ether. The combined organic layer and extracts were washed with brine, dried (MgSO$_4$) and concentrated. Chromatography of the residue with pentane yielded three components.

26: (25 mg, 10%, based on allylzinc), R_F 0.62 (Found: C, 63.6; H, 11.6. Calc. for $C_{12}H_{26}Si_2$: C, 63.6; H, 11.6); ν_{max}(thin film)/cm^{-1} 3098w (=CH$_2$), 2955, 2900s (CH), 1588m (C=C), 1414m, 1249s, 1162m, 840s and 697s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 4.92 [2 H, s, (C=C*H*H)$_2$], 4.73 [2 H, s, (C=CH*H*)$_2$], 1.75 [4 H, s, C*H*$_2$TMS)$_2$] and 0.00 [18 H, s, Si(CH$_3$)$_3$]; δ_C(67.8 MHz; CDCl$_3$; Me$_4$Si) 145.81 (2 × C), 110.98 (2 × CH$_2$), 24.08 (2 × CH$_2$) and −1.07 (6 × CH$_3$); *m*/*z* (EI) 226 (M$^+$, 20%), 211 (M$^+$ − Me, 11), 123 (32) and 73 (TMS, 100); *m*/*z* (HRMS) 226.1572 (Calc. for $C_{12}H_{26}Si_2$: 226.1573).

24: (56 mg, 14%), R_F 0.48; ν_{max}(thin film)/cm^{-1} 3065w (ArH), 3030w (=CH), 2958, 2900s (C–H), 1633m (C=C), 1248s, 850s and 699s; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 7.40–7.18 (5 H, m, ArH), 4.69 (1 H, s, C=C*H*H), 4.62 (1 H, s, C=CH*H*), 3.32 (2 H, s, ArC*H*$_2$), 1.55 (2 H, s, C*H*$_2$TMS) and 0.10 [9 H, s, Si(CH$_3$)$_3$]; δ_C(67.8 MHz; CDCl$_3$; Me$_4$Si) 146.75 (C), 139.85 (C), 129.10 (2 × CH), 128.22 (2 × CH), 126.01 (CH), 109.44 (CH$_2$), 45.04 (CH$_2$), 26.11 (CH$_2$) and −1.25 (3 × CH$_3$); *m*/*z* (EI) 204 (M$^+$, 20%) and 73 (TMS, 100); *m*/*z* (HRMS) 204.1339 (Calc. for $C_{13}H_{20}Si$: 204.1334).

25: (99 mg, 54%, based on benzyl bromide), R_F 0.29; δ_H(270 MHz; CDCl$_3$; Me$_4$Si) 7.46–7.23 (10 H, m, ArH) and 3.03 (4 H, s, ArC*H*$_2$); *m*/*z* (EI) 182 (M$^+$, 42%) and 91 (PhCH$_2$$^+$, 100).

3-*tert*-Butyl(diphenyl)silyl-2-bromoprop-1-ene 27. *tert*-Butyl(diphenyl)silyl chloride (7.7 cm^3, 30 mmol) was added to a stirred suspension of lithium wire (2% sodium) (1.26 g, 180 mmol) in THF (30 cm^3) at 0 °C. The colour began to darken after 10 min. The mixture was stirred for 4 h to yield a dark-brown solution which was titrated against butylated hydroxytoluene with fluorene as indicator. The titre indicated the solution was 0.82 mol dm^{-3}. To copper(I) cyanide (1.16 g, 13 mmol) in THF (20 cm^3) at 0 °C was added the *tert*-butyl(diphenyl)silyllithium (31.7 cm^3, 26 mmol) over 5 min. The colour initially became mauve and then rapidly darkened. The resulting black solution was stirred for 30 min and then cooled to −78 °C. 2,3-Dibromopropene (2.7 cm^3, 26 mmol) [which had been freshly distilled (64–65 °C at 49 mmHg)] in THF (10 cm^3) was added over 10 min to the mixture which was then stirred at −70 to −78 °C for 10 min. It was then allowed to warm to room temperature over 2 h before being diluted by the slow addition of saturated aqueous ammonium chloride to quench the reaction. The mixture was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue in hexane (R_F 0.22) yielded the title compound in 91% purity by GC analysis (6.05 g, 59%); ν_{max}(thin film)/cm^{-1} 3052w (ArH), 2930, 2858m (CH), 1618m, 1427s, 1104s and 696s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.72–7.60 (4 H, m, ArH), 7.47–7.30 (6 H, m, ArH), 5.16 (2 H, s, C=CH_2), 2.73 (2 H, s, $SiCH_2$) and 1.05 (9 H, s, Bu^t); δ_C(100 MHz; $CDCl_3$; Me_4Si) 136.17 (4 × CH), 133.22 (2 × C), 130.00 (C), 129.39 (2 × CH), 127.56 (4 × CH), 117.73 (CH_2), 27.66 (3 × CH_3), 26.78 (CH_2) and 18.51 (C); *m*/*z* (EI) (consistent with 1 bromine) 303/301 (M^+ − Bu, 18/15%), 263/261 (Ph_2Si^+Br, 100/96), 239 (16), 197 (28), 181 (31), 135 (73) and 105 (29); *m*/*z* (CI) 361/359 (MH^+, < 1/< 1%) and 256 (100); *m*/*z* 301.0073 (Calc. for M^+ − Bu: $C_{15}H_{14}BrSi$ 301.0048).

2-*tert*-Butyl(diphenyl)silylmethyl-4,5-epoxy-4-methylhept-1-en-3-ol 28. To a suspension of magnesium (0.60 g, 25 mmol) and 1,2-dibromoethane (43 cm^3, 0.5 mmol) in THF (20 cm^3) was added the prop-2-enylsilane **27** (4.44 cm^3, 26 mmol) dropwise over 30 min, a gentle reflux being maintained after initiation had occurred. Upon cooling to 0 °C the reaction mixture, an opaque olive solution, provided a gelatinous precipitate. The aldehyde (1.14 cm^3, 0.01 mol) in THF (5 cm^3) was added dropwise to the Grignard solution over 20 min and the reaction mixture allowed to warm to room temperature over 1 h. Saturated aqueous ammonium chloride was added carefully with stirring to the mixture until no precipitate remained after which it was filtered and the aqueous layer separated and extracted with ether. The combined organic layer and extracts were dried ($MgSO_4$), filtered through a silica plug, evaporated and the residue dried *in vacuo*. Chromatography of the residue with 20% ether–hexane as the eluent yielded the two diastereoisomeric products.

28a: (0.48 g, 12%), R_F 0.30; ν_{max}(thin film)/cm^{-1} 3462br m (OH), 3073m (ArH), 2966, 2935, 2861s (CH), 1958, 1898, 1821w (ArH), 1640w (C=C), 1468m, 1428m, 1106s, 738s and 701s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.73–7.61 (4 H, m, ArH), 7.45–7.29 (6 H, m, ArH), 4.87 (1 H, s, C=C*H*H), 4.73 (1 H, s, C=CH*H*), 3.63 [1 H, s, C(*H*)OH], 2.98 (1 H, t, *J* 7, C*H*CH_2), 2.33 (1 H, d, *J* 15, C*H*HTBDPS), 2.08 (1 H, d, *J* 15, CH*H*TBDPS), 1.77 (1 H, s, OH), 1.64 (1 H, dpent, *J* 14 and 7, CHC*H*HCH_3), 1.51 (1 H, dpent, *J* 14 and 7, CHCH*H*CH_3) and 1.09–0.97 (15 H, m, 5 × CH_3); δ_C(100 MHz; $CDCl_3$; Me_4Si) 144.31 (C), 136.30 (2 × CH), 136.18 (2 × CH), 134.47 (C), 134.05 (C), 129.19 (2 × CH), 127.50 (2 × CH), 127.48 (2 × CH), 114.02 (CH_2), 77.39 (CH), 61.74 (C), 61.13 (CH), 27.74 (3 × CH_3), 21.58 (CH_2), 18.45 (C), 14.84 (CH_2), 13.74 (CH_3) and 10.55 (CH_3); *m*/*z* (EI) 337 (M^+ − Bu, 4%), 319 (2), 279 (100), 199 (94) and 135 (79); *m*/*z* (CI) 412 (M + NH_4^+, 100%), 395 (MH^+, 9), 337 (100) and 317 (80); *m*/*z* (HRMS) 394.2336 (Calc. for $C_{25}H_{34}O_2Si$: 394.2328).

28b: (1.79 g, 45%), R_F 0.21 (Found: C, 75.8; H, 8.75. Calc. for $C_{25}H_{34}OSi$: C, 75.7; H, 8.5); ν_{max}(thin film)/cm^{-1} 3462br m (OH), 3072 (m, ArH), 2965, 2930, 2857s (CH), 1957, 1887, 1823w (ArH), 1641w (C=C), 1464m, 1428m, 1107s, 736s and 702s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.72–7.55 (4 H, m, ArH), 7.45–7.28 (6 H, m, ArH), 5.00 (1 H, s, C=C*H*H), 4.79 (1 H, s, C=CH*H*), 3.24 [1 H, d, *J* 4, C(*H*)OH], 2.64 (1 H, t, *J* 7, C*H*CH_2), 2.32 (1 H, d, *J* 15, C*H*HTBDPS), 1.89 (1 H, d, *J* 15, CH*H*TBDPS), 1.58 (1 H, d, *J* 4, OH), 1.61 (1 H, dpent, *J* 14 and 7, CHC*H*HCH_3), 1.47 (1 H, dpent, *J* 14 and 7, CHCH*H*CH_3), 1.10 (3 H, s, CH_3), 1.02 [9 H, s, C(CH_3)$_3$] and 1.00 (3 H, t, *J* 7, CHCH_2C*H*$_3$); δ_C(100 MHz; $CDCl_3$; Me_4Si) 143.88 (C), 136.23 (2 × CH), 136.16 (2 × CH), 134.20 (C), 134.10 (C), 129.32 (CH), 129.26 (CH), 127.55 (2 × CH), 127.52 (2 × CH), 112.25 (CH_2), 79.17 (CH), 63.14 (CH), 62.59 (C), 27.74 (3 × CH_3), 21.43 (CH_2), 18.44 (C), 15.89 (CH_2), 11.63 (CH_3) and 10.48 (CH_3); *m*/*z* (EI) 337 (M^+ − Bu, 2%), 319 (2), 279 (93), 199 (100) and 135 (92); *m*/*z* (CI) 412 (M + NH_4^+, 100%), 395 (MH^+, 9), 337 (62) and 317 (51); *m*/*z* (HRMS) 394.2336 (Calc. for $C_{25}H_{34}O_2Si$: 394.2328).

2-*tert*-Butyl(diphenyl)silyl-5,6-epoxy-5-methyloct-1-en-4-ol 29. A solution of 2-(bromoprop-2-enyl)-*tert*-butyl(diphenyl)-silane (3.6 g, 10 mmol) in ether (10 cm^3) at −70 °C was treated with Bu^{t}Li (1.5 mol dm^{-3} in pentane solution; 13.5 cm^3, 20 mmol) over 10 min (exotherm to −50 °C). The pale yellow solution was stirred for 5 min at −70 °C after which it was treated with a solution of zinc dichloride (1.0 mol dm^{-3} in ether solution; 10.5 cm^3, 10.5 mmol), added over 10 min (exotherm to −50 °C). The mixture was stirred for 10 min at −70 °C after which it was made up to 30 cm^3 with ether (aliquots of this solution were added to different reactions). For example, the organozinc reagent was stirred at ambient temperature for 2.5 h before being added (1.5 mmol) to the aldehyde **6** (116 g, 1 mmol) in ether (5 cm^3) (pre-dried with molecular sieves). The mixture was stirred for 10 min and treated with saturated aqueous ammonium chloride to quench the reaction. The aqueous layer was separated and extracted with ether and the combined organic layer and extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue in 20% ether–hexane yielded two diastereoisomeric products.

29a: A clear colourless oil (149 mg, 38%), R_F 0.29; ν_{max}(thin film)/cm^{-1} 3491br s (OH), 3070w (ArH), 2967, 2859s (CH), 1469m, 1426s, 1104s, 909s, 734s and 702s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.70–7.57 (4 H, m, Ph), 7.45–7.29 (6 H, m, Ph), 6.17 (1 H, d, *J* 0.5, C=C*H*H), 5.83 (1 H, d, *J* 1, C=CH*H*), 3.38 (1 H, br d, *J* 10, C*H*OH), 2.82 (1 H, t, *J* 7, C*H*CH_2), 2.43 (1 H, br d, *J* 14, H*H*CCHOH), 2.08 (1 H, dd, *J* 14 and 10, *H*HCCHOH), 1.99 (1 H, br s, OH), 1.53 (1 H, dpent, *J* 14 and 7, C*H*HCH_3), 1.40 (1 H, dpent, *J* 14 and 7, CH*H*CH_3), 1.15 (9 H, s, Bu^t), 0.93 (3 H, t, *J* 7, CH_2C*H*$_3$) and 0.84 (3 H, s, CH_3); δ_C(67.8 MHz; $CDCl_3$; Me_4Si) 142.56 (C), 136.42 (2 × CH), 136.24 (2 × CH), 134.43 (C), 134.28 (C), 132.49 (CH_2), 129.19 (CH), 129.18 (CH), 127.71 (2 × CH), 127.64 (2 × CH), 70.78 (CH), 62.47 (C), 60.58 (CH), 41.01 (CH_2), 28.64 (3 × CH_3), 21.29 (CH_2), 18.59 (C), 13.53 (CH_3) and 10.37 (CH_3); GC–MS *m*/*z* (EI) 337 (M^+ − Bu, 1%), 319 (5), 279 (72), 251 (48), 201 (100), 199 (55), 183 (37) and 173 (36); *m*/*z* (CI) 412 (M + NH_4^+, 1%), 361 (48), 354 (100), 259 (97) and 256 (73); *m*/*z* (HRMS) 319.1523 (Calc. for M^+ − Bu − H_2O: 319.1518).

29b: A clear colourless oil (64 mg, 16%), R_F 0.15; ν_{max}(thin film)/cm^{-1} 3460br s (OH), 3070w (ArH), 2967, 2859s (CH), 14m, 1426s, 1104s, 1054m, 909s, 734s and 702s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.72–7.55 (4 H, m, Ph), 7.45–7.29 (6 H, m, Ph), 6.15 (1 H, d, *J* 0.5, C=C*H*H), 5.86 (1 H, d, *J* 1, C=CH*H*), 2.88 (1 H, br d, *J* 10, C*H*OH), 2.36 (1 H, br d, *J* 14, H*H*CCHOH), 2.23 (1 H, dd, *J* 14 and 10, *H*HCCHOH), 2.08 (1 H, t, *J* 7, C*H*CH_2), 1.78 (1 H, br s, OH), 1.51–1.20 (2 H, m, C*H*$_2$$CH_3$), 1.12 (9 H, s, Bu^t), 1.03 (3 H, s, CH_3) and 0.84 (3 H, t, *J* 7, CH_2C*H*$_3$); δ_C(67.8 MHz; $CDCl_3$; Me_4Si) 142.43 (C), 136.37 (2 × CH), 136.24 (2 × CH), 134.41 (C), 134.09 (C), 132.87 (CH_2), 129.32 (CH), 129.25 (CH), 127.78 (2 × CH), 127.76 (2 × CH), 74.46 (CH), 63.30 (C), 62.42 (CH), 41.70 (CH_2), 28.61 (3 × CH_3), 21.23 (CH_2), 18.66 (C), 11.24 (CH_3) and 10.35 (CH_3); GC–MS *m*/*z* (EI) 319 (5%), 279 (100), 251 (45), 201 (100), 199 (70), 183 (30), 181 (38) and 173 (36); *m*/*z* (CI) 412 (M + NH_4^+, 1%), 361 (22), 354 (31), 259 (100) and 256 (38); *m*/*z* (HRMS) 319.1523 (Calc. for M^+ − Bu − H_2O: 319.1518).

Acknowledgements

We acknowledge the assistance of Mr Adrian Shell in the preparation of this manuscript and to Peter Heath, J. Nangle, P. Stanley and M. Kipps for detailed NMR studies.

References

1 B. M. Trost and I. Fleming, *Comprehensive Organic Synthesis*, Pergamon, Oxford, 1991, vol. 1, ch. 1.

2 (*a*) E. D. Hughes, C. K. Ingold and G. A. Mair, *J. Chem. Soc.*, 1948, 2072; (*b*) T. Imamoto, T. Kasumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka and M. Yokoyama, *J. Org. Chem.*, 1984, **49**, 3904.

3 (*a*) K. V. Baker, J. M. Brown, N. Hughes, A. J. Skarnulis and A. Sexton, *J. Org. Chem.*, 1991, **56**, 698–703; (*b*) C. Petrier, J. C. de Souza Barbosa, C. Dupuy and J.-L. Luche, *J. Org. Chem.*, 1985, **50**, 5761–5765; (*c*) P. Knochel, M. C. P. Yeh, S. C. Berk and J. Talbert, *J. Org. Chem.*, 1988, **53**, 2390; (*d*) E. Erdik, *Tetrahedron*, 1987, **43**, 2203; (*e*) R. D. Rieke, *Acc. Chem. Res.*, 1977, **10**, 301.

4 H. O. House, W. L. Respess and G. M. Whitesides, *J. Org. Chem.*, 1966, **31**, 3128.

5 A. Yanagisawa, K. Yasue and H. Yamamoto, *Synlett*, 1992, 593.

6 (*a*) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, 1952, **74**, 5828; (*b*) J. W. Cornforth, R. H. Cornforth and K. K. Mathew, *J. Chem. Soc.*, 1959, 112; (*c*) M. Chèrest, H. Felkin and N. Prudent, *Tetrahedron Lett.*, 1968, **9**, 2199; (*d*) N. T. Anh, *Top. Curr. Chem.*, 1980, **88**, 145; (*e*) M. T. Reetz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 1035.

7 (*a*) I. Fleming and M. Rowley, *Tetrahedron*, 1989, **45**, 413; (*b*) A. Barbero, P. Cuadrado, A. M. Gonzalez, F. J. Pulido and I. Fleming, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2811; (*c*) F. J. Blanco, P. Cuadrado, A. M. Gonzalez, F. J. Pulido and I. Fleming, *Tetrahedron Lett.*, 1994, **35**, 8881.

8 L. E. Overman and P. A. Renhowe, *J. Org. Chem.*, 1994, **59**, 4138.

9 H. Nishiyama, H. Yokoyama, S. Narimatsu and K. Itoh, *Tetrahedron Lett.*, 1982, **23**, 1267.

10 B. M. Trost and B. P. Coppola, *J. Am. Chem. Soc.*, 1982, **104**, 3733, 4299, 6879.

11 J. J. Eshelby, P. J. Crowley and P. J. Parsons, *Synlett*, 1993, 277.

12 J. J. Eshelby, P. J. Crowley and P. J. Parsons, *Synlett*, 1993, 279.

13 (*a*) P. Knochel and R. D. Singer, *Chem. Rev.*, 1993, **93**, 2117; (*b*) P. Knochel and J. F. Normant, *Tetrahedron Lett.*, 1984, **25**, 4383.

14 (*a*) H. Achenbach, A. Muhlenfeld, U. Fauth and H. Zahner, *Ann. N. Y. Acad. Sci.*, 1988, **544**, 128, (*b*) H. Nakayama, T. Takatsu, Y. Abe, A. Shimazu, K. Furihata, K. Ikeda, K. Furihata, H. Seto and N. Otake, *Agric. Biol. Chem.*, 1987, **51** (3), 853.

15 M. G. B. Drew, A. Jahans, J. Eshelby and P. J. Parsons, manuscript in preparation.

16 (*a*) C. H. Behrens, S. Y. Ko, B. Sharpless and F. J. Walker, *J. Org. Chem.*, 1985, **50**, 5687; (*b*) G. B. Payne, *J. Org. Chem.*, 1962, **27**, 3819.

17 F. M. Dayrit, D. E. Gladkowski and J. Schwartz, *J. Am. Chem. Soc.*, 1980, **102**, 3976.

18 (*a*) E. Erdik, *Tetrahedron*, 1992, **48**, 9577; (*b*) E. Negishi, A. O. King and N. Okukado, *J. Org. Chem.*, 1977, **42**, 1821.

19 K.-T. Kang, J. C. Lee and J. S. U, *Tetrahedron Lett.*, 1992, **34**, 4953.

20 (*a*) I. Shimizu, K. Hayashi, N. Ide and M. Oshima, *Tetrahedron*, 1991, **47**, (18/19), 2991; (*b*) R. Sturmer, *Liebigs Ann. Chem.*, 1991, 311; (*c*) B. E. Rossiter, T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc.*, 1981, **103**, 464.

Paper 5/04032I
Received 22*nd June* 1995
Accepted 6*th September* 1995