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STEREOSPECIFIC SYNTHESES AND REACTIONS OF ALLYL- AND ALLENYL-SILANES *

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Summary

The stereospecifically *anti* synthesis of allyl- and allenyl-silanes by the reaction of a silylcuprate reagent with allyl and propargyl acetates is described. The S_E2' reactions of these silanes with various electrophiles are shown to proceed with predominantly *anti* stereoselectivity, offset to a greater or lesser extent by other steric factors.

Introduction

The S_E2' reaction of allylsilanes is a well-known, synthetically useful process which is regiochemically reliable [1]. The synthetic utility of the process could be extended if it were shown to be equally stereochemically reliable. However, such investigations have been hampered by the dearth of stereochemically defined allylsilanes. Two that were known were cyclic allylsilanes from our work, and reactions of these with various electrophiles gave products of both *syn* [2] and *anti* [3] stereochemistry. We felt at the time that the stereochemical constraints of the ring system were likely to be the dominant influence on the stereochemistry. However we did discover [4] some reactions of cyclic allylsilanes where the stereochemical preference of the ring system appeared to have been overridden by an *anti* preference of the allylsilane.

The first result in an open chain allylsilane was the *syn* acylative desilylation reported by Wetter [5]. This result has proved to be an anomaly, as the proto- and deutero-desilylation [6] of the same allylsilane is mainly *anti*.

Results by Eschenmoser [7], and more recently by Kumada [8] and by Kitching [9] have shown that allylsilanes will react with a range of electrophiles with high *anti* selectivity.

* Dedicated to Professor Raymond Calas on the occasion of his 70th birthday in recognition of his outstanding research in Organometallic Chemistry during more than thirty years.

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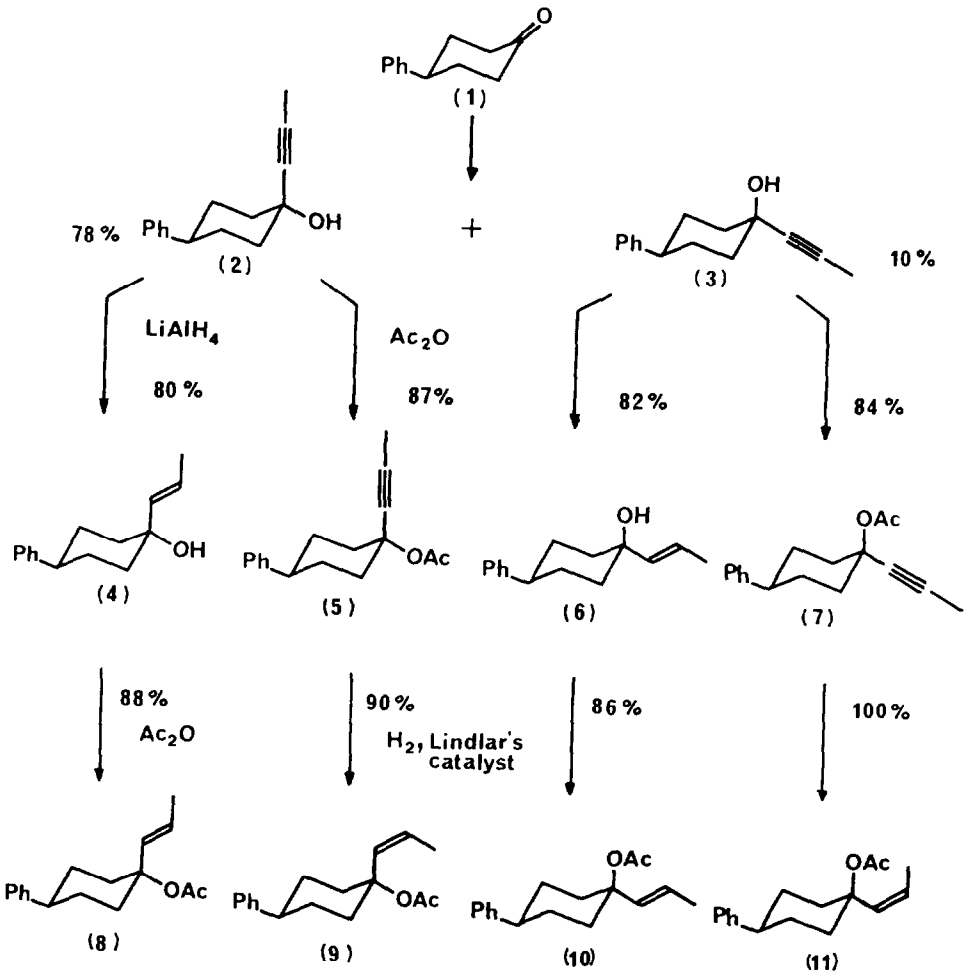
As reported in our preliminary communications [10], we have developed a stereospecific synthesis of acyclic allylsilanes, which have allowed us not only to study the intrinsic stereochemistry of the S_E2' reaction, but also to gain some insight into just how powerfully controlled the stereochemistry is when it is set in competition with other forces. We now report the experimental details of this work.

Results and discussion

A new stereospecific synthesis of allyl- and allenyl-silanes

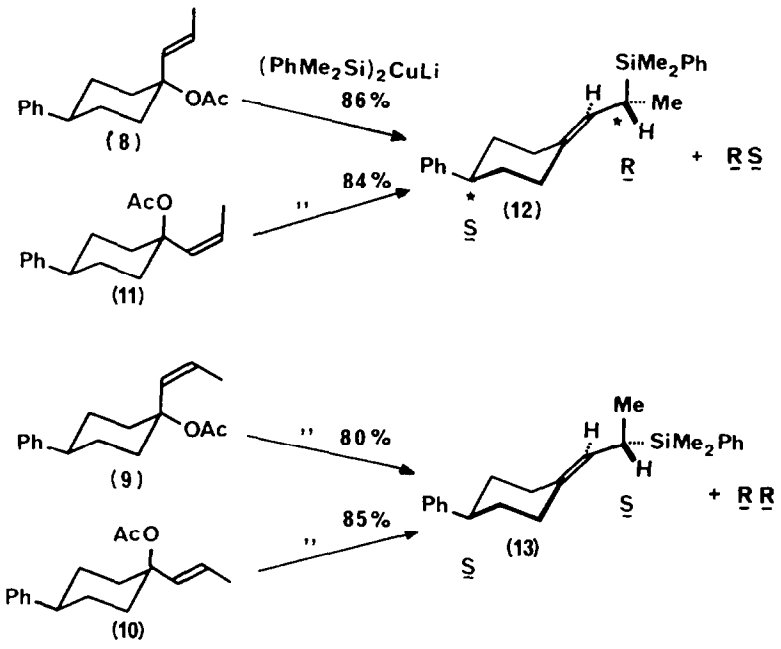
To prepare allylsilanes of known stereochemistry, we exploited the reaction of our silylcuprate reagent with allyl acetates [11]. We prepared the four tertiary allyl acetates (**8**, **9**, **10** and **11**) by routine methods from 4-phenylcyclohexanone (**1**) (Scheme 1). The stereochemistry of the two propargyl alcohols (**2** and **3**) was determined by the method of Rader [12], the ratio of isomers being similar to that



SCHEME 1

observed by Rocquet [13] in the reaction of propynylmagnesium bromide with 4-methylcyclohexanone.

The reaction of the acetates (**8**, **9**, **10** and **11**) with dimethylphenylsilylcuprate [11 and 14] was straightforward and gave a single allylsilane (**12** or **13**) in each case with no cross-contamination detectable by ^{13}C NMR (Scheme 2).



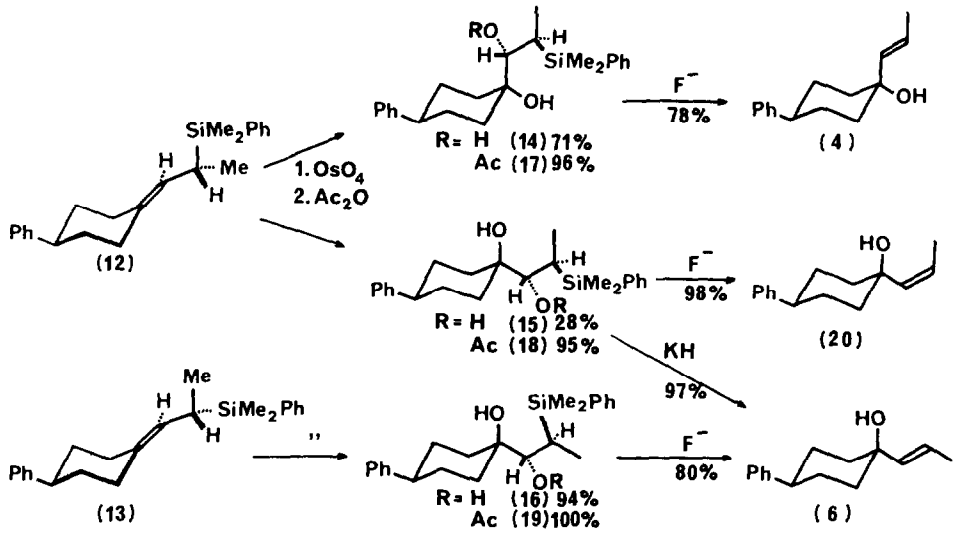
SCHEME 2

The relative configurations of the two allylsilanes were determined by a series of reactions of known stereospecificity to give identifiable products (Scheme 3). Osmylation, a known *syn* [15] process and hydrolysis of the osmate esters gave the silyl-diols (**14**, **15** and **16**). It was hoped to convert these to identifiable allyl alcohols by the Peterson elimination [16], but unfortunately only the silyl-diol (**15**) gave an isolable product, the allyl alcohol (**6**). To confirm the stereochemical assignment which this result gave us, we converted all three diols to their mono acetates (**17**, **18** and **19**), and induced elimination by treatment with fluoride ion to give the alcohols (**4**, **20** and **6**, respectively). We assumed this elimination to be an *anti* process, but there is no literature proof for the stereochemistry of this elimination; analogies do exist [17], and we have obtained further proof for *anti* stereospecifity in other, but unrelated work [18].

Knowing the relative configurations of the allylsilanes we have shown that the silyl-cupration is overall an *anti* process, as expected, by analogy with the known [19] stereochemistry of alkyl-cuprate reactions with allyl acetates.

By the analogous reactions of the propargyl acetates (**5** and **7**) with the silyl-cuprate reagent, we prepared the allenylsilanes (**21** and **22**) again with no discernible cross-contamination evident by ^{13}C NMR (Scheme 4).

The structures of these compounds were determined by an X-ray crystal structure



SCHEME 3

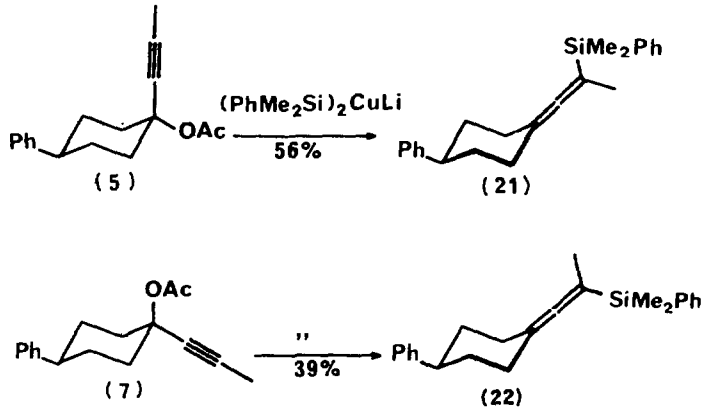
[20] on the crystalline isomer (**21**), and the reaction was thus shown to be again stereospecifically *anti*.

The S_E2' reaction

Having prepared allyl- and allenyl-silanes of known stereochemistry, we examined their reactions with three representative electrophiles.

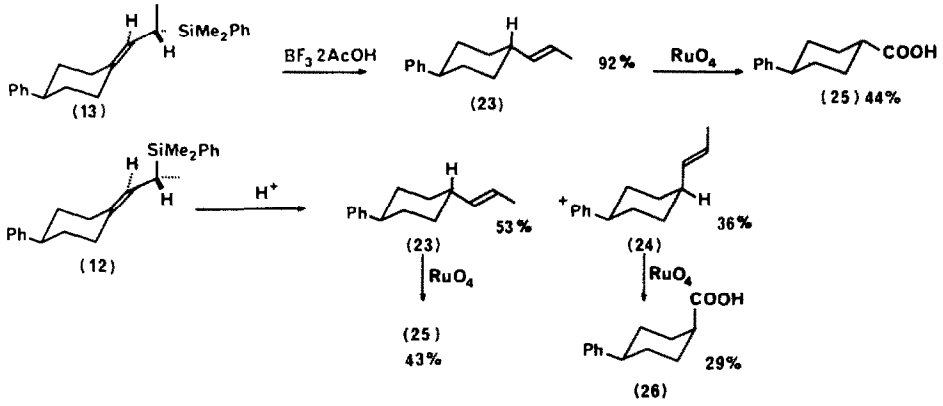
Protodesilylation

Protodesilylation of the allylsilane (**13**) with boron trifluoride-acetic acid was cleanly *anti* and axial, giving rise solely to the *E*-alkene (**23**). This geometry of the alkene is presumably produced by the allylsilane reacting in a conformation in which the hydrogen is the only group small enough to eclipse the double bond (Scheme 5).



SCHEME 4

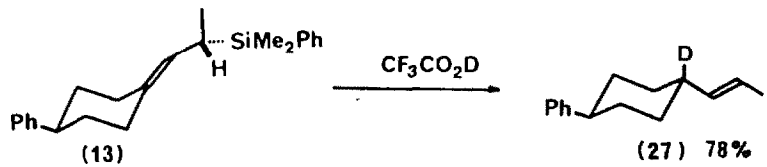
In contrast to this straightforward results, protodesilylation of the diastereomeric allylsilane (**12**) gave a mixture of axial and equatorial *E* alkenes (**23** and **24**). In both



SCHEME 5

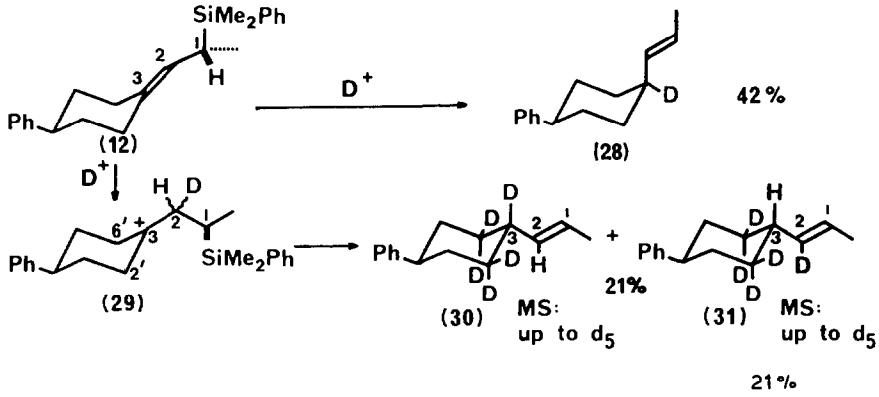
cases, the stereochemistry of the alkenes was determined by NMR, and by oxidation to the known [21] carboxylic acids (**25** and **26**).

Deuterodesilylation of the allylsilanes revealed more about the pathways in these reactions (Scheme 6). The first allylsilane (**13**) reacted cleanly to give the monodeuterated (> 97% d_1 incorporation: ^{2}H NMR, MS. ^{13}C NMR showed a very small, broadened signal for the deuterated carbon C-3, due to the α-effect [22]) alkene (**27**). The diastereomeric allylsilane (**12**) again gave a mixture of products. Chromatographic separation of the axial and equatorial isomers allowed us to examine the deuterium incorporation. While the reaction gave the equatorially deuterated alkene



SCHEME 6

(**28**) in a straightforward S_E2' fashion, the isomeric alkene was a mixture of axially deuterated and protonated *E* alkenes (**30** and **31**). (The position of the deuterium in these isomers was assigned on the basis of the relative intensity of the ^{13}C NMR signal for the methine carbon, C-3; the upfield shifted signal of the olefinic carbon, C-1, due to the β-effect [23]; and the relative intensity of the deuterium signals from the ^{2}H NMR). Thus the anomalous (apparently *syn*) product (**30** and **31**) was revealed to have arisen via an indirect deuteration pathway. As we have observed previously [24] with 3,3-disubstituted allylsilanes, the deuteron has attacked C-2 of the allyl system to give a tertiary cation (**29**) (Scheme 7). This cation can lose protons (and regain deuterons) from C-2′ and C-6′, and will eventually undergo 1,2-hydride or deuteride shift and loss of the silyl group to give the alkenes (**30** and **31**), each of which was a mixture of mono-, di-, tri-, tetra-, and penta-deuterated species. ^{2}H NMR indicated that there was a trace (< 3%) of equatorially protonated alkene product, probably formed by a similar mechanism. The predominance of the axially

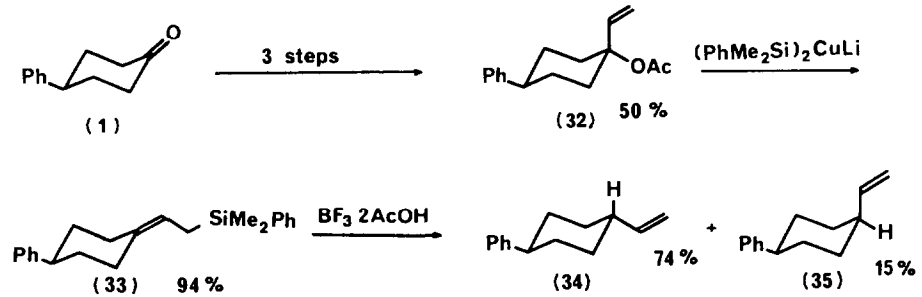


SCHEME 7

protonated alkene over any equatorially protonated product implies that 1,2-hydride (or deuteride) shift took place preferentially on the axial face, to give the thermodynamically more stable equatorial *E* alkene.

The above results imply that in addition to the *anti* selectivity of the allylsilane, the cyclohexyl ring has a preference for axial protonation, and when this axial preference opposes the *anti* selectivity of the allylsilane, the molecule finds an alternative reaction in which stereospecificity is lost.

To investigate the stereoselectivity of the cyclohexyl ring, we prepared the allylsilane (**33**) (Scheme 8) without the methyl group on C-1. Protodesilylation of this allylsilane gave a 5/1 ratio of axially to equatorially protonated products (**34** and **35**).

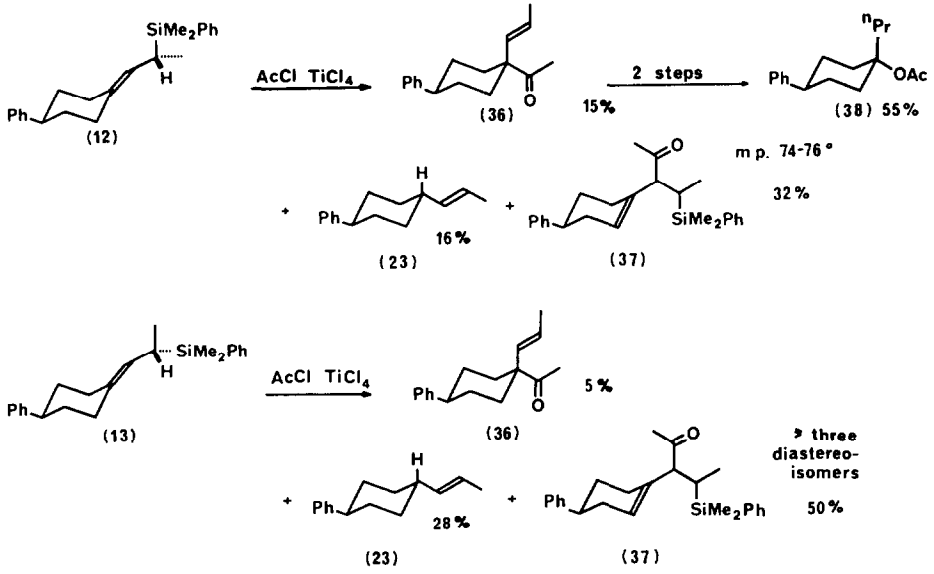


SCHEME 8

Acetylation

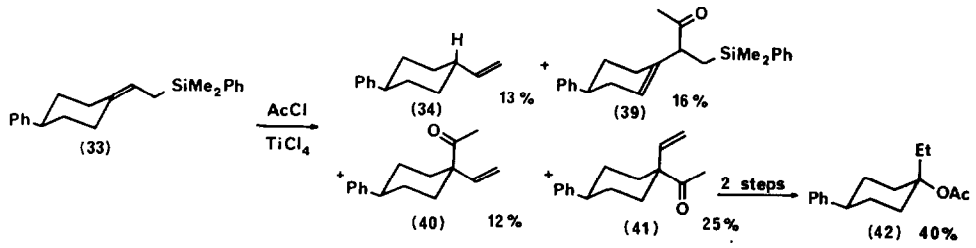
Titanium tetrachloride catalysed acetylation of the allylsilanes gave complicated reaction mixtures. The allylsilane (**12**) gave the ketone (**36**) only as a minor reaction product despite its being the product of an *anti* S_E2' reaction (Scheme 9). The major component of the mixture was the product of acylation on C-2, isolated, surprisingly, as a single diastereoisomer (**37**) of indeterminate stereochemistry. Protodesilylation to give the alkene (**23**) was another major pathway. The diastereomeric

allylsilane (**13**) gave a smaller quantity of the ketone (**36**), now the product of a *syn* S_E2' reaction. We observed none of the isomeric ketone formed by the *anti* S_E2'



SCHEME 9

pathway. Acylation on C-2 was a major pathway, giving a mixture of at least three diastereoisomers (**37**). Protodesilylation was again evident from the alkene (**23**). In so far as stereocontrol is present, there appears to be a preference for equatorial acetylation. This is confirmed by the acetylation of the allylsilane (**33**), which gave, in addition to acylation on C-2, twice as much equatorial ketone (**41**) as axial ketone (**40**) (Scheme 10).



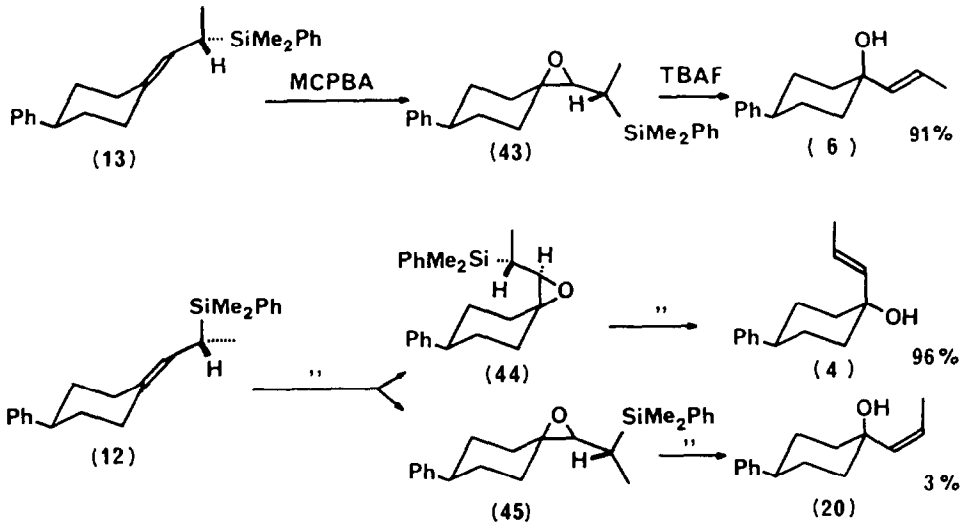
SCHEME 10

The stereochemistry of the ketones (**36** and **41**) was determined by hydrogenation and Baeyer–Villager oxidation to the acetates (**38** and **42**). These were identical to the products derived by hydrogenation of the previously prepared acetates (**9** and **32**).

Epoxidation

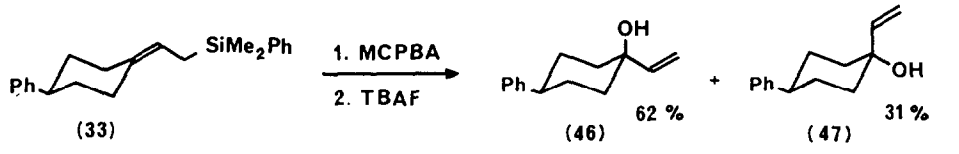
Unlike proto- and acylative-desilylation, epoxidation was a well-behaved reaction.

Treatment of the allylsilanes with *m*-chloroperoxybenzoic acid gave stable, isolable epoxysilanes (**43**, **44** and **45**), but to determine their stereochemistry, we found it more convenient to convert them directly to the recognisable allyl alcohols (**6**, **4** and **20**) by fluoride catalysed desilylation, an *anti* process (Scheme 11). The epoxidations were cleanly *anti* overall and, although there was a small preference for axial attack by the epoxidising species, the overall stereochemistry was very largely determined by the allylsilane group. The axial preference of the cyclohexyl group was confirmed



SCHEME 11

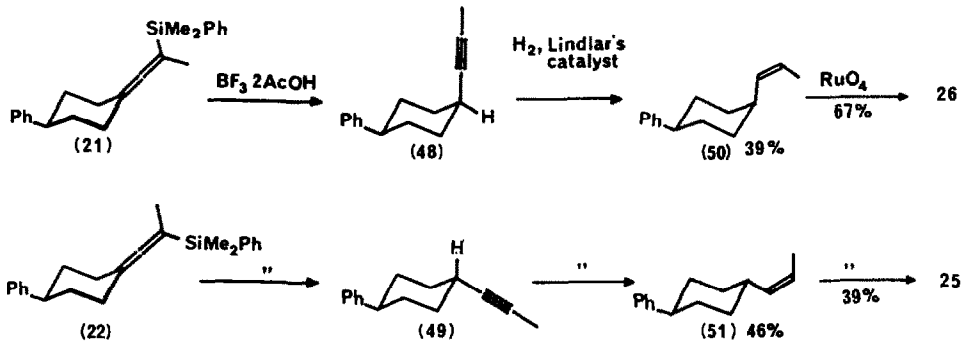
by the corresponding reactions of the allylsilane (**33**), which gave axial and equatorial alcohols (**46** and **47**) in a ratio of 2/1 (Scheme 12).



SCHEME 12

Protodesilylation of the allenylsilanes

Protodesilylation of the allenylsilanes (**21** and **22**) took place in rather poor yield, but with largely *anti* stereochemistry (Scheme 13). The configurations of the products were determined by reduction of the acetylenes (**48** and **49**) to the alkenes (**50** and **51**) and oxidation to the known carboxylic acids [21] (**26** and **25**). The poor yields are not too surprising in view of some of the unusual reactions [25] which allenylsilanes show.



SCHEME 13

Conclusions

In conclusion we have demonstrated a new method for the stereospecific preparation of allyl- and allenylsilanes. In the findings that the S_E2' reaction is *anti* selective, we have supported earlier results, and we are now in a better position to assess how powerful the *anti* selectivity is when it is set in competition with other constraints. In particular, we note that whereas protodesilylation and acylation can be easily led astray, bridging electrophiles such as peracid and osmium tetroxide are very selective for an overall *anti* reaction. It is noteworthy that in our earlier work on cyclic allylsilanes [4], the two electrophiles which reacted *anti* in opposition to the bicyclic framework were peracid, and another bridging electrophile, phenylsulphenyl chloride. The clean formation of an *E* double bond in an *anti* reaction augurs well for the usefulness of the S_E2' reaction in the control of stereochemistry in open-chain systems.

Experimental

General

Infrared spectra were recorded on a Perkin–Elmer 297 grating spectrophotometer. Proton nuclear magnetic resonance spectra were recorded on Varian EM 360A or EM 390 spectrometers. ^{13}C and ^{2}H NMR spectra were recorded on a Bruker WM-250 spectrometer. Chemical shifts were measured in ppm relative to tetramethylsilane (δ 0.00) or dichloromethane (δ 5.35) as internal standard. Mass spectra were recorded on an AEI MS9 or MS30 spectrometer. High resolution mass spectra were recorded on an AEI MS902 spectrometer. Melting points were taken on a Kofler hot-stage melting point apparatus and are uncorrected. Column chromatography was carried out using Merck Kieselgel 60 (70–230 mesh ASTM) or (230–400 mesh ASTM); thin-layer chromatography was performed on plates coated to a thickness of 1.0 mm with Kieselgel 60 PF_{254}. Tetrahydrofuran (THF) was freshly distilled from lithium aluminium hydride under nitrogen: all solvents were distilled before use.

cis- and trans-4-Phenyl-1-(1-propynyl)cyclohexanol (2 and 3)

Propyne (4 l, 0.167 mol) was condensed into a solution of ethylmagnesium

bromide (0.150 mol) (bromoethane 16.4 g and magnesium 3.6 g) in dry THF (175 ml) under argon at −78°C. The mixture was allowed to warm to room temperature and then heated under reflux for 1 h. 4-Phenylcyclohexanone (**1**) (20 g) in dry THF (75 ml) was added dropwise over 10 min. The mixture was stirred for 15 h, poured into water and extracted with ether. The extract was dried ($MgSO_4$) and evaporated in vacuo to give a mixture of the two isomeric alcohols. Separation of the isomers by crystallisation (from hexane) and column chromatography of the mother liquors on silica gel (150 g) eluting with ethyl acetate/light petroleum (b.p. 60–80°C) (1/4, v/v) gave the *cis*-alcohol (**2**) (19.2 g, 78%) as prisms, m.p. 78–80°C (from hexane) (Found: C, 83.8; H, 8.50. $C_{15}H_{18}O$ calcd.: C, 84.1; H, 8.45%), R_F (20% EtOAc/hexane) 0.10, ν_{max} (CH_2Cl_2) 3585 sharp (OH), 3445 broad (OH), and 2245 cm^{-1} (C≡C), δ ($CDCl_3$) 7.4–7.0 (5H, m, Ph), 1.82 (3H, s, Me) and 2.8–1.3 (10H, m, remainder), *m/z* 214 (9%, M^+), 196 (100, $M - H_2O$), 181 (88, $M - Me - H_2O$), and 95 (84, C_6H_7O), and the *trans*-alcohol (**3**) (2.5 g, 10%) as needles, m.p. 91.5–93.5°C (from hexane) (Found: C, 83.9; H, 8.60. $C_{15}H_{18}O$ calcd.: C, 84.1; H, 8.45%), R_F (20% EtOAc/hexane) 0.25, ν_{max} (CH_2Cl_2) 3600 sharp (OH), 3460 broad (OH), and 2240 cm^{-1} (C≡C), δ($CDCl_3$) 7.25–6.7 (5H, m, Ph), 1.85 (3H, s, Me), and 2.6–1.2 (10H, m, remainder), *m/z* 214 (23%, M^+), 199 (15, $M - Me$), 185 (32, $M - C_2H_4$), 171 (8, $M - Me - H_2O$), and 95 (100, C_6H_7O).

cis-(E)-4-Phenyl-1-(1-propenyl)cyclohexanol (4)

Lithium aluminium hydride (4.1 g) and sodium methoxide (6.8 g) were suspended in dry THF (150 ml) and the propargyl alcohol (**2**) (12 g) in dry THF (50 ml) was added dropwise. The mixture was heated under reflux for 2 h and then cautiously poured into water. The product was extracted into ether, the ether dried ($MgSO_4$) and evaporated in vacuo to give the alcohol (**4**) (9.6 g, 80%) as prisms, m.p. 98.5–100°C (from hexane) (Found: C, 83.1; H, 9.30. $C_{15}H_{20}O$ calcd.: C, 83.3; 9.30%), R_F (20% EtOAc/hexane) 0.80, ν_{max} (CCl_4) 3600 sharp (OH), and 3400 cm^{-1} broad (OH), δ ($CDCl_3$) 7.33 (5H, s, Ph), 5.84 (1H, d, *J* 17 Hz, C*H*=CHMe), 5.80 (1H, dq, *J* 17 and 6 Hz, CH=C*H*Me), 2.8–2.4 (1H, m, PhC*H*), 1.78 (3H, d, *J* 6 Hz, CH=CH*Me*), and 2.1–1.5 (9H, m, remainder), *m/z* 216 (15%, M^+), 198 (32, $M - H_2O$), and 97 (100, $M - C_9H_{11}$).

General method for the acetylation of alcohols

The alcohol (1 mmol) and 4-dimethylaminopyridine (0.2 mmol) were dissolved in dry dichloromethane (50 ml). Triethylamine (1 mmol) and acetic anhydride (1 mmol) were added and the mixture was stirred for 2–24 h. The solvent was evaporated in vacuo, and an ether solution of the product washed with 1 *N* hydrochloric acid and sodium hydrogen carbonate solution. The ether was dried ($MgSO_4$) and evaporated in vacuo to give the acetate.

cis-4-Phenyl-1-(1-propynyl)cyclohexyl acetate (5)

The propargyl alcohol (**2**) was acetylated by the general method to give the acetate (**5**) (87%) as plates, m.p. 106.5–108°C (from hexane) (Found: C, 79.7; H, 7.85. $C_{17}H_{20}O_2$ calcd.: C, 79.7; H, 7.85%), R_F (33% EtOAc/hexane) 0.55, ν_{max} (CH_2Cl_2) 2250 (C≡C), and 1738 cm^{-1} (C=O), δ ($CDCl_3$) 7.09 (5H, s, Ph), 2.01 (3H, s, COMe), 1.89 (3H, s, C≡CMe), and 2.7–1.5 (9H, m, remainder), *m/z* 256 (26%, M^+), 214 (100, $M - CH_2CO$), 196 (33, M − AcOH), and 181 (22, $M - Me$ − AcOH).

trans-(E)-4-Phenyl-1-(1-propenyl)cyclohexanol (6)

Lithium aluminium hydride reduction of the alcohol (**3**) gave the alcohol (**6**) (2.1 g, 82%) as needles, m.p. 80–82°C (from hexane) (Found: C, 83.5; H, 9.20. $C_{15}H_{20}O$ calcd.: C, 83.3; H, 9.30%), R_F (20% EtOAc/hexane) 0.20, ν_{max} (CH_2Cl_2) 3610 sharp (OH), 3480 broad (OH), and 976 cm^{-1} (CH=CH), δ ($CDCl_3$) 7.32 (5H, s, Ph), 5.70 (1H, dq, *J* 7 and 16 Hz, CH=C*H*Me), 5.68 (1H, d, *J* 16 Hz, C*H*=CHMe), 2.6–2.2 (1H, m, PhC*H*), 2.68 (3H, d, *J* 7Hz, Me), 1.20 (1H, s, OH), and 2.15–1.30 (8H, m, remainder), *m/z* 216 (28%, M^+), and 97 (100, $M - C_9H_{11}$).

trans-4-Phenyl-1-(1-propynyl)cyclohexyl acetate (7)

The propargyl alcohol (**3**) was acetylated by the general method to give the acetate (**7**) (3.0 g, 84%) as prisms, m.p. 116.5–118°C (from hexane) (Found: C, 79.8; H, 7.60. $C_{17}H_{20}O_2$ calcd.: C, 79.7; H, 7.85%), R_F (20% EtOAc/hexane) 0.35, ν_{max} (CH_2Cl_2) 2255 (C≡C), and 1742 cm^{-1} (C=O), δ ($CDCl_3$) 7.22 (5H, s, Ph), 2.11 (3H, s, COMe), 1.87 (3H, s, C≡CMe), and 2.9–1.4 (9 H, m, remainder), *m/z* 256 (8%, M^+), 214 (31, $M - CH_2CO$), and 196 (100, M – AcOH).

cis-(E)-4-Phenyl-1-(1-propenyl)cyclohexyl acetate (8)

The alcohol (**4**) was acetylated by the general method to give the acetate (**8**) (88%) as prisms, m.p. 56–57°C (from hexane) (Found: C, 79.2; H, 8.65. $C_{17}H_{22}O_2$ calcd.: C, 79.0; H, 8.60%), R_F (hexane) 0.10, ν_{max} (film) 1732 (C=O), and 1665 cm^{-1} (C=C), δ ($CDCl_3$), 7.17 (5H, s, Ph), 5.95–5.6 (2H, m, CH=CH), 1.94 (3H, s, COMe), 1.74 (3H, d, *J* 5 Hz, CH=CH*Me*), and 2.9–1.1 (9H, m, remainder), *m/z* 258 (1%, M^+), and 198 (100%, M – AcOH).

cis-(Z)-4-Phenyl-1-(1-propenyl)cyclohexyl acetate (9)

The propargyl acetate (**5**) (10 g) was dissolved in ethanol (350 ml) and stirred with Lindlar's catalyst (0.5 g) under hydrogen at 20°C and one atmosphere for 0.5 h. The catalyst was removed by filtration and the solvent was evaporated in vacuo to afford the acetate (**9**) (9 g, 90%) as prisms, m.p. 49.5–51.5°C (from hexane) (Found: C, 78.8; H, 8.35. $C_{17}H_{22}O_2$ calcd.: C, 79.0; H, 8.60%), R_F (35% EtOAc/hexane) 0.60, ν_{max} (CH_2Cl_2) 1738 (C=O), and 1656 cm^{-1} (C=C), δ ($CDCl_3$) 7.02 (5H, s, Ph), 5.56 (1H, d, *J* 10 Hz, C*H*=CHMe), 5.48 (1 H, dq, *J* 10 and 6 Hz, CH=*CH*Me), 1.97 (3H, s, COMe), 1.75 (3H, d, *J* 6 Hz, CH=CH*Me*), and 2.8–1.3 (9H, m, remainder), *m/z* 258 (1%, M^+), and 198 (100%, M – AcOH).

trans-(E)-4-Phenyl-1-(1-propenyl)cyclohexyl acetate (10)

The alcohol (**6**) was acetylated by the general method to give the acetate (**10**) (86%) as prisms, m.p. 31–33°C (from methanol) (Found: C, 78.9; H, 8.60. $C_{17}H_{22}O_2$ calcd.: C, 79.0; H, 8.60%), R_F (15% EtOAc/hexane) 0.50, ν_{max} (CH_2Cl_2) 1736 cm^{-1} (C=O), δ ($CDCl_3$) 7.22 (5H, s, Ph), 5.75 (1H, dq, *J* 5 and 15 Hz, CH=C*H*Me), 5.72 (1H, d, *J* 15 Hz, C*H*=CHMe), 2.05 (3H, s, COMe), 1.70 (3H, d, *J* 5 Hz, CH=CH*Me*), and 2.9–1.2 (9H, m, remainder), *m/z* 258 (3%, M^+), and 198 (100, M – AcOH).

trans-(Z)-4-Phenyl-1-(1-propenyl)cyclohexyl acetate (11)

The propargyl acetate (**7**) (1 g) was dissolved in ethanol (60 ml) and stirred with Lindlar's catalyst (50 mg) under hydrogen at room temperature and pressure for 30 min. The catalyst was removed by filtration and the solvent was evaporated in vacuo

to afford the acetate (**11**) (1.01 g, 100%) as an oil, R_F (33% EtOAc/hexane) 0.60, ν_{max} (CH_2Cl_2) 1736 cm^{-1} (C=O), δ ($CDCl_3$) 7.18 (5H, s, Ph), 5.43 (1H, dq, *J* 5 and 12 Hz, CH=C*H*Me), 5.40 (1H, d, *J* 12 Hz, C*H*=CHMe), 2.08 (3H, s, COMe), 1.70 (3H, d, *J* 5 Hz, CH=CH*Me*), and 2.8–1.2 (9 H, m, remainder) (Found: M^+, 258.1619. $C_{17}H_{22}O_2$ calcd.: *M*, 258.1620), *m/z* 258 (0.25%, M^+), 256 (1, $M - H_2$), and 198 (100, M – AcOH).

General procedure for the preparation of the allylsilanes and allenylsilanes

Phenyldimethylsilyllithium [26] (4.3 mmol) in THF (10 ml) was added to a suspension of dry copper(I) cyanide (191 mg) in dry THF (7 ml) under argon at 0°C. After 30 min, the temperature was reduced to −50°C and the acetate (2.0 mmol) in dry THF (10 ml) was added dropwise. After 3 h the mixture was poured into basic ammonium chloride solution and extracted with hexane. The hexane was washed several times with basic ammonium chloride solution, dried ($MgSO_4$), and evaporated in vacuo. The resulting oil was purified by flash column chromatography on silica gel eluting with hexane, to afford: (*S,R*)- and (*R,S*)-dimethylphenyl-[1-methyl-2-(4-phenylcyclohexylidenyl)ethyl]silane (**12**) [from the (*E*)-propenyl acetate (**8**) (86%), and from the (*Z*)-propenyl acetate (**11**) (84%)] as prisms, m.p. 39–40°C (from ether/methanol) (Found: C, 82.6; H, 8.90. $C_{23}H_{30}Si$ calcd.: C, 82.6; H, 9.05%), R_F (Hexane) 0.25, ν_{max} (CH_2Cl_2) 1246 (SiMe), and 1116 cm^{-1} (SiPh), $\delta(CCl_4)$ 7.8–6.8 (10H, m, 2 × Ph), 5.03 (1H, d, *J* 11 Hz, C=CH), 1.18 (3H, d, *J* Hz, CMe), 0.48 (6H, s, 2 × SiMe), and 3.0–0.8 (10H, m, remainder), δ ($CDCl_3$) 147.3, 138.4, 135.0, 134.2, 128.9, 128.3, 127.6, 126.9, 125.9, 125.0, 44.9, 37.4, 36.3, 34.5, 28.6, 21.1, 15.6, −4.9, and −5.0, *m/z* 334 (21%, M^+), 198 (69, $M - PhMe_2SiH$), and 135 (100, $PhMe_2Si$), and (*S,S*)- and (*R,R*)-dimethylphenyl-[1-methyl-2-(4-phenylcyclohexylidenyl)-ethyl]silane (**13**) [from the (*E*)-propenyl acetate (**10**) (85%), and from the (*Z*)-propenyl acetate (**9**) (80%)] as an oil, R_F (hexane) 0.25, ν_{max} (CH_2Cl_2) 1247 (SiMe) and 1115 cm^{-1} (SiPh), δ (CCl_4) 7.8–7.1 (10H, m, 2 × Ph), 5.12 (1H, d, *J* 11 Hz, C=CH), 1.20 (3H, d, *J* 7 Hz, CMe), 0.48 (6 H, s, 2 × SiMe), and 3.1–1.1 (10H, m, remainder), $\delta(CDCl_3)$ 147.3, 138.3, 135.1, 134.1, 128.8, 128.3, 127.5, 126.8, 125.9, 125.3, 44.9, 37.0, 36.0, 35.2, 28.9, 21.2, 15.8, −4.6, and −5.3, (Found: M^+, 334.2107. $C_{23}H_{38}Si$ calcd.: *M*, 334.2117), *m/z* 334 (8%, M^+), and 135 (100, $PhMe_2Si$).

*trans-(R,R) (S,S)- and cis-(S,R)(R,S)-4-Phenyl-1-[1-hydroxy-2-(dimethylphenylsilyl)propyl]cyclohexanol (**14** and **15**)*

The allylsilane (**12**) (130 mg) was dissolved in pyridine (0.5 ml) and osmium tetroxide (100 mg) in pyridine (2 ml) was added. After 18 h at room temperature, sodium metabisulphite (100 mg) in water (0.5 ml) was added and the mixture was stirred for a further 5 h. More water was added and the mixture was extracted with ether, the ether was dried ($MgSO_4$) and evaporated in vacuo. Separation by preparative thin layer chromatography on silica gel eluting with ethyl acetate/hexane (1/3, v/v) gave the *trans*-silyldiol (**15**) (38 mg, 28%) as an oil, R_F (25% EtOAc/hexane) 0.45, ν_{max} (film) 3450 broad (OH), 1248 (SiMe), and 1114 cm^{-1} (SiPh), $\delta(CCl_4)$ 7.7–7.1 (10H, m, 2 × Ph), 3.30 (1H, d, *J* 5 Hz, C*H*OH), 1.22 (3H, d, *J* 6 Hz, CMe), 0.55 (6H, s, 2 × SiMe), and 2.8–1.1 (12H, m, remainder) (Found: *m/z* 335.1809. $C_{22}H_{27}OSi$ calcd.: $M - Me - H_2O$, 335.1831), *m/z* 335 (0.5%, $M - Me - H_2O$), and 135 (100, $PhMe_2Si$), and the *cis*-silyldiol (**14**) (97 mg, 71%) as prisms, m.p. 115–116°C (from hexane) (Found: C, 75.2; H, 8.50. $C_{23}H_{32}O_2Si$ calcd.: C,

75.0; H. 8.75%), R_F (25% EtOAc/hexane) 0.25, ν_{max} (CH_2Cl_2) 3610 (OH), 3570 (OH), and 1116 cm^{-1} (SiPh), δ(CCl_4) 7.7–6.6 (10H, m, 2 × Ph), 4.02 (1H, m, C*H*OH), 1.42 (3H, s, CMe), 0.71 (6H, d, 2 × SiMe), and 2.9–1.0 (12H, m, remainder), *m/z* 135 (100%, $PhMe_2Si$), and 115 (54, $C_6H_{11}O_2$).

trans-(R,S)(S,R)-4-Phenyl-1-[1-hydroxy-2-(dimethylphenylsilyl)propyl]cyclohexanol (16)

The allylsilane (**13**) (130 mg) was dissolved in pyridine (0.5 ml) and osmium tetroxide (100 mg) in pyridine (2 ml) was added. After 15 h at room temperature, sodium metabisulphite (100 mg) in water (0.5 ml) was added and the mixture was stirred for a further 5 h. More water (20 ml) was added and the mixture was extracted with ether, the ether was dried ($MgSO_4$) and evaporated in vacuo. Purification by preparative thin layer chromatography on silica gel eluting with ethyl acetate/hexane (1/4, v/v) gave the silyldiol (**16**) (124 mg, 94%) as prisms, m.p. 95–97°C (from hexane) (Found: C, 74.9; H, 8.50. $C_{23}H_{32}O_2Si$ calcd.: C, 75.0; H, 8.75%), R_F (20% EtOAc/hexane) 0.15, ν_{max} (CH_2Cl_2) 3615 (OH), 3575 (OH), and 1115 cm^{-1} (SiPh), δ ($CDCl_3$) 7.6–6.8 (10H, m, 2 × Ph), 3.45 (1H, m, C*H*OH), 1.14 (3H, d, *J* 6 Hz, CMe), 0.38 (6H, s, 2 × SiMe), and 2.7–0.7 (12H, m, remainder) *m/z* 135 (100%, $PhMe_2Si$), and 115 (53, $C_6H_{11}O_2$).

The Peterson elimination

The silyldiol (**15**) (21 mg) was dissolved in dry THF (3 ml) and potassium hydride (20% dispersion in oil) (50 mg) was added to the solution. The mixture was stirred at room temperature for 30 min, water was added and the product extracted into ether. The ether was dried ($MgSO_4$), and evaporated in vacuo to give an oil. Purification by preparative thin layer chromatography on silica gel, eluting with ethyl acetate/hexane (1/4, v/v), gave the *trans*-(*E*)-4-phenyl-1-(1-propenyl)cyclohexanol (**6**) (12 mg, 97%) identical (m.p., mixed m.p., IR, and TLC) to an authentic sample of (**6**).

cis-(S,R)(R,S)-4-Phenyl-1-[1-acetoxy-2-(dimethylphenylsilyl)propyl]cyclohexanol (17)

This was prepared from the silyldiol (**14**) by the general method for acetylation to give the mono-acetate (**17**) (96%) as prisms, m.p. 134–136°C (from hexane) (Found: C, 73.0; H, 8.45. $C_{25}H_{34}O_3Si$ calcd.: C, 73.1; H, 8.35%), R_F (25% EtOAc/hexane) 0.30, ν_{max} (CH_2Cl_2) 3600 (OH), 1740 (CO), and 1236 cm^{-1} (SiMe), δ(CCl_4) 7.8–7.0 (10H, m, 2 × Ph), 5.58 (1H, s, C*H*OAc), 2.03 (3H, s, COMe), 1.52 (3H, s, CMe), 0.53 (6H, d, 2 × SiMe), and 2.9–1.2 (11H, m, remainder), *m/z* 350 (1%, *M* − AcOH), and 135 (100, $PhMe_2Si$).

trans-(R,R)(S,S)-4-Phenyl-1-[1-acetoxy-2-(dimethylphenylsilyl)propyl]cyclohexanol (18)

This was prepared from the silyldiol (**15**) by the general method for acetylation to give the mono-acetate (**18**) (95%) as prisms, m.p. 108–110°C (from hexane) (Found: C, 72.8; H, 8.40. $C_{25}H_{34}O_3Si$ calcd.: C, 73.1; H, 8.35%), R_F (10% EtOAc/hexane) 0.20, ν_{max} (CH_2Cl_2) 3590 (OH), 1732 (CO), 1225 (SiMe), and 1114 cm^{-1} (SiPh), δ(CCl_4) 7.7–7.0 (10H, m, 2 × Ph), 4.87 (1H, d, *J* 5 Hz, C*H*OAc), 1.98 (3H, s, COMe), 1.27 (3H, d, *J* 7 Hz, CMe), 0.46 (6H, s, 2 × SiMe), and 2.9–1.3 (11H, m, remainder) (Found: *m/z*, 309.1676. $C_{20}H_{25}OSi$ calcd.: *M* − AcOH − C_3H_5, 309.1675), *m/z* 309 (28%, *M* − AcOH − C_3H_5), and 135 (100, $PhMe_2Si$).

trans-(R,S)(S,R)-4-Phenyl-1-[1-acetoxy-2-(dimethylphenylsilyl)propyl]cyclohexanol (19)

This was prepared from the silyldiol (**16**) by the general method for acetylation to give the mono-acetate (**19**) (100%) as an oil, R_F (25% EtOAc/hexane) 0.45, ν_{max} (CH_2Cl_2) 3600 (OH), 1737 (CO), 1235 (SiMe), and 1116 cm^{-1} (SiPh), $\delta(CCl_4)$ 7.7–7.0 (10H, m, 2 × Ph), 4.93 (1H, m, C*H*OAc), 1.99 (3H, s, COMe), 1.31 (3H, d, *J* 6 Hz, CMe), 0.47 (6H, s, 2 × SiMe), and 2.8–1.2 (11H, m, remainder) (Found: *m/z*, 350.208 8. $C_{23}H_{30}OSi$ calcd.: *M* − AcOH, 350.2065), *m/z* 350 (0.5%, *M* − AcOH), 335 (0.5, *M* − AcOH − Me), and 135 (100, $PhMe_2Si$).

trans-(Z)-4-Phenyl-1-(1-propenyl)cyclohexanol (20)

The mono-acetate (**18**) (19 mg) was dissolved in THF (2 ml), and tetrabutylammonium fluoride in THF (0.075 mmol) was added. After standing for 3 h at room temperature, the mixture was put directly onto a preparative thin layer chromatogram of silica gel, and eluted with ethyl acetate/hexane (1/9, v/v) to give the allyl alcohol (**20**) (9.7 mg, 98%) as an oil, R_F (25% EtOAc/hexane) 0.45, ν_{max} (CH_2Cl_2) 3610 cm^{-1} (OH), δ ($CDCl_3$) 7.33 (5H, s, Ph), 5.50 (1H, dq, *J* 5 and 12 Hz, CH=C*H*Me), 5.48 (1H, d, *J* 12 Hz, C*H*=CHMe), 2.8–2.2 (1H, m, PhC*H*), 1.89 (3H, d, *J* 5 Hz, CH=CH*Me*), 1.48 (1H, s, OH), and 2.2–1.3 (8H, m, remainder) (Found: M^+, 216.1515. $C_{15}H_{20}O$ calcd.: *M*, 216.151 4), *m/z* 216 (12%, M^+), 198 (7, *M* − H_2O), and 97 (100, C_6H_9O).

cis-(E)-4-Phenyl-1-(1-propenyl)cyclohexanol (4)

Prepared from the mono-acetate (**17**) by the method above to give the allyl alcohol (**4**) (78%).

trans-(E)-4-Phenyl-1-(1-propenyl)cyclohexanol (6)

Prepared from the mono-acetate (**19**) by the method above to give the allyl alcohol (**6**) (80%).

cis-1-(Dimethylphenylsilyl)-1-methyl-3,3-(3-phenylpentamethylene)allene (21)

Prepared from the propargyl acetate (**5**) by the general method, to give the allenylsilane (**21**) (56%) as needles, m.p. 63–64°C (from methanol) (Found: C, 83.2; H, 8.55. $C_{23}H_{28}Si$ calcd.: C, 83.1; H, 8.50%), R_F (hexane) 0.25, ν_{max} (CH_2Cl_2) 1945 (C=C), 1244 (SiMe), and 1114 cm^{-1} (SiPh), $\delta(CDCl_3)$ 7.8–7.0 (10H, m, 2 × Ph), 1.68 (3H, s, CMe), 0.41 (6H, s, 2 × SiMe), and 2.8–1.1 (9H, m, remainder), δ ($CDCl_3$) 202.9, 147.1, 133.9, 128.9, 128.3, 127.7, 126.8, 125.9, 94.8, 88.5, 44.2, 34.9, 31.3, 16.1, and −2.9, (Found: M^+ 332.194 6. $C_{23}H_{28}Si$ calcd.: *M*, 332.1961), *m/z* 332 (70%, M^+), and 135 (100, $PhMe_2Si$).

trans-1-(Dimethylphenylsilyl)-1-methyl-3,3-(3-phenylpentamethylene)allene (22)

Prepared from the propargyl acetate (**7**) by the general method, to give the allenylsilane (**22**) (39%) as an oil, R_F (hexane) 0.25, ν_{max} (CH_2Cl_2) 1948 (C=C), and 1118 cm^{-1} (SiPh), $\delta(CDCl_3)$ 7.6–7.0 (10H, m, 2 × Ph), 1.67 (3H, s, CMe), 0.34 (6H, s, 2 × SiMe), and 2.7–1.4 (9H, m, remainder), $\delta(CDCl_3)$ 203.0, 147.2, 138.8, 133.8, 128.8, 128.3, 127.7, 126.9, 126.0, 95.1, 88.3, 44.2, 35.1, 31.0, 16.6, and −3.0, (Found: M^+, 332.1945. $C_{23}H_{28}Si$ calcd.: *M*, 332.1961), *m/z* 332 (42%, M^+), and 135 (100, $PhMe_2Si$).

Protodesilylation of the allylsilanes

The allylsilane (**13**) (200 mg) and boron trifluoride in acetic acid (0.08 ml of a 40% solution) were kept in dichloromethane (5 ml) at 0°C for 20 min and at 20°C for 40 min. Sodium bicarbonate solution was added in excess and the organic product worked up with hexane in the usual way to give *trans*-(*E*)-1-phenyl-4-(1-propenyl)cyclohexane (**23**) (110 mg, 92%) as colourless needles, m.p. 43–44°C (from methanol) (Found: C, 89.7; H, 9.80. $C_{15}H_{20}$ calcd.: C, 89.9; H, 10.05%), R_F (hexane) 0.45, ν_{max} (CCl_4) 985 cm^{-1} (CH=CH), δ ($CDCl_3$) 7.12 (5H, s, Ph), 5.45–5.15 (2H, m, CH=CH), 1.6 (3H, d, *J* 5 Hz, Me), and 2.6–0.9 (10H, m, remainder), δ ($CDCl_3$) 147.7(d), 137.2(d), 128.3(d), 126.8(d), 125.8(d), 122.4(d), 44.1(d), 40.4(d), 34.0(t), 33.4(t), and 18.0(q), (Found: M^+, 200.1561. $C_{15}H_{20}$ calcd.: *M*, 200.1565), *m/z* 200 (70%, M^+) and 104 (100%, C_8H_8).

The allylsilane (**12**) was protodesilylated as above to give the *trans*-alkene (**23**) (53%) and the *cis*-(*E*)-1-phenyl-4-(1-propenyl)cyclohexane (**24**) (36%) as a colourless oil, R_F (hexane) 0.45, δ($CDCl_3$) 147.6(d), 134.6(d), 128.3(d), 126.9(d), 125.7(d), 124.0(d), 43.6(d), 35.6(d), 31.0(t), 29.2(t), and 18.2(q).

Oxidation of the alkenes

The alkene (0.5 mmol) was dissolved in acetone (30 ml) and sodium periodate (5.0 mmol) and ruthenium dioxide (0.02 mmol) were added in water (5 ml). After being stirred at 20°C for 4 h, 2*N* hydrochloric acid (20 ml) was added and the mixture extracted with ethyl acetate. A sodium carbonate extraction, acidification of the aqueous phase and extraction with ethyl acetate in the usual manner gave the carboxylic acid products.

In this way, the alkene (**23**) gave the *trans*-4-phenylcyclohexane carboxylic acid (**25**) (44%) as colourless plates, m.p. 202–204°C (from ethyl acetate) (lit. [21] m.p. 201–203°C), R_F (50% EtOAc/hexane) 0.4, ν_{max} (Nujol) 3200–2400 (OH), and 1690 cm^{-1} (C=O), δ (acetone-d_6) 7.36 (5H, m, Ph), and 2.8–1.4 (10H, m, remainder).

Oxidation of the mixture of alkenes (**23** and **24**) from protodesilylation of the allylsilane (**12**) gave the *trans*-carboxylic acid (**25**) (43%) and the *cis*-4-phenylcyclohexane carboxylic acid (**26**) (29%) as colourless needles, m.p. 128–129°C (from hexane) (lit. [21] m.p. 129–130°C) R_F (50% EtOAc/hexane) 0.48, ν_{max} (Nujol) 3200–2300 (OH), and 1700 cm^{-1} (C=O), δ (acetone-d_6) 7.31 (5H, m, Ph), and 2.8–1.5 (10H, m, remainder).

Deuterodesilylation of the allylsilanes

The allylsilane (**13**) (208 mg) was dissolved in dichloromethane (5 ml) and ^{2}H-trifluoroacetic acid (1 ml) and kept at 20°C for 2.5 h. Evaporation of the solvent and chromatography on silica gel eluting with hexane gave *trans*-(*E*)-1-deutero-4-phenyl-1-(1-propenyl)cyclohexane (**27**) (78%) as colourless needles, m.p. 43–44°C (from methanol), R_F (hexane) 0.45, δ ($CDCl_3$) 7.3–7.1 (5H, m, Ph), 5.5–5.4 (2H, m, CH=CH), 2.5–2.4 (1H, m, PhC*H*), 1.7 (3H, d, *J* 4.5 Hz, Me), and 1.9–1.2 (8H, m, remainder), δ ($CDCl_3$) 147.7(d), 137.2(d), 128.3(d), 126.8(d), 125.8(d), 122.4(d), 44.1(d), 34.0(t), 33.4(t), and 18.0(q), δ(^{2}H NMR) ($CHCl_3$) 1.4, (Found: M^+, 201.1644. $C_{15}H_{19}D$ calcd.: *M*, 201.1643).

By the same method, deuterodesilylation of the allylsilane (**12**) and chromatography of the products on silica gel eluting with hexane gave *cis*-(*E*)-1-deutero-4-phenyl-1-(1-propenyl)cyclohexane (**28**) (42%) as a colourless oil, R_F (hexane) 0.45, δ

($CDCl_3$) 147.6(d), 134.6(d), 128.3(d), 126.9(d), 125.7(d), 124.0(d), 43.6(d), 31.0(t), 29.2(t), and 18.2(q), δ (^2H NMR) ($CHCl_3$) 1.9 (> 97%, deuterium on methine carbon), and 5.1 (< 3%, deuterium on olefinic carbon), (Found: M^+, 201.1644. $C_{15}H_{19}D$ calcd.: M, 201.1643), and an inseparable mixture of mono-, di-, tri-, tetra-, and penta-deutero-*trans*-(*E*)-1-deutero-4-phenyl-1-(1-propenyl)cyclohexane (**30**) (21%) and *trans*-(*E*)-1-(1-deutero-1-propenyl)-4-phenylcyclohexane (**31**) (21%) as a colourless oil, R_F (hexane) 0.45, δ ($CDCl_3$) 147.7, 137.2, 128.3, 126.8, 125.8, 122.4 (C-1 of olefin in (**30**) 50%), 122.3 (β-shifted signal of C-1 of olefin (**31**) 50%), 44.1, 40.4 (C-3 reduced in intensity due to α-effect), 34.0, 33.9 (β-effect shifted signal), 33.4 (reduced intensity due to α-effect), 33.3 (β-effect shifted signal reduced in intensity due to α-effect), and 18.0, δ (^2H NMR) ($CHCl_3$) 5.0 (C^2H=CH of (**31**)), 1.4 (^2H on C-3 of (**30**)), 1.3 and 0.7 (^2H on ring methylene carbons), *m/z* 201 (22%, $C_{15}H_{19}D$), 202 (34%, $C_{15}H_{18}D_2$), 203 (10%, $C_{15}H_{17}D_3$), 204 (5%, $C_{15}H_{16}D_4$), and 205 (2%, $C_{15}H_{15}D_5$).

cis-4-Phenyl-1-vinylcyclohexyl acetate (32)

Lithium acetylide-ethylene diamine complex (1.6 g) was suspended in dry THF (10 ml) and 4-phenylcyclohexanone (**1**) (2 g) was added in dry THF (15 ml). The mixture was stirred at 20°C for 3 h and then subjected to aqueous work-up and ether extraction. Purification by flash column chromatography on silica gel eluting with ethyl acetate/hexane (1/4 v/v) gave *cis*-1-ethynyl-4-phenylcyclohexanol (1.20 g, 52%) as needles, m.p. 101–103°C (from hexane), R_F (20% EtOAc/hexane) 0.25, ν_{max} ($CHCl_3$) 3595 sharp (OH), 3400 broad (OH), 3310 (C≡CH), and 2100 cm^{-1} (C≡C), δ ($CDCl_3$) 7.15 (5H, s, Ph), 2.50 (1H, s, C≡CH), and 2.8–0.7 (10H, m, remainder) (Found: M^+, 200.1200. $C_{14}H_{16}O$ calcd.: M, 200.1200), *m/z* 200 (3%, M^+), 182 (82, $M - H_2O$), 167 (68, $M - Me - H_2O$), and 104 (100, $PhCH{=}CH_2$). Acetylation of this alcohol gave *cis*-1-ethynyl-4-phenylcyclohexyl acetate (96%) as colourless prisms, m.p. 98–99°C (from hexane) (Found: C, 79.5; H, 7.55. $C_{16}H_{18}O_2$ calcd.: C, 79.3; H, 7.50%), R_F (20% EtOAc/hexane) 0.40, ν_{max} ($CHCl_3$) 3310 (C≡CH), 2110 (C≡C) and 1738 cm^{-1} (C=O), δ ($CDCl_3$) 7.18 (5H, s, Ph), 2.65 (1H, s, C≡CH), 2.05 (3H, s, CH_3CO), and 2.8–1.3 (9H, m, remainder) (Found: M^+, 242.130 9. $C_{16}H_{18}O_2$ requires M, 242.130 7), *m/z* 242 (3%, M^+), 200 (31, M–CH_2CO), 182 (75, M – AcOH), and 104 (100, $PhCH{=}CH_2$), Hydrogenation over Lindlar's catalyst gave *cis*-4-phenyl-1-vinylcyclohexyl acetate (**32**) (99%) as colourless plates, m.p. 49–50°C (from water/methanol) (Found: C, 78.6; H, 8.40. $C_{16}H_{20}O_2$ calcd.: C, 78.7; H, 8.25%), R_F (20% EtOAc/hexane) 0.45, ν_{max} ($CHCl_3$) 1725 (C=O), and 698 cm^{-1} (Ph), δ ($CDCl_3$) 7.12 (5H, s, Ph), 6.15 (1H, dd, *J* 10 and 18 Hz, C*H*=CH_2), 5.22 (1H, dd, *J* 2 and 18 Hz, CH=C*H*H), 5.20 (1H, dd, *J* 2 and 10 Hz, CH=CH*H*), 1.95 (3H, s, CH_3CO), and 2.8–1.2 (9H, m, remainder) (Found: M^+, 244.1467. $C_{16}H_{20}O_2$ calcd.: M 244.1463), *m/z* 244 (14%, M^+), 184 (53, M – AcOH), and 108 (100, $PhCH{=}CH_2$).

Dimethylphenyl-[1-(4-phenylcyclohexylidenyl)ethyl]silane (33)

The acetate (**32**) was reacted with the silylcuprate by the standard method to give the allylsilane (**33**) as a colourless oil (94%), R_F (hexane) 0.3, ν_{max} (CCl_4) 1248 (SiMe), 1116 (SiPh) and 798 cm^{-1} (Ph), δ ($CDCl_3$) 7.5–6.9 (10H, m, 2 × Ph), 5.1 (1H, t, *J* 9 Hz, C=CH), 0.3 (6H, s, 2 × SiMe), and 2.8–1.1 (11H, m, remainder), (Found: M^+, 320.1961. $C_{22}H_{28}Si$ calcd.: 320.1961), *m/z* 320 (12%, M^+), and 135 (100, $PhMe_2Si$).

Protodesilylation of the allylsilane (33)

The allylsilane (**33**) was protodesilylated with boron trifluoride in acetic acid to give an inseparable mixture (5/1) of *trans*- and *cis*-1-ethenyl-4-phenylcyclohexane (**34** and **35**) (89%) as a colourless oil, R_F (hexane) 0.45, ν_{max} (film) 1640 (C=C), 995 ($CH=CH_2$) and 910 cm^{-1} ($CH=CH_2$), δ ($CDCl_3$) 7.3–7.1 (5 H, m, Ph), 6.1–4.5 (3 H, m, $CH=CH_2$), and 2.9–0.7 (10H, m, remainder), δ ($CDCl_3$) 147.5 (*trans*), 144.4 (*trans*), 142.2 (*cis*), 128.3 (*cis* and *trans*), 126.9 (*cis*), 126.8 (*trans*), 125.9 (*trans*), 125.8 (*cis*), 113.8 (*cis*), 112.0 (*trans*), 44.1 (*trans*), 43.6 (*cis*), 41.3 (*trans*), 36.5 (*cis*), 33.9 (*trans*), 32.8 (*trans*), 30.4 (*cis*), and 29.2 (*cis*), (Found: M^+, 186.1400. $C_{14}H_{18}$ requires 186.1409), *m/z* 186 (97%, M^+), and 104 (100, $PhCH=CH_2$).

Acetylation of the allylsilane 12

A solution of titanium tetrachloride (184 mg) in dichloromethane (1 ml) was cooled to −78°C and added to a solution of the allylsilane (**12**) (294 mg) and acetyl chloride (82 mg) in dichloromethane (3 ml) at −78°C. After 1 h the mixture was poured into saturated sodium bicarbonate solution, and the products were extracted into dichloromethane. Separation by chromatography on silica gel eluting with ethyl acetate/hexane (1/9 v/v) gave *trans*-(*E*)-1-phenyl-4-(1-propenyl)cyclohexane (**23**) (16%), *cis*-(*E*)-1-(4-phenyl-1-(1-propenyl)cyclohexyl)ethan-1-one (**36**) (15%) as a colourless oil, R_F (10% EtOAc/hexane) 0.35, ν_{max} (film, 1705 (C=O), and 974 cm^{-1} (CH=CH), δ ($CDCl_3$) 7.3–7.1 (5H, m, Ph), 5.65 (1H, dq, *J* 16 and 6.5 Hz, CH=C*H*Me), 5.40 (1H, d, *J* 16 Hz, C*H* = CHMe), 2.45 (1H, m, PhC*H*), 2.1 (3H, s, COMe), 1.8 (3H, d, *J* 6.5 Hz, CH=CH*Me*), and 2.3–1.6 (8H, m, remainder), (Found: M^+, 242.1666. $C_{17}H_{22}O$ calcd.: *M*, 242.1621), *m/z* 242 (16%, M^+), 199 (97, $M^+ - MeCO$), and 91 (100, C_7H_7), and 4-(dimethylphenylsilyl)-3-(4-phenylcyclohex-1-enyl)pentan-2-one (**37**) (32%) as colourless prisms m.p. 74–76°C (from hexane) (Found: C, 79.7; H, 8.60. $C_{25}H_{32}OSi$ calcd.: C, 79.7; H, 8.55%), R_F (10% EtOAc/hexane) 0.40, ν_{max} (film) 1715 (C=O), 1428 (SiPh), 1248 (SiMe), and 1113 cm^{-1} (SiPh), δ ($CDCl_3$) 7.4 (5H, m, SiPh), 7.2 (5H, m, CH*Ph*), 5.6 (1H, m, C=CH), 3.1 (1H, d, *J* 11 Hz, MeCOC*H*), 2.05 (3H, s, MeCO), 0.9 (3H, d, *J* 8 Hz, *Me*CH), 0.35 (6H, s, $SiMe_2$), and 2.6–1.2 (8H, m, remainder), δ ($CDCl_3$) 208.9, 146.7, 139.2, 134.5, 134.0, 128.8, 128.3, 127.6, 127.5, 126.7, 126.0, 64.5, 38.9, 33.6, 29.6, 29.3, 26.4, 18.9, and 14.2, (Found: M^+, 376.2225. $C_{25}H_{32}OSi$ calcd.: 376.2223), *m/z* 376 (32%, M^+) and 135 (100, $PhMe_2Si$).

Acetylation of the allylsilane 13

The allylsilane (**13**) was acetylated by the above method to give the alkene (**23**) (28%), the ketone (**36**) (5%), and the silylketone (**37**) (50%) as a mixture of at least three diastereoisomers.

Acetylation of the allylsilane 33

The allylsilane (**33**) was acetylated by the above method to give *trans*-1-ethenyl-4-phenylcyclohexane (**34**) (13%), 1-(dimethylphenylsilyl)-2-(4-phenylcyclohex-1-enyl)butan-3-one (**39**) (16%) as a colourless oil, R_F (10% EtOAc/hexane) 0.45, ν_{max} 1712 (C=O), 1426 (SiPh), 1246 (SiMe), and 1112 cm^{-1} (SiPh), δ ($CDCl_3$) 7.4 (5H, m, SiPh), 7.2 (5H, m, CHPh), 5.5 (1H, m, C=C*H*), 3.1 (1H, t, *J* 6 Hz, MeCOC*H*), 2.05 (3H, s, MeCO), 0.3 (6H, s, $SiMe_2$), and 2.5–0.9 (9H, m, remainder), (Found: M^+, 347.1836. $C_{24}H_{30}OSi$ calcd.: 347.1831), *m/z* 362 (17%, M^+), and 135 (100, $PhMe_2Si$),

cis-1-(1-ethenyl-4-phenylcyclohexyl)ethan-1-one (**41**) (25%) as colourless plates, m.p. 43–45°C (from hexane) (Found: C, 84.3; H, 8.85. $C_{16}H_{20}O$ calcd.: C, 84.2; H, 8.85%), R_F (10% EtOAc/hexane) 0.40, ν_{max} ($CHCl_3$) 1705 cm^{-1} (C=O), δ ($CDCl_3$) 7.1 (5H, m, Ph), 6.1–4.9 (3H, m, CH=CH_2), 2.12 (3H, s, Me), 2.6–1.5 (9H, m, remainder), (Found: M^+, 228.1510. $C_{16}H_{20}O$ calcd.: M, 228.1514), m/z 228 (36%, M^+), 210 (27, $M^+ - H_2O$), 104 (55, PhCH=CH_2), and 91 (100, C_7H_7), and *trans*-1-(1-ethenyl-4-phenylcyclohexyl)ethan-1-one (**40**) (12%) as a colourless oil, R_F (10% EtOAc/hexane) 0.5, ν_{max} (film) 1705 cm^{-1} (C=O), δ ($CDCl_3$) 7.0 (5H, m, Ph), 5.7–4.8 (3H, m, CH=CH_2), 2.1 (3H, s, MeCO), and 2.8–1.1 (9H, m, remainder), (Found: M^+, 228.1516. $C_{16}H_{20}O$ calcd.: M, 228.1514).

*Determination of the stereochemistry of the ketone **36***

The ketone (**36**) (17 mg) was dissolved in ethanol (3 ml) and hydrogenated over 5% palladium on carbon for 2.5 h. The catalyst was removed by filtration and the solvent evaporated to give the propyl substituted cyclohexylethanone. The ketone was dissolved in dichloromethane (5 ml) and stirred with *p*-nitroperoxybenzoic acid (85%, 18.5 mg), disodium hydrogen phosphate (15 mg) and 3-t-butyl-4-hydroxy-5-methylphenyl sulphide (0.1 mg). The mixture was heated under reflux for 24 h and then poured into sodium hydrogen carbonate solution and extracted with dichloromethane. Evaporation and chromatography on silica gel eluting with ethyl acetate-hexane (1/9 v/v) gave *cis*-4-phenyl-1-propylcyclohexyl acetate (**38**) (55%) as a colourless oil, R_F (10% EtOAc/hexane) 0.50, ν_{max} (film) 1725 cm^{-1} (C=O), δ ($CDCl_3$) 7.2 (5H, m, Ph), 2.0 (3H, s, MeCO), and 2.8–0.8 (16H, m, remainder), (Found: M^+, 217.1217. $C_{17}H_{24}O_2$ calcd.: M, 217.1228), identical TLC, IR and MS to a sample prepared by the hydrogenation of the acetate (**9**).

*Determination of the stereochemistry of the ketone **41***

The ketone (**41**) was hydrogenated and oxidised by the above method to give *cis*-1-ethyl-4-phenylcyclohexyl acetate (**42**) (40%) as colourless needles, m.p. 64–65°C (from hexane) (Found: C, 78.1; H, 9.00. $C_{16}H_{22}O_2$ calcd.: C, 78.0; H, 9.00%), R_F (20% EtOAc/hexane) 0.48, ν_{max} (film) 1725 cm^{-1} (C=O), δ ($CDCl_3$) 7.15 (5H, m, Ph), 1.95 (3H, s, MeCO), 1.8 (3H, t, J 7 Hz, CH_3CH_2), and 2.7–1.5 (11H, m, remainder), (Found: M^+, 217.1233. $C_{14}H_{17}O_2$ calcd.: M, 217.1229), m/z 246 (2%, M^+), 186 (100, M – AcOH), and 104 (80, PhCH=CH_2), identical by TLC, IR, MS and m.p. to a sample prepared by the hydrogenation of the acetate (**32**).

General method for the epoxidation of allylsilanes

The allylsilane (1 mmol) and *m*-chloroperoxybenzoic acid (1 mmol) were dissolved in dichloromethane (2 ml) and stirred with disodium hydrogen phosphate (1 mmol) at 0°C for 1 h. Filtration of the mixture and evaporation of the solvent gave a mixture that was dissolved in ether and washed with sodium hydrogen carbonate solution. Evaporation of the ether gave the epoxysilane.

*Epoxidation of the allylsilane **13***

Epoxidation of the allylsilane (**13**) gave the epoxysilane (**43**) which was treated with tetrabutylammonium fluoride in THF at 20°C. After 18 h the solvent was evaporated and chromatography on silica gel eluting with ethyl acetate/hexane (1/3 v/v) to give *trans*-(*E*)-4-phenyl-1-(1-propenyl)cyclohexanol (**6**) (91%).

Epoxidation of the allylsilane 12

Epoxidation of the allylsilane (**12**) and treatment of the product with tetrabutylammonium fluoride gave *cis*-(*E*)-4-phenyl-1-(1-propenyl)cyclohexanol (**4**) (96%) and *trans*-(*Z*)-4-phenyl-1-(1-propenyl)cyclohexanol (**20**) (3%).

Epoxidation of the allylsilane 33

The allylsilane (**33**) was epoxidised with *m*-chloroperoxybenzoic acid to give a mixture of epoxides as a colourless oil. The oil was treated with tetrabutylammonium fluoride solution in THF to give *cis*-4-phenyl-1-vinylcyclohexanol (**47**) (31%) as colourless needles m.p. 95–97°C (from hexane), (Found: C, 83.2; H, 9.20. $C_{14}H_{18}O$ calcd.: C, 83.1; H, 8.95%), R_F (20% EtOAc/hexane) 0.20, ν_{max} ($CHCl_3$) 3595 sharp (OH), 3430 broad (OH), and 690 cm^{-1} (Ph), δ ($CDCl_3$) 7.10 (5H, s, Ph), 6.02 (1H, dd, *J* 10 and 18 Hz, C*H*=CH_2), 5.18 (1H, dd, *J* 2 and 18 Hz, CH=C*H*H), 5.10 (1H, dd, *J* 2 and 10 Hz, CH=CH*H*), and 2.8–0.9 (10H, m, remainder) (Found: M^+, 202.1355. $C_{14}H_{18}O$ calcd.: *M*, 202.1357), *m/z* 202 (3%, M^+), 184 (86, $M - H_2O$), and 104 (100, PhCH=CH_2), and *trans*-4-phenyl-1-vinylcyclohexanol (**46**) (62%) as colourless plates m.p. 48–50°C (from hexane), (Found: C, 83.4; H, 8.85. $C_{14}H_{18}O$ calcd.: C, 83.1; H, 8.95%), R_F (10%) EtOAc/hexane) 0.30, ν_{max} ($CHCl_3$) 3595 sharp (OH), 3440 broad (OH), 1639 (C=C), and 695 cm^{-1} (Ph), δ ($CDCl_3$) 7.15 (5H, s, Ph), 5.85 (1H, dd, *J* 13 and 17 Hz, C*H*=CH_2), 5.15 (1H, dd, *J* 2 and 17 Hz, CH=C*H*H), 4.87 (1H, dd, *J* 2 and 13 Hz, CH=CH*H*), and 2.7–1.0 (10H, m, remainder) (Found: M^+, 202.1356. $C_{14}H_{18}O$ calcd.: *M*, 202.1357), *m/z* 202 (24%, M^+), 184 (29, $M - H_2O$), 104 (100, PhCH=CH_2), and 91 (99, C_7H_7).

Protodesilylation of the allenylsilane 21

The allenylsilane (**21**) was protodesilylated with boron trifluoride in acetic acid in the usual manner to give the acetylene (**48**). The acetylene was directly hydrogenated over Lindlar's catalyst to give *cis*-(*Z*)-1-phenyl-4-(1-propenyl)cyclohexane (**50**) (39%) as a colourless oil, R_F (hexane) 0.50, ν_{max} (film) 718 cm^{-1} (Ph), δ ($CDCl_3$) 7.4–7.2 (5H, m, Ph), 5.8 (1H, dd, *J* 9 and 10 Hz, C*H*=CHMe), 5.5 (1H, dq, *J* 10 and 6 Hz), 2.8 (1H, m, PhC*H*), 2.6 (1H, m, C*H*CH=C), 1.7 (3H, d, *J* 6 Hz, Me), and 2.1–1.7 (8H, m, remainder), δ ($CDCl_3$) 147.6(d), 133.5(d), 128.3(d), 126.9(d), 125.7(d), 123.1(d), 43.6(d), 31.1(t), 30.7(d), 29.3(t), and 12.9(q), (Found: M^+, 200.156 2. $C_{15}H_{20}$ requires *M*, 200.1565), *m/z* 200 (89%, M^+), and 104 (100, PhCH=CH_2), and *cis*-(*E*)-1-phenyl-4-(1-propenyl)cyclohexane (**24**) (4%). The alkenes were oxidised with ruthenium dioxide and sodium periodate by the general method above to give *cis*-4-phenylcyclohexane carboxylic acid (**26**) (67%).

Protodesilylation of the allenylsilane 22

The allenylsilane (**22**) was protodesilylated with boron trifluoride in acetic acid in the usual manner to give the acetylene (**49**). The acetylene was directly hydrogenated over Lindlar's catalyst to give *trans*-(*Z*)-1-phenyl-4-(1-propenyl)cyclohexane (**51**) (46%) as a colourless oil, R_F (hexane) 0.60, ν_{max} (film) 1656 cm^{-1} (C=C), δ($CDCl_3$) 7.4–7.2 (5H, m, Ph), 5.45 (1H, dq, *J* 10 and 7 Hz, CH=C*H*Me), 5.3 (1H, dd, *J* 9 and 10 Hz, C*H* = CHMe), 1.7 (3H, d, *J* 7 Hz, Me), and 2.6–1.2 (10H, m, remainder), δ ($CDCl_3$) 147.8(d), 136.6(d), 128.3(d), 126.9(d), 125.9(d), 122.4(d), 44.1(d), 35.8(d), 34.0(t), 33.5(t), and 13.0(q), (Found: M^+, 200.1559. $C_{15}H_{20}$ calcd.: 200.1565), *m/z* 200 (92%, M^+), and 104 (100, PhCH=CH_2), and *cis*-(*Z*)-1-phenyl-4-(1-

propenyl)cyclohexane (**50**) (5%). The alkenes were oxidised with ruthenium dioxide and sodium periodate by the general method above to give *trans*-4-phenylcyclohexane carboxylic acid (**25**) (39%).

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