The Phenyldimethylsilyl Group as a Masked Hydroxy Group

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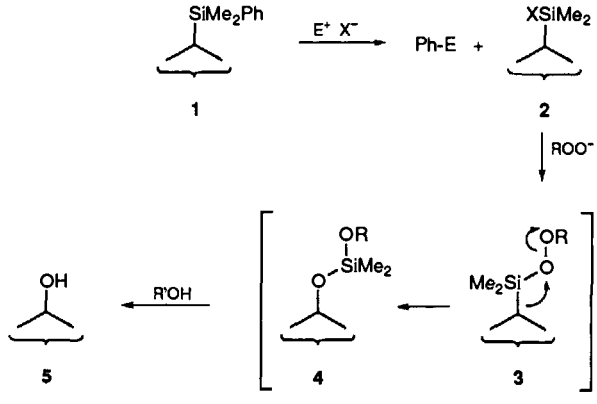
A phenyldimethylsilyl group attached to carbon can be converted into a hydroxy group **1**→**5**, with retention of configuration at the migrating carbon, by any of three main methods. The first involves protodesilylation, to remove the phenyl ring from the silicon atom, followed by oxidation of the resulting functionalised silicon atom using peracid or hydrogen peroxide. The second uses mercuric acetate for the same purpose, and can be combined in one pot with the oxidative step using peracetic acid. This method has a variant in which the mercuric ion is combined with palladium(II) acetate, both in less than stoichiometric amounts. The third uses bromine, which can also be used in one pot in conjunction with peracetic acid. In this method, but not in the method based on mercuric acetate, the peracetic acid may be buffered with sodium acetate. The method using bromine as the electrophile for removing the benzene ring has a more agreeable variant in which it is administered in the form of potassium bromide, which is oxidised to bromine by the peracetic acid. The scope and limitations of each of these methods are reported with a range of examples possessing between them many of the common functional groups. Simple benzene rings, alcohols, ethers, esters, amides and nitriles are compatible with all three methods, and ketones do not undergo Baeyer–Villiger reaction under any of the conditions. Amines, however, are oxidised to amine oxides. Ketones may be brominated in the third of the three main recipes. The absence of acid in the third method makes it especially valuable when the phenyldimethylsilyl group has a neighbouring nucleofugal group such as hydroxy or acetoxy. Carbon–carbon double bonds are incompatible with the methods, except for terminal monosubstituted double bonds, which can survive the conditions used in the first of the three methods.

We have established in a series of papers that a silyl group on a stereogenic centre exerts considerable influence on the diastereoselectivity of reactions taking place at an adjacent double bond. Some of these reactions are S_E2' reactions of allylsilanes,[1] in which the silyl group is removed from the molecule, and its stereochemical information transferred to the newly created stereogenic centre. However, in other reactions that we studied, notably in the alkylations of enolates having a β silyl group[2] and in the hydroboration of allylsilanes,[3] the silyl group remained in the molecule. For such reactions to be useful in synthesis we needed to convert the silyl group into something else with the stereochemical information that it carries intact. We reported in two preliminary communications[4,5] that a phenyldimethylsilyl group can be converted in two steps into a hydroxy group **1**→**5** with retention of configuration. We now report the experimental details of this work.

The transformation **1**→**5** makes the phenyldimethylsilyl group a *masked* hydroxy group, possessing very different properties from a hydroxy group or from any *protected* form of the hydroxy group. It is comparatively unreactive in most of the conditions commonly used in organic synthesis, it has no loan pairs with which to indulge in coordination, its influence on its neighbourhood is that of an electropositive rather than an electronegative group, and it is substantially larger. It can be easily introduced into organic molecules either as an electrophile, using the commercially available or easily synthesised phenyldimethylsilyl chloride, or as a nucleophile, using our bis(phenyldimethylsilyl)cuprate reagent,[6] which reacts with most kinds of α,β-unsaturated carbonyl compound,[7] acetylenes.[8] allylic acetates,[9] allenes,[10] epoxides[11,12] and alkyl bromides.[12] The use of the phenyldimethylsilyl group as a masked hydroxy group has already found several applications both in our own synthetic work[13] and in that of others.[14–21]

The first inspiration for our work came from Eaborn's extensive studies of the protodesilylation of arylsilanes.[22] We



realised that the protodesilylation of our compounds would trivially give benzene (E = H), but the more interesting corollary was that the silyl group in the product **2** would carry whatever electronegative counterion was present in the reaction mixture. Thus, Kumada has used the protodesilylation of a phenylsilane for the synthesis of a silyl chloride.[23] This fed into the second inspiration for our work, which was Buncel and Davies's report[24] that phenyldimethylsilyl chloride reacted with perbenzoic acid, in the presence of ammonia, to cleave off one or more of the phenyl and methyl groups from the silicon atom in a rearrangement that bears some resemblance to the Baeyer–Villiger reaction, and even more to the oxidation of boranes with alkaline hydrogen peroxide. Whereas a borane, with an empty p orbital, needs no nucleofugal group, a silyl halide was needed for this reaction to occur, in order that the peracid could displace it **2**→**3** (R = PhCO, X = Cl) and establish a bond to the silicon atom. Silanes with four alkyl or aryl groups are unreactive towards peracid. Once the peracid is bonded to the silicon, a rearrangement can take place **3**→**4**, in

which a carbon group on the silicon migrates to the first oxygen atom with departure of the second, possibly in a cyclic process with the nucleofugal group RO^- attaching itself to the silyl group. The final step either takes place in the hydroxylic medium with the silyl ether **4** giving the free alcohol **5** directly, or can be encouraged by treating the crude product with tetrabutylammonium fluoride or methanolic hydrochloric acid.

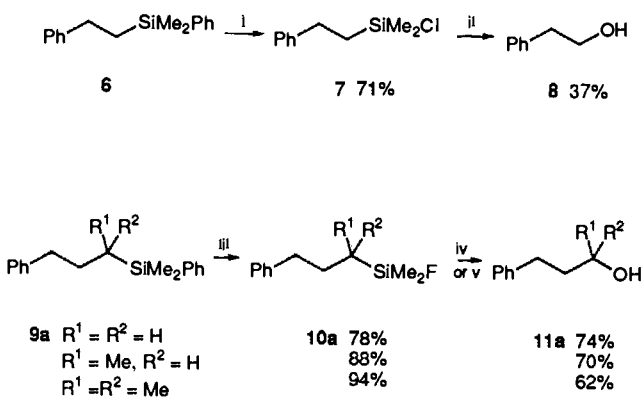
Our choice of the phenyldimethylsilyl group in our synthetic work had originally been made because it was so much easier to make phenyldimethylsilyllithium[25] than trimethylsilyllithium.[26] Now we had a bonus—many of the phenyldimethylsilyl compounds that we had been making ought to be convertible into the corresponding hydroxy compounds. This would be especially important in our work setting up stereochemical relationships, but clearly the potential for this kind of group was much larger—there was nothing like it in the synthetic armoury.

Concurrently with our work and subsequent to it, Tamao studied the oxidation step **2**→**5**, and found a number of different conditions under which it could be carried out.[27,28] He found that the nucleofugal group X on the silicon atom in the intermediate **2** could be an ether, or an amine, or even a hydrogen atom, in addition to a halide. He also found that the oxidant ROOH could be hydrogen peroxide as well as peracid, and the base could be fluoride or hydrogen carbonate ion. Added to Davies's original recipe and ours, which uses *m*-chloroperbenzoic acid (MCPBA) and triethylamine, there is now a bewildering variety of methods for carrying out the oxidation step. Since we were developing our reactions without the benefit of Tamao's discoveries, the recipes reported in this paper using MCPBA, although effective, are not necessarily the best, and we recommend Tamao's procedures for the oxidation step following protodesilylation.

Later, we tried other aromatic electrophilic substitutions for the first step, in addition to protodesilylation ($E^+ = H^+$), and found that mercuri-desilylation ($E^+ = Hg^{2+}$) and bromodesilylation ($E^+ = {}^{+}Br$) had advantages, the most notable being that the whole operation could now be carried out in one pot, with peracetic acid (R = Ac) as the oxidant, since these electrophiles were compatible with the peracid. Thus, we have three procedures among which to choose, each of which has advantages and disadvantages which should become clear in the discussion. We begin by discussing, in sections 1–4, the method using protodesilylation for the removal of the benzene ring, which has the advantage that the intermediate fluorosilane can be examined by NMR spectroscopy to check that only protodesilylation has taken place. It also has the advantage that other phenyl rings in the molecule will survive without having been changed in any way as a result of having been attacked by the electrophile. We then discuss in sections 5–7 the one-pot procedures, which are normally to be preferred, and which would undoubtedly have worked in most of the examples we quote from our earlier work.

Results and Discussion

(1) *Simple Reactions with Minimal Competing Functional Groups* (Scheme 1).—We first established that the two-step procedure could be made to work at all using the phenethyl substrate **6**. Protodesilylation using dry hydrogen chloride took place in chloroform solution over 22.5 h at room temperature, and needed no aluminium chloride, as Kumada had used.[23] The rearrangement step, passing ammonia through an ether solution of the chloride 7 with *1 equivalent* of MCPBA at 0°C, gave a mixture of products, which clearly showed in their ^1H NMR spectra that both phenethyl and methyl migration had taken place (an approximate triplet at δ 3.8 and a sharp singlet at δ 3.6). It was known that aryl migration was faster than alkyl migration,[24] but there had been no indication in the literature whether a substituted alkyl group might migrate significantly faster than a methyl. We were not able to measure ratios reliably, but it was clear that there was significant methyl migration. Use of an excess of MCPBA gave the alcohol **8** in encouraging but unimpressive overall yield. Accordingly, we have always used at least 3 equivalents of peracid in all our work since, in order to encourage all three groups on the silicon atom to migrate.

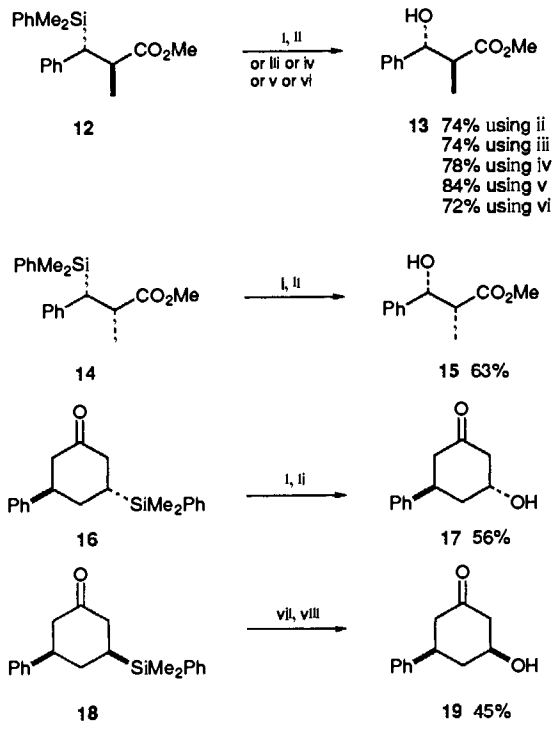


Scheme 1 *Reagents:* i, HCl; ii, MCPBA, NH_3; iii, HBF_4·OEt_2; iv, MCPBA, Et_3N; v, MCPBA, KF, DMA

We then tried the same reaction in the phenylpropyl series **9**, where we discovered that tetrafluoroboric acid–diethyl ether in chloroform removed the phenyl group typically in a little over 1 h at room temperature. Furthermore, the fluoride products **10** could be minimally purified by washing the organic layer with alkali, whereas the chloride **7** could not. Furthermore, the success of the protodesilylation could be easily monitored by the appearance of doublets in the δ 0.5–0.0 region of the ^1H NMR spectrum, arising from the methyl groups on the silicon atom carrying a fluorine atom. However, these doublets, one or two depending upon whether the methyl groups were diastereotopic or not, only appeared *after* the aqueous wash. The primary and secondary alkylsilyl fluorides **10a** and **10b** then proved to be easily oxidised using MCPBA and various amines. Ammonia had been inconvenient but triethylamine proved to work well, evidently catalysing the rearrangement steps fast enough before it was itself oxidised by the peracid. We also succeeded using Barton's *N-tert*-butyl-*N*,*N*,*N*′,*N*″-tetramethylguanidine,[29] which was known to be slow to react with peracid, but there appeared to be no advantage to using it.

The tertiary silane **10c**, although undergoing the protodesilylation step fast enough, was very slow in the oxidation step, requiring, in our best run, 12 equivalents of MCPBA added slowly over 4 h at 60 °C to a solution of the silyl fluoride and potassium fluoride in dimethylacetamide containing Kishi's radical inhibitor.[30]

(2) *Simple Reactions with Unexceptional Functional Groups and Proof of the Stereochemistry of the Rearrangement* (Schemes 2 and 3).—We thought it likely that ester groups would be compatible with the conditions of both steps. Since we had been able to prove the relative stereochemistry of the esters **12** and **14** independently,[31] we were now able to show that converting the silyl groups into hydroxy groups took place with retention of configuration in the migrating group—they gave the known esters **13** and **15**, respectively. We proved the stereospecificity of the reaction a second time using the cyclohexanones **16** and **18**, with configurations known from the method of synthesis. The stereochemistry of the alcohols **17** and **19** derived from them was evident from the half-height width of the signals in the ^1H NMR spectra for the protons adjacent to the hydroxyl group,

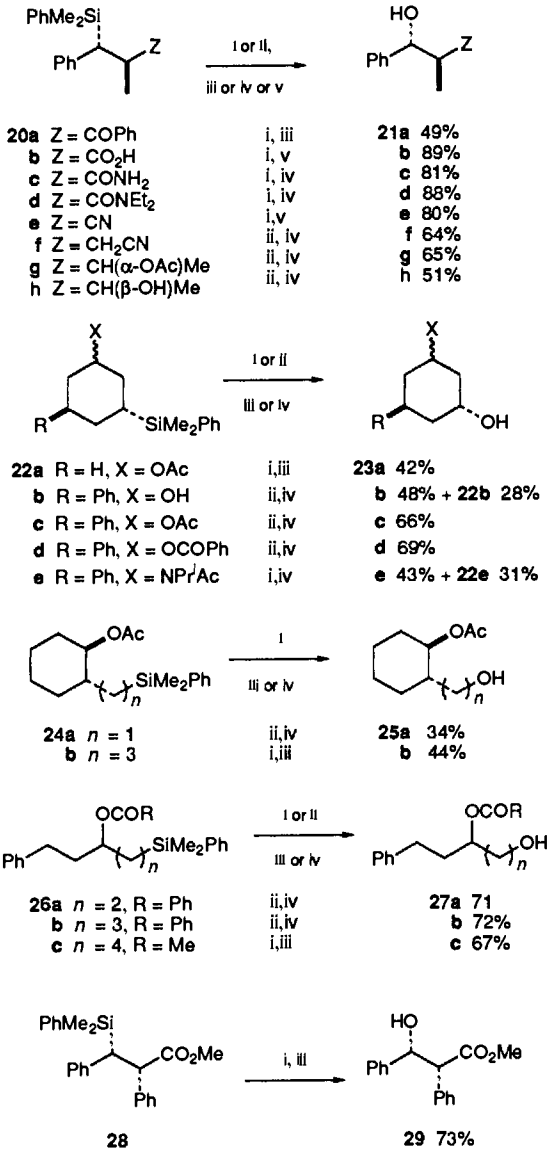


Scheme 2 *Reagents:* i, HBF_4·OEt_2; ii, MCPBA, Et_3N; iii, $Hg(OAc)_2$, AcO_2H, AcOH; iv, 0.2$Hg(OAc)_2$, 0.1$Pd(OAc)_2$, AcO_2H, AcOH; v, Br_2, AcO_2H, AcOH; vi, KBr, AcO_2H, AcOH; vii, BF_3·2AcOH; viii, MCPBA, KF, DMF

making the reasonable assumption that the phenyl group is equatorial. We saw no signs of competing Baeyer–Villiger reaction with these compounds—the yields are low because of the ease of dehydration of the β-hydroxy ketones **17** and **19**. Kumada and Tamao have also proved that the rearrangement takes place with retention of configuration.[28] We have therefore used this reaction since on many occasions to prove with considerable confidence the relative configuration of phenyldimethylsilyl-containing compounds.

Other compounds containing ketone, ester, carboxylic acid, amide (both primary and tertiary), nitrile and secondary alcohol groups, all proved to be compatible with the two-step procedure as summarised in the reactions in Scheme 3. The conditions used in these reactions vary from compound to compound, occasionally because one method worked where another did not, but mostly the only method used was the one quoted, chosen by the whim of the moment. None, except the carboxylic acid **20b** giving the known β-hydroxy acid **21b**, can be described as having been optimised, but that one case was investigated with care, and scaled up to a 48 mmol scale, in order to demonstrate that the reaction can be made to work in high yield. In addition to the earlier use of tetrafluoroboric acid, we found that the boron trifluoride–acetic acid complex, typically taking a few hours in dichloromethane at room temperature, was often better for the protodesilylation step, and Ito has used trifluoroacetic acid for the same purpose.[20] We also found that peracetic acid was sometimes better for the oxidation step, especially when the reaction is to be carried out on a larger scale, as it was with the acid **20b**. The only slight complication with these functional groups was the formation of the corresponding 5-membered ring cyclic silyl ether in place of the silyl fluoride in the protodesilylation step on the alcohol **20h**. Since this silyl ether smoothly went through to the alcohol **21h**, there was no overall problem with the silyl-to-hydroxy conversion.

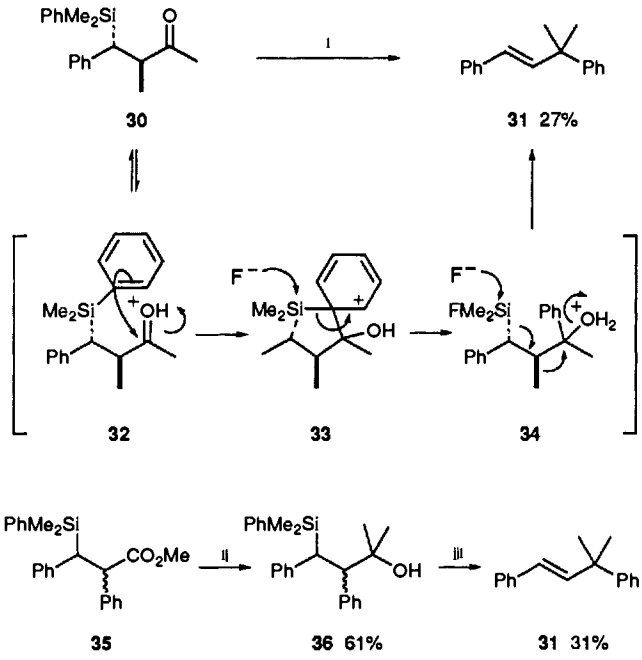
We prepared the substrates **24** by copper(I)-catalysed opening of cyclohexene oxide using phenyldimethylsilylmethyl



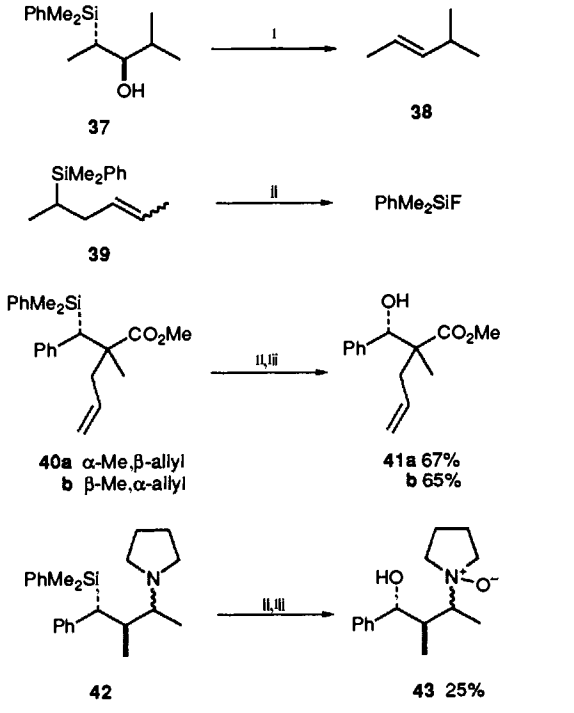
Scheme 3 *Reagents:* i HBF_4·OEt_2; ii, BF_3·2AcOH; iii, MCPBA, Et_3N, Et_2O; iv, MCPBA, KF, DMF; v, AcOOH, Et_3N

and phenyldimethylsilylpropyl Grignard reagents. We prepared the substrates **26** from hydrocinnamaldehyde; for **26b** and **26c** we used the phenyldimethylsilylpropyl and phenyldimethylsilylbutyl Grignard reagents, and for the lower homologue **26a**, we used phenyldimethylsilylethynyllithium followed by hydrogenation. In none of these syntheses were the overall yields of the silanes **24** and **26** good enough for us to make much of a claim for these reagents as ω-hydroxyalkyl synthons.

(3) *Problematical Functional Groups* (Schemes 4 and 5).—We had worried that a ketone group might react with the peracid in a Baeyer–Villiger reaction as fast as or faster than the rearrangement. This proved not to be the case, as discussed above, but a different problem, one that we had not expected, did materialise with one ketone, not in the second step, but in the first. When we treated the ketone **30** with tetrafluoroboric acid there appeared to be some of the appropriate fluorosilane in the crude product, but the major product that we isolated was the alkene **31**. We believe that this product is formed by acid-catalysed attack of the ketone group on the phenyl group of the phenylsilane **32**→**33**→**34** (arrows), followed by acid-catalysed rearrangement **34** (arrows) closely similar to many rearrangements that we have seen before.[32] Indeed, we



Scheme 4 *Reagents*: i, HBF_4·OEt_2; ii, MeMgI; iii, BF_3·2AcOH



Scheme 5 *Reagents*: i, BF_3·2AcOH; ii, HBF_4·OEt_2; iii, MCPBA, KF, DMF

confirmed the structure of the alkene **31** by making it using our route[32] from the mixture of diastereoisomeric alcohols **36**.

In subsequent work, we have also seen this type of reaction when we tried to carry out the Lewis acid-catalysed reaction between an allenylsilane and an aldehyde having a β-phenyldimethylsilyl group,[33] and Ito has found similar phenyl-transfer reactions with other electrophilic centres than the carbonyl group.[20] However, when the carbonyl group is less electrophilic, as with the phenyl ketone **20a**, we did not see this type of reaction, although the yield of the fluorosilane in this step (70%) is notably lower than with compounds having no problematical functional groups, and accounts for the low overall yield of the alcohol **21a** reported in Scheme 3.

A second problem that we did foresee was that hydroxy groups, and other nucleofugal groups, β to the silyl group would undergo desilylative elimination faster than the phenyl group was attacked in the protodesilylation step. To confirm that this was indeed the case we treated the β-hydroxysilane **37** with acid, and could detect cleanly in the ^{1}H NMR spectrum only the alkene **38**.[3] The solution to this problem is discussed in section (7).

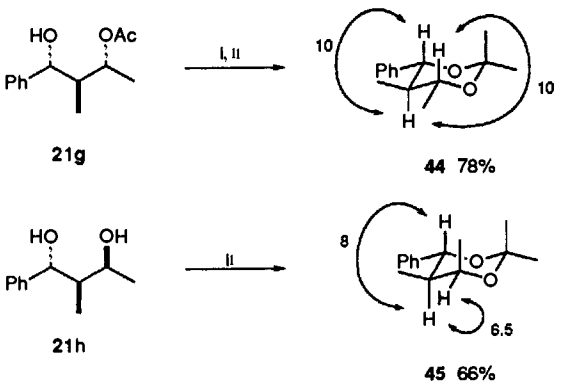
A third problem was that a double bond in the molecule might not survive the treatment with acid or whatever other electrophile we used for the removal of the benzene ring; this problem would be most acute when the double bond was conjugated to the silyl group as an allylsilane, and indeed Roush has met precisely this problem with an allylsilane that he wanted to convert into an allyl alcohol.[16] We have found that even cyclopropylmethylsilanes[34] and a cyclopropylsilane[35] are too unstable to acid, reacting by protonation of the cyclopropane ring before attack takes place on the phenyl ring. Fuchs succeeded in this transformation to a limited extent with a more hindered cyclopropylsilane, but found it better to use an allyl group as the removable group rather than a phenyl ring.[18]

In the hope that a disubstituted double bond not conjugated to the silyl group just might survive the conditions of the protodesilylation, we treated the mixture of alkenes **39** with tetrafluoroboric acid–etherate in dichloromethane for 2 h at 0 °C. This gave a mixture of products, which we did not attempt to analyse, but amongst them we could detect the characteristic sharp doublet at δ 0.7 from phenyldimethylsilyl fluoride, and none of the signals that would have been appropriate for the product of the protodesilylation that we wanted. This problem was not likely to be solved by changing the electrophile. We have now solved this problem by developing a silyl group that carries an exceptionally reactive allylsilane substituent, enabling it to be removed faster than attack takes place on double bonds like that in the alkene **39**.[36] Another solution to the problem is to have a silyl group already carrying a nucleofugal group, as Tamao has shown for diethylaminosilanes[37] and isopropoxysilanes.[38] These can be oxidised directly with hydrogen peroxide without disturbing the double bond of an allyl group attached to the silicon. An exceptional case is the aminomethyl-substituted silane that Chan has shown can be oxidised directly without disturbing a C=C double bond even when the silicon atom carries four carbon groups.[39]

Our only success in preserving a double bond while removing the phenyl group from a phenyldimethylsilane has been with a monosubstituted terminal double bond in the conversion **40**→**41** and with an α,β-unsaturated ketone,[35] when we did get low yields of alcohols in which the double bonds had survived. Hart has also seen a terminal double bond survive this conversion,[17] and Fuchs[18] and Ley[19] have similarly seen an enone survive.

The fourth problem was that sulfides and amines might be oxidised by the peracid faster than the rearrangement. We tested this possibility using the mixtures of stereoisomeric amines **42**, which gave the mixture of *N*-oxides **43** in low yield, but none of the corresponding amine. With further work to improve the yield, this might be an acceptable outcome, since the *N*-oxide can always be reduced to restore the amine, but evidently amines, and presumably sulfides, cannot always be carried through the conversion. However, Polniaszek and Dillard have succeeded in carrying through a tertiary amine unchanged by using Tamao's hydrogen peroxide and potassium fluoride conditions for the oxidation step.[15]

(4) *Proof of Relative Configuration* (Scheme 6).—The relative stereochemistry shown in Scheme 2 was already known for the β-silyl esters **12** and **14**, and we assigned the relative stereochemistry to the β-silyl ketones **16** and **18** based on their



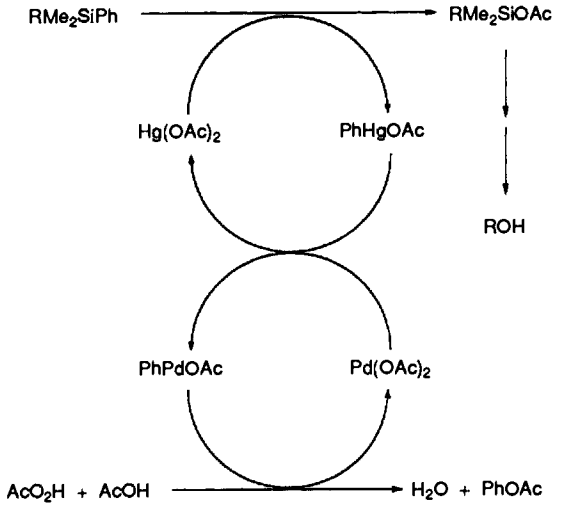
Scheme 6 *Reagents:* i, $LiAlH_4$; ii, $(MeO)_2CMe_2$, TsOH

method of synthesis. Although not critical to this work, we were able to assign stereochemistry to the alcohols **20g** and **20h** using the diagnostic coupling constants of the acetals **44** and **45** derived from the alcohols **21g** and **21h**, respectively.

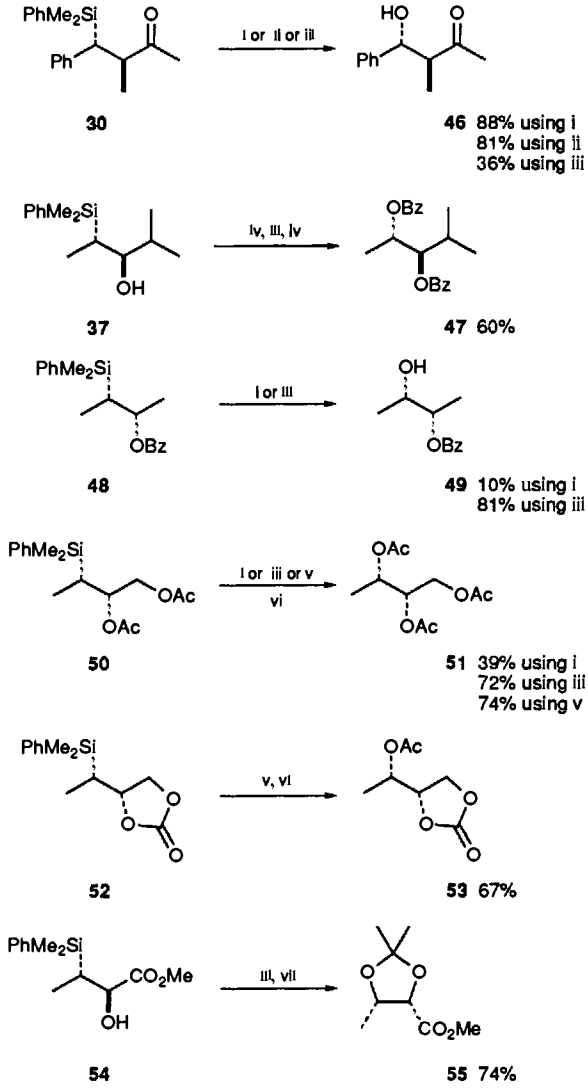
(5) *One-pot Procedures for removing the Phenyl Ring by Mercuridesilylation* (Schemes 2 and 8).—The protic acid that we had used in the earlier procedures described above had to be used in aprotic solvents for it to have the necessary strength as an electrophile to attack the benzene ring. It was, therefore, not possible to combine this step in one operation with the rearrangement step, especially when using the relatively cheap peracetic acid dissolved in acetic acid, which we recommend for larger scale work. The solution to this problem is to use other electrophiles, and we have succeeded with mercuric ion and with bromine. However, unlike protodesilylation, this type of reaction could take place on an aromatic ring elsewhere in the molecule of interest and not leave it unscathed.

Mercuric ion has been studied as an electrophile for mercuridesilylation of phenylsilanes.[40] Mercuridesilylation is known to be faster than mercurideprotonation,[41] and so should allow the reaction we want to be compatible with the presence of a phenyl group elsewhere in the molecule, but it might present problems with any more reactive aromatic rings. Furthermore, it needs protic acid catalysis, usually provided in our case by the sulfuric acid present in commercial peracetic acid solutions, and is not therefore compatible with acid-sensitive functional groups. We tested this reagent using the ester **12** and 1 equivalent of mercury(II) acetate in an excess (20 equivalents) of commercial 15% peracetic acid in acetic acid, stirring for 5 h, and obtained directly the alcohol **13** in 74% yield. Ley has used mercury(II) trifluoroacetate in a mixture of trifluoroacetic acid and acetic acid for this type of reaction with a more hindered phenyldimethylsilyl group, which had not reacted fast enough with mercury(II) acetate.[19]

(6) *A One-pot Procedure for removing the Phenyl Ring by Mercuridesilylation Catalytically* (Schemes 2, 7 and 8).—The 1 equivalent of mercuric ion was necessary. Protodemercuriation of arylmercuric salts, which might have regenerated mercuric ion, is slower than the protodesilylation of arylsilanes,[42] and the phenylsilane **12** did not undergo protodesilylation when we performed the same reaction without the mercuric acetate. It is also known that arylmercuric salts are quite unreactive towards oxidising agents.[43] However, one method by which this route might be rendered catalytic in mercuric ion, an environmentally and economically desirable goal, was to find an electrophile that did react with the arylmercuric salt to give another arylmetal ion more susceptible to oxidation by the peracid. Palladium(II) ions are known to replace mercuric ion from arylmercuric salts



Scheme 7



Scheme 8 *Reagents:* i, $Hg(OAc)_2$, AcO_2H, AcOH; ii, $0.2Hg(OAc)_2$, $0.1Pd(OAc)_2$, AcO_2H, AcOH; iii, KBr, AcO_2H, NaOAc, AcOH; iv, $(PhCO)_2O$; v, Br_2, AcO_2H, NaOAc, AcOH; vi, Ac_2O; vii, $(MeO_2)CMe_2$, TsOH

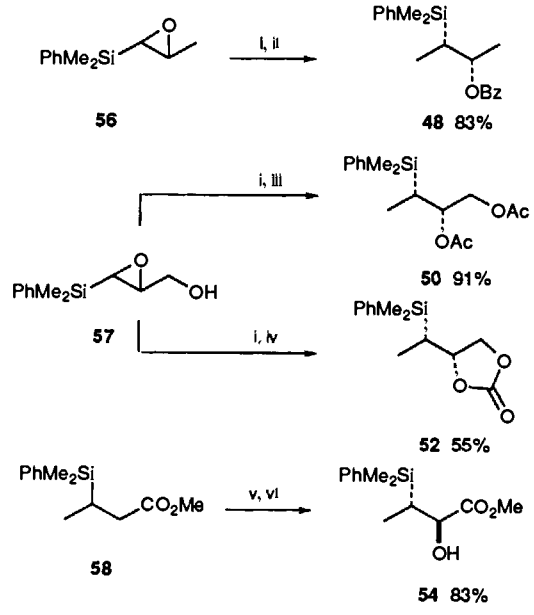
readily in acetic acid solution,[44] and it is also known that arylpalladium acetate can be oxidised.[45] We find that this

works—0.2 equivalents of mercuric acetate, 0.1 equivalents of palladium acetate and an excess of peracetic acid gave the alcohol **13** in 78% yield. The catalytic cycles are illustrated in Scheme 7. The problem with this method is that palladium acetate also catalyses the decomposition of the peracetic acid, and it is a race between the turning cycles of Scheme 7 and the disappearance of the peracetic acid that drives it. As evidence that Scheme 7 is a reasonable pathway, we found that both metal ions were needed. In the absence of mercuric acetate, no reaction took place, and in the absence of the palladium acetate, the reaction stopped after the mercuric acetate had been consumed. We also isolated phenyl acetate in 30% yield as one of the products from the same reaction, using 0.1 equivalents of mercuric acetate and 0.02 equivalents of palladium acetate, carried out on phenyltrimethylsilane, and saw no trace of biphenyl in this reaction. In the absence of the peracid, however, mercuric acetate and palladium acetate reacted with phenyltrimethylsilane to give biphenyl in 62% yield. This reaction is nearly stoichiometric in palladium, which precipitates as the colloidal metal.

(7) *One-pot Procedures for removing the Phenyl Ring by Bromodesilylation* (*Schemes 2 and 8*).—Halogenodesilylation of arylsilanes is also well known. Chlorine replaces a silyl group and hydrogen at comparable rates, and would not seem to be suitable.[46] Iodine itself favours *ipso* iododesilylation, but is rather slow, requiring heating.[47] Iodine monochloride is faster[48] and has been used by Koreeda.[49] Bromodesilylation also appeared to be ideal. It needs no acid catalysis, it is known to take place in acetic acid cleanly enough to be used for quantitative assessment of phenylsilanes, it is enormously faster than bromodeprotonation, by a factor of 10^7 for phenyltrimethylsilane relative to benzene and the bromide ion produced will be oxidised to bromine by the peracetic acid, so that only 0.5 equivalent of bromine will be needed.[50] In practice, addition of bromine in acetic acid to a solution of the silane **12** in an excess (12 equivalents) of commercial peracetic acid caused an exothermic reaction to take place, and the starting material was nearly completely consumed after 0.5 equivalent had been added. Adding a little more bromine until the starting material was no longer detectable, and working up after 5 h, gave the alcohol **13** in 84% yield. Even more convenient, addition of an excess of peracetic acid to a solution of the silane **12** in acetic acid containing sodium acetate, as a buffer, and potassium bromide as a source of bromine, gave the alcohol in 72% yield. There was no sign of bromination of the resident phenyl ring in this substrate, although we have seen this happen in other cases, when the amount of bromine or bromide is excessive. No starting material was recovered and the by-product was bromobenzene, fortunately volatile enough to be little trouble in the work-up. The buffering sodium acetate is not needed in this case, but is a definite advantage when either the substrate or product is acid-sensitive.

Thus we have two one-pot recipes for achieving the oxidation of a phenyldimethylsilyl group, both of which are more convenient than the two-step procedure. Which to use in any particular situation has usually been a matter of whim, and sometimes of trial and error, but there are a few guidelines, associated especially with the two situations which had not worked with the earlier method, namely the problem of the rearrangement **30**→**31** and the elimination **37**→**38**. The mercuric acetate procedure, stoichiometric or catalytic, with the ketone **30** gave the hydroxy ketone **46** in good yield (Scheme 8). Evidently this mixture is not acidic enough to set off the rearrangement. On the other hand, the bromine-based method with this substrate did not work well, giving only a 36% yield, presumably because either or both of the ketones **30** and **46** are too easily brominated. On the other hand, the buffered bromine-based recipe is the method of choice for the β-silyl alcohol **37**, which cleanly gave the diol derivative **47**, as we have reported elsewhere.[3] The problem with the mercuric ion-based method with this kind of substrate is almost certainly that the necessary acidity of the medium sets off the β-elimination **37**→**38**. We find that the mercuric ion method gives low yields with β-silyl alcohol derivatives in general, and specifically with the examples **48**, **50**, **52** and **54**, whereas the bromine-based method works well with each of them, giving the diol derivatives **49**, **51**, **53** and **55**. The presence of the sodium acetate buffer is not always essential, even for these substrates, but we recommend it as a sensible precaution in such cases.

(8) *Synthesis of the β-Silyl Alcohols* (Scheme 9).—The β-silyl alcohol derivatives **48**, **50**, **52** and **54** were used as models for various syntheses of sugars that we planned. They were prepared by the methods illustrated in Scheme 9, which also



Scheme 9 *Reagents:* i, Me_2CuLi; ii, $(PhCO)_2O$; iii, Ac_2O; iv, $COCl_2$; v, KNHMDS; vi, $PhC\overline{O}\overline{N}SO_2Ph$

demonstrates two of the ways in which the relative stereochemistry between the silicon-bearing and oxygen-bearing carbons can be established. The relative stereochemistry of the enolate hydroxylation leading to the alcohol **54** is the same as that for carbon electrophiles reacting with β-silyl enolates,[2] but this was our first example with a heteroatom electrophile. We proved the relative stereochemistry by reducing the alcohol **54** with lithium aluminium hydride, which gave a diol different from the intermediate in the sequence between **57** and the acetate **50**.

(9) *Conclusion and Comparison with Other Work.*—The conversion of the phenyldimethylsilyl group into a hydroxy group can be achieved by several different methods. Protodesilylation to remove the benzene ring, and hence functionalise the silyl group, has been carried out using hydrochloric acid, tetrafluoroboric acid or, best, boron trifluoride–acetic acid. Other methods that have been used include treatment with trifluoroacetic acid,[20] and, in exceptional cases, where there is a γ-hydroxy group, treatment with sodium hydride.[21] If the aromatic ring is furyl instead of phenyl, fluoride ion alone is effective, and singlet oxygen is another reagent for removing this group.[51] Alternative electrophiles for the removal of the phenyl ring are mercury(II) acetate in acidic solution, in a reaction that can be made formally catalytic in mercuric ion by using

palladium(II), also in catalytic amounts. Mercury(II) trifluoroacetate is more reactive in difficult cases.[19] Halogenodesilylation can be achieved with bromine, either administered directly, or administered as bromide ion in peracetic acid. Iodine, and especially iodine monochloride, with[52] and without[20] silver ion catalysis, may be superior on occasion. Aromatic electrophilic desilylations have been reviewed.[53]

The oxidation step may be carried out with peracids such as MCPBA or peracetic acid, in the presence of bases such as triethylamine or fluoride ion. Alternative procedures use hydrogen peroxide with fluoride ion and hydrogencarbonate ion.[27,28] If protodesilylation is the method by which the phenyl ring is removed, any of these methods will work for the oxidation step. If bromine or mercuric ion is used to remove the phenyl ring, the method using peracetic acid *in situ* is usually best, because it allows both steps to be carried out in one pot, but occasionally[19] there may be some advantage to using one of these electrophiles in the two-step procedure. The mechanism of the oxidation step has been investigated by Tamao, Hayashi and Ito.[54]

Many functional groups are compatible with the conditions—alcohol, ester, amide, carboxylic acid and nitrile groups appear rarely to be problematic. The ketone group however can give trouble both from its electrophilic nature and from its capacity to react with bromine in the bromine-based method. A phenyl ring, at least one that lacks donor substituents, is compatible even with the mercuric ion and bromine-based methods, but a cyclopropane directly attached to the silicon[35] is not, Amines and presumably sulfides, may be oxidised. The most serious deficiency is the incompatibility of a C=C double bond, unless it is either conjugated to a carbonyl group[18,19] or only monosubstituted, but this problem is met by Tamao's diethylaminodiphenylsilyl group[37] or by our 2-methylbut-2-enyl(diphenyl)silyl group,[36] both of which can be introduced as cuprates, or by alkoxydimethylsilyl,[38] allyldimethylsilyl[18,55] or furyldimethylsilyl groups,[51] which cannot. A recent addition to the armoury is the pentamethyldisilyl group, which can be introduced as a silyllithium reagent and may or may not be introduced as a cuprate.[56]

Experimental

Starting Materials.—The esters **12**, **14**, **28**, **40a** (as an 80:20 mixture of **40a** and **40b**), **40b** (as an 83:17 mixture of **40b** and **40a**) and **58**, the ketone **20a**, the acid **20b**, the amide **20c** and the nitrile **20e**, were prepared as described in our earlier papers.[2]

Dimethyl(phenyl)(2-phenylethyl)silane **6**.—Following Gilman and Marshall,[57] dimethyl(phenyl)silyl chloride (18.0 g) was added at room temperature to 2-phenylethylmagnesium bromide, prepared from the bromide (12.5 cm^3, 15.4 g) and magnesium (2.5 g) in dry ether (36 cm^3) by refluxing for 3.5 h. The mixture was stirred at room temperature for 1 h and then heated on an oil-bath at 78 °C for 64 h. After this it was diluted with ether (50 cm^3), filtered and evaporated under reduced pressure, to give the silane (9.92 g, 50%), b.p. 112–114 °C/0.3 mmHg (lit.,[58] 117–120 °C/2 mmHg); δ(CCl_4, 60 MHz) 7.75–7.25 (5 H, m, SiPh), 7.25 (5 H, br s, CPh), 2.85 (2 H, m, PhCH_2), 1.45 (2 H, m, CH_2Si) and 0.60 (6 H, s, $SiMe_2$).

Chloro(dimethyl)(2-phenylethyl)silane 7.—Following Gilman and Marshall,[57] dichlorodimethylsilane (26.0 cm^3, 27.7 g) in ether (20 cm^3) was added to 2-phenethylmagnesium chloride, prepared from the chloride (9.36 cm^3, 10.01 g) and magnesium (2.06 g) in dry ether (26 cm^3) by refluxing for 3.25 h. The mixture was refluxed for 19 h, filtered, evaporated under reduced pressure and the residue distilled to give the chlorosilane (9.97 g, 71%), b.p. 60–62 °C/0.1 mmHg.

1-*Dimethyl(phenyl)silyl*-3-*phenylpropane* **9a**.—Chlorodimethyl(phenyl)silane (10.0 g) in ether (10 cm^3) was added to 3-phenylpropylmagnesium bromide prepared from the bromide (9.95 g) and magnesium (1.3 g) in dry ether (10 cm^3) by refluxing for 2.25 h. The mixture was refluxed for 23.5 h on an oil bath at 60 °C, filtered, evaporated under reduced pressure and the residue distilled to give the silane[59] (8.99 g, 70%), b.p. 134–136 °C/0.6 mmHg; δ(CCl_4, 90 MHz) 7.8–7.2 (10 H, Ph and SiPh), 2.8 (2 H, t, *J* 8, CH_2Ph), 2.1–1.7 (2 H, m, CCH_2C), 1.1–0.9 (2 H, m, CH_2Si) and 0.45 (6 H, s, $SiMe_2$); *m/z* 239 (24%, M − Me) and 135 (100, $PhMe_2Si$) (Found: M − Me, 239.1253. $C_{17}H_{22}Si$ requires *M* − Me, 239.1256).

3-*Methyl*-1-*phenylbut*-2-*en*-1-*one*.—1-Phenyl-1-(trimethylsiloxy)ethene (11.97 g) in dichloromethane (200 cm^3) was added dropwise over 1.75 h to acetone (3.99 g, 5.04 cm^3) and titanium tetrachloride (13.72 g, 7.95 cm^3) in dry dichloromethane (500 cm^3) under argon at room temperature and the mixture stirred for 6 h. It was then diluted with water and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to give the hydroxy ketone (10.7 g). The crude hydroxy ketone (10.7 g) and toluene-*p*-sulfonic acid (4.8 g) in dry benzene (300 cm^3) were refluxed for 5.25 h in a Dean–Stark apparatus and the solvent then evaporated. The residue in ether was washed with aqueous sodium hydrogen carbonate, dried ($Na_2SO)_4$, and evaporated and the residue distilled to give the title compound (4.25 g, 43%), b.p. 50–70 °C/0.15 mmHg (lit.,[60] 136–138 °C/15 mmHg); δ(CCl_4, 60 MHz) 7.75 (2 H, m, *o*-H PhCO), 7.35 (3 H, m, *m,p*-HPhCO), 6.40 (1 H, s, C=CH), 2.15 (3 H, s, *cis Me*C=CCO) and 2.00 (3 H, s, *trans Me*C=CCO).

Conjugate Addition of the Silyl-cuprate Reagent to Enone Systems.—Typically, the enone (20 mmol) was added dropwise to a stirred solution of the silyl-cuprate[6] (21.6 mmol) under nitrogen at −23 °C and the mixture stirred for 5.25 h. It was then warmed to room temperature and stirred for a further 45 min before being quenched with basic aqueous ammonium chloride and extracted with light petroleum (b.p. 60–80 °C). The extract was washed with basic aqueous ammonium chloride until no further blue colouration was produced, dried (Na_2SO_4) and evaporated to give the β-silyl ketone or β-silyl ester. The following compounds were prepared by this method, with column chromatography [typically SiO_2, EtOAc–light petroleum, 1:3] where necessary.

3-*Dimethyl(phenyl)silyl*-1-*phenylbutan*-1-*one* (69%) as needles, m.p. 85.5–86 °C (from hexane); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.58; ν_{max}($CHCl_3$)/cm^{-1} 1680 (C=O), 1600 and 1580 (Ph), 1250 (SiMe) and 1115 (SiPh); δ($CDCl_3$, 90 MHz) 7.90–7.25 (10 H, m, Ph and SiPh), 3.05 (1 H, dd, *J* 4 and 15, CH_AH_BCO), 2.65 (1 H, dd, *J* 12 and 15, CH_AH_BCO), 1.65 (1 H, ddq, *J* 4, 8 and 12, MeC*H*), 1.00 (3 H, d, *J* 8, *Me*CH) and 0.35 (6 H, s, $SiMe_2$) (Found: M^+, 282.1454. $C_{18}H_{22}OSi$ requires *M*, 282.1440); *m/z* 282 (25%, M^+) and 135 (100, $PhMe_2Si$) (Found: C, 76.1; H, 7.8. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.85%).

3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohex*-2-*enone from* 3-*chloro*-5-*phenylcyclohex*-2-*enone*[61] (73%); R_F(hexane–EtOAc, 10:1) 0.19; ν_{max}(film)/cm^{-1} 1685 (C=O), 1116 (SiPh) and 1615 (C=C); δ(CH_2Cl_2) 7.37 (5 H, m, SiPh), 7.20 (5 H, m, Ph), 6.30 (1 H, m, C=CH), 3.22 (1 H, m, PhC*H*), 2.74–2.37 (4 H, m) and 0.54 (6 H, s, $SiMe_2$); *m/z* 306 (25%, M^+) and 135 (100%, $SiMe_2Ph$) (Found: M^+, 306.1433. $C_{20}H_{22}OSi$ requires *M*, 306.1439).

trans 3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohexanone* **16** (89%); R_F(hexane–EtOAc, 5:1) 0.33; ν_{max}(film)/cm^{-1} 1715 (C=O), 1605 (Ph) and 1430 (SiPh); δ(CH_2Cl_2) 7.33 (5 H, m, Ph), 7.19 (5 H, m, SiPh), 3.47 (1 H, m, PhCH), 2.87–1.90 (6 H, m), 1.70 (1 H, m, SiCH) 0.40 (3 H, s, $SiMe_AMe_B$) and 0.38 (3 H, s,

$SiMe_AMe_B$); *m/z* 308 (3%, M^+), 230 (29%, M − C_6H_6) and 135 (100%, $SiMe_2Ph$) (Found: M^+, 308.1597. $C_{20}H_{24}OSi$ requires *M*, 308.1597).

3-*Dimethyl(phenyl)silyl*-3-*methyl*-1-*phenylbutan*-1-*one* (57%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.70; ν_{max}($CHCl_3$)/cm^{-1} 1675 (C=O), 1600 (Ph) and 1580 (Ph); δ(CCl_4, 90 MHz) 8.1–7.4 (10 H, m, PhCO and PhSi), 3.0 (2 H, s, CH_2), 1.3 (6 H, s, Me_2C) and 0.6 (6 H, s, Me_2Si); *m/z* 296 (27%, M^+), 281 (35, M − Me) and 135 (100, $PhMe_2Si$) (Found: M^+, 296.1595. $C_{19}H_{24}OSi$ requires *M*, 296.1596).

Methyl (2RS,3SR)-3-*Dimethyl(phenyl)silyl*-2,3-*diphenylpropionate* **35** (81% as a mixture of diastereoisomers); the major (2*RS*,3*SR*) isomer was separated by crystallisation, as needles, m.p. 96–97 °C (from Et_2O–pentane); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:10] 0.32; ν_{max}(film)/cm^{-1} 1745 (C=O), 1600 and 1500 (Ph); δ(CCl_4, 90 MHz) 7.7–7.0 (15 H, m, Ph and SiPh), 4.2 (1 H, d, *J* 13, CHCO), 3.4 (3 H, s, OMe), 3.3 (1 H, d, *J* 13, SiCH), 0.0 (3 H, s, $SiMe_AMe_B$) and −0.1 (3 H, s, $SiMe_AMe_B$); *m/z* 374 (24%, M^+) and 135 (100, $PhMe_2Si$) (Found: C, 77.3; H, 6.8; M^+, 374.1710. $C_{24}H_{26}O_2Si$ requires C, 77.0; H, 7.00%; *M*, 374.1702).

3-*Dimethyl(phenyl)silylbutanal* (44%); R_F[Et_2O–light petroleum (b.p. 40–60 °C), 1:5] 0.41; δ(CCl_4, 90 MHz). 9.67 (1 H, dd, *J* 1 and 3, CHO), 7.65–7.4 (5 H, m, Ph), 2.6–2.0 (2 H, m, CH_2CHO), 1.57 (1 H, m, SiCH), 1.07 (3 H, d, *J* 7, Me) and 0.39 (6 H, s, $SiMe_2$).

Dimethyl(phenyl)(4-*phenylbutan*-2-*yl*)*silane* **9b**.—A mixture of 3-dimethyl(phenyl)silyl-1-phenylbutan-1-one (0.56 g), Raney nickel[62] (1.4 cm^3, 2.1 g) and ethanol (10 cm^3) were stirred at 90 °C for 20 h and then centrifuged. The combined washings were evaporated and chromatographed [TLC, EtOAc–light petroleum (b.p. 60–80 °C), 1:12] to give the *silane* (0.40 g, 75%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:12] 0.78; ν_{max}($CHCl_3$)/cm^{-1} 1605 and 1495 (Ph), 1.255 (SiMe) and 1115 (SiPh); δ(CCl_4, 90 MHz) 7.7–7.2 (10 H, m, Ph and SiPh), 3.2–2.5 (2 H, m, CH_2Ph), 2.25–1.50 (2 H, m, CH_2CMe), 1.30 (3 H, d, *J* 5, CH*Me*), 1.25–1.00 (1 H, m, C*H*Me) and 0.50 (6 H, s, $SiMe_2$); *m/z* 253 (0.4%, M − Me) and 135 (100, $PhMe_2Si$) (Found: M − Me, 253.1417. $C_{18}H_{24}Si$ requires *M* − Me, 253.1412).

3-*Dimethyl(phenyl)silyl*-3-*methyl*-1-*phenylbutane* **9c**.—3-Dimethyl(phenyl)silyl-3-methyl-1-phenylbutan-1-one (2.80 g) was similarly reduced to give the *silane* (2.39 g, 90%); R_F(EtOAc–light petroleum (b.p. 60–80 °C) 1:12] 0.78; ν_{max}($CHCl_3$)/cm^{-1} 1600 and 1500 (Ph), 1255 (SiMe) and 1115 (SiPh); δ(CCl_4, 90 MHz) 7.75–7.15 (10 H, m, Ph and SiPh), 2.8–2.6 (2 H, m, PhCH_2), 1.85–1.65 (2 H, m, CH_2CMe_2), 1.2 (6 H, s, CMe_2) and 0.55 (6 H, s, $SiMe_2$); *m/z* 267 (0.3%, M − Me) and 135 (100, $PhMe_2Si$) (Found: M − Me, 267.1570. $C_{19}H_{26}Si$ requires *M* − Me, 267.2569).

(3RS,5RS)-3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohexanone* **18**.—3-Dimethyl(phenyl)silyl-5-phenylcyclohexenone (1.0 g, 3.3 mmol) in ethanol (40 cm^3) was hydrogenated over palladium on charcoal (10%, 0.14 g) at atmospheric pressure and room temperature for 2 h. Filtration and evaporation of the reaction mixture under reduced pressure gave the crude ketone (0.97 g, 96%) as a *ca.* 5.3:1 mixture of the *cis* and *trans* isomers.

This mixture (3.1 mmol), toluene-*p*-sulfonic acid (0.1 g) and ethylene glycol (0.5 g) in benzene (50 cm^3) was refluxed for 3 h with a Dean–Stark head. After cooling, the mixture was washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and evaporated and the residue chromatographed (SiO_2, EtOAc–hexane, 1:20) to give cis-7-*dimethyl(phenyl)silyl*-9-*phenyl*-1,4-*dioxaspiro*[4.5]*decane* (0.83 g, 75%); R_F(EtOAc–hexane, 1:20) 0.11; ν_{max}(CCl_4)/cm^{-1} 1600 (Ph), 1495 (Ph) and 1250 ($SiMe_2$); δ(CCl_4, 90 MHz) 7.7–7.2 (10 H, m, SiPh and Ph), 3.98 (4 H, m, CH_2O), 2.98 (1 H, tt, *J* 3 and 12, PhC*H*), 2.1–1.15 (7 H, m, CH_2 and SiCH) and 0.40 (6 H, s, $SiMe_2$); *m/z* 352 (2%, M^+), 175 (100) and 135 (27, $SiMe_2Ph$) (Found: M^+, 352.1869. $C_{22}H_{28}O_2Si$ requires *M*, 352.1858). The *trans* isomer (0.17 g, 15%) had R_F 0.16; δ(CCl_4, 60 MHz) 7.7–7.05 (10 H, m, SiPh and Ph), 3.95 (4 H, br s, CH_2O), 3.01 (1 H, m, PhC*H*), 2.15–1.45 (7 H, m, CH_2 and SiCH), 0.64 (3 H, s, $SiMe_AMe_B$) and 0.62 (3 H, s, $SiMe_AMe_B$).

The *cis* ketal (0.83 g, 2.4 mmol) and toluene-*p*-sulfonic acid (0.1 g) in dry acetone (50 cm^3) was refluxed for 4 h. After evaporation of most of the solvent, the residue was taken up in ether, washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and evaporated to give the cis *ketone* **18** (0.68 g, 93%); ν_{max}(CCl_4)/cm^{-1} 1720 (C=O), 1605 (Ph), 1495 (Ph) and 1255 ($SiMe_2$); δ(CCl_4, 90 MHz) 7.65–7.15 (10 H, m, SiPh and Ph), 3.06 (1 H, m, PhCH), 2.65–1.35 (7 H, m, CH_2 and SiCH) and 0.41 (6 H, s, $SiMe_2$); *m/z* 308 (11%, M^+), 232 (22, M − C_6H_4), 230 (10, M − C_6H_6) and 135 (100, $SiMe_2Ph$) (Found: M^+, 308.1604. $C_{20}H_{24}OSi$ requires *M*, 308.1596).

N,N-*Diethyl* (2RS,3RS)-3-*Dimethyl(phenyl)silyl*-2-*methyl*-3-*phenylpropionamide* **20d**.—Dicyclohexylcarbodiimide (DCC) (0.38 g, 1.84 mmol), diethylamine (0.25 cm^3, 2.2 mmol) and the acid **20b** (0.5 g, 1.68 mmol) were stirred in dry dichloromethane (7 cm^3) at room temperature overnight. The mixture was diluted with light petroleum (b.p. 60–80 °C), filtered, washed with dilute hydrochloric acid and with aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and evaporated and the residue chromatographed (SiO_2, EtOAc–hexane, 2:5) to give the *amide* (0.372 g, 63%); R_F(EtOAc–hexane, 2:5) 0.37; ν_{max}($CHCl_3$)/cm^{-1} 1625 (C=O), 1485 (Ph) and 1260 ($SiMe_2$); δ($CDCl_3$, 90 MHz) 7.5–6.95 (10 H, m, SiPh and Ph), 3.34 (5 H, m, CH_2N and CHCO), 2.93 (1 H, d, *J* 10, C*H*Ph), 1.16 (6 H, t, *J* 7, *Me*CH_2N), 1.01 (3 H, d, *J* 6, *Me*CH), 0.35 (3 H, s, $SiMe_AMe_B$) and 0.19 (3 H, s, $SiMe_AMe_B$); *m/z* 353 (41%, M^+), 338 (75, M − Me), 324 (13, M − C_2H_5), 262 (58) and 135 (100, $SiMe_2Ph$) (Found: M^+, 353.2194. $C_{22}H_{31}NOSi$ requires *M*, 353.2175).

(2RS,3RS)-4-*Dimethyl(phenyl)silyl*-3-*methyl*-4-*phenylbutanonitrile* **20f**.—The alcohol **20** (Z=CH_2OH)[63] (2.56 g, 90 mmol) was converted into its toluene-*p*-sulfonate using toluene-*p*-sulfonyl chloride (2 g, 10 mmol) in pyridine (10 cm^3) at 0 °C for 10 h, and the crude product used directly after an acidic aqueous work-up. The toluenesulfonate (4 g, 90 mmol) was stirred with sodium cyanide (0.5 g, 100 mmol) in DMSO (35 cm^3) at room temperature for 72 h and then briefly at 60 °C, the reaction being followed by TLC. A conventional aqueous work-up and flash chromatography gave the *nitrile* (0.5 g, 19%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.5; ν_{max}(film)/cm^{-1} 2255 (CN), 1600 and 1490 (Ph), 1250 ($SiMe_2$) and 1115 (SiPh); δ(CCl_4, 90 MHz) 7.45–6.85 (10 H, m, SiPh and Ph), 2.48 (2 H, m, CH_2N), 2.32–2.10 (2 H, m, C*H*$CHCH_2$), 1.09 (3 H, d, *J* 7, *Me*CH), 0.47 (3 H, s, $SiMe_AMe_B$) and 0.23 (3 H, s, $SiMe_AMe_B$); *m/z* 293 (39%, M^+), 202 (20, M − $PhCH_2$), 175 (33) and 135 (100, $SiMe_2Ph$) (Found: M^+, 293.1584. $C_{19}H_{23}NSi$ requires *M*, 293.1599).

(2SR,3SR,4SR)*and*(2RS,3SR,4SR)-4-*Dimethyl(phenyl)silyl*-3-*methyl*-4-*phenylbutan*-2-*ol*.—The ketone[31] (3.5 g, 11.8 mmol) in dry ether (25 cm^3) was refluxed with lithium aluminium hydride (0.25 g) in dry ether (25 cm^3) for 3 h, after which the mixture was cooled. Water was added to it carefully, followed by the dropwise addition of dilute sulfuric acid until the precipitate had redissolved. The aqueous layer was extracted with ether and the combined organic phases were washed with brine, dried ($MgSO_4$) and evaporated to give the *alcohols* (3.6 g) as a *ca.* 1:1 mixture of isomers, which were used without further

purification or separation; $\nu_{max}(CHCl_3)/cm^{-1}$ 3570 (OH), 3420 (OH), 1595 (Ph), 1480 (Ph) and 1245 ($SiMe_2$); $\delta(CDCl_3$, 90 MHz) 7.7–7.1 (10 H, m, SiPh and Ph), 3.97 (1 H, dq, *J* 3 and 6, C*H*OH one isomer), 3.67 (1 H, quintet, *J* 7, C*H*OH other isomer), 2.64 (1 H, d, *J* 7, C*H*Ph one isomer) and 2.55 (1 H, d, *J* 9, C*H*Ph other isomer), 2.11 (1 H, m, SiCC*H*COH), 1.43 (1 H, br s, OH), 1.18–0.85 (6 H, m, CH*Me*), 0.44, 0.21 and 0.11 (6 H, 3 × S, $SiMe_2$).

(2SR,3SR,4SR)- *and* (2RS,3SR,4SR)-4-*Dimethyl(phenyl)silyl*-3-*methyl*-4-*phenylbut*-2-*yl Acetate*.—The mixture of alcohols (1.5 g, 5 mmol) in dry dichloromethane (15 cm^3) was stirred with pyridine (1 cm^3), 4-*N*,*N*-dimethylaminopyridine (DMAP) (0.1 g) and acetic anhydride (1 cm^3) at room temperature overnight. After work-up, the crude mixture of acetates was chromatographed [SiO_2, light petroleum (b.p. 60–80 °C)–Et_2O, 10:1] to give the (2RS,3RS,4RS)-*acetate* **20g** (0.81 g, 49% from ketone); R_F[light petroleum (b.p. 60–80 °C)–Et_2O, 10:1] 0.26; $\nu_{max}(CCl_4)/cm^{-1}$ 1730 (C=O), 1595 (Ph), 1490 (Ph) and 1250 ($SiMe_2$/C–O); $\delta(CCl_4$, 90 MHz) 7.75–7.05 (10 H, m, SiPh and Ph), 5.13 (1 H, dq, *J* 5 and 7, C*H*OAc), 2.42 (1 H, ddq, *J* 5, 9 and 8, SiCC*H*COAc), 2.24 (1 H, d, *J* 9, C*H*Ph), 2.06 (3 H, s, MeCOO), 0.86 (3 H, d, *J* 6, *Me*CH), 0.84 (3 H, d, *J* 7, *Me*CH), 0.58 (3 H, s, $SiMe_AMe_B$) and 0.15 (3 H, s, $SiMe_AMe_B$); *m*/*z* 340 (2%, M^+), 281 (3, M – OAc), 146 (100, M – $SiMe_2$Ph/OAc), 135 (84, $SiMe_2$Ph) and 131 (97) (Found: M^+, 340.1849. $C_{21}H_{28}O_2Si$ requires *M*, 340.1858); and the (2RS,3SR,4SR)-*acetate* (0.75 g, 45% from ketone); R_F 0.20; $\nu_{max}(CCl_4)/cm^{-1}$ 1730 (C=O), 1595 (Ph), 1490 (Ph) and 1250 ($SiMe_2$/C–O); $\delta(CCl_4$, 90 MHz) 7.65–7.05 (10 H, m, SiPh and Ph), 4.97 (1 H, dq, *J* 4 and 6, C*H*OAc), 2.53 (1 H, d, *J* 8, C*H*Ph), 2.17 (1 H, ddq, *J* 5, 8 and 6, SiCC*H*COAc), 1.87 (3 H, s, MeCO), 1.24 (3 H, d, *J* 6, *Me*CH), 1.03 (3 H, d, *J* 7, *Me*CH), 0.38 (3 H, s, $SiMe_AMe_B$) and 0.30 (3 H, s, $SiMe_AMe_B$); *m*/*z* 262 (0.2%, M – C_6H_6), 146 (100, M – $SiMe_2$Ph/OAc), 135 (76, $SiMe_2$Ph) and 131 (87) (Found: M^+, 340.1861).

(2RS,3SR,4SR)-4-*Dimethyl(phenyl)silyl*-3-*methyl*-4-*phenylbutan*-2-*ol* **20h**.—The (2*RS*,3*SR*,4*SR*)-acetate (0.74 g, 2.2 mmol) in dry ether (10 cm^3) was refluxed with lithium aluminium hydride (0.1 g) in dry ether (3 cm^3) for 2 h. After the reaction mixture had been cooled and quenched with dilute sulfuric acid, the aqueous layer was extracted with ether and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (0.65 g, 100%); R_F[light petroleum (b.p. 60–80 °C)–Et_2O, 10:1] 0.07; $\nu_{max}(CHCl_3)$/cm^{-1} 3560 (OH), 3430 (OH), 1595 (Ph), 1485 (Ph) and 1255 ($SiMe_2$); $\delta(CDCl_3$, 90 MHz) 7.8–7.15 (10 H, m, SiPh and Ph), 4.00 (1 H, dq, *J* 3 and 6, C*H*OH), 2.59 (1 H, d, *J* 9, C*H*Ph), 2.10 (1 H, m, SiCC*H*COH), 1.26 (1 H, s, OH), 1.17 (3 H, d, *J* 6, *Me*CHOH), 0.93 (3 H, d, *J* 7, *Me*CHCSi), 0.46 (3 H, s, $SiMe_AMe_B$) and 0.15 (3 H, $SiMe_AMe_B$); *m*/*z* 281 (6%, M – OH), 146 (68, M – $SiMe_2$Ph/OH), 135 (100, $SiMe_2$Ph) and 131 (75) (Found: M – OH, 281.1722. $C_{19}H_{26}OSi$ requires *M* – OH, 281.1725).

3-*Dimethyl(phenyl)silylcyclohexanol*.—3-Dimethyl(phenyl)-silylcyclohexanone [7] (0.79 g) in ether (5 cm^3) was added over 5 min to a stirred solution of lithium aluminium hydride (0.20 g) in ether (10 cm^3) and the mixture stirred for a further 1.25 h. Dilute aqueous hydrochloric acid was then added slowly to the mixture. The aqueous layer was separated and extracted with ether and the combined extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:3] to give the mixture of silyl alcohols [3] (0.60 g, 75%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.30; ν_{max}(film)/cm^{-1} 3350 (OH) and 1255 (SiMe); $\delta(CCl_4$, 90 MHz) 7.6–7.4 (5 H, m, Ph), 3.7–3.3 (1 H, m, C*H*OH), 3.1 (1 H, br s, OH), 2.1–1.8 (9 H, m, ring) and 0.4 (6 H, s, $SiMe_2$); *m*/*z* 234 (0.8%, M^+) and 137 (100, PhMeSiOH) (Found: M^+, 234.1450. $C_{14}H_{22}OSi$ requires *M*, 234.1440).

3-*Dimethyl(phenyl)silylcyclohexyl Acetate* **22a**.—Pyridine (30 cm^3), the 3-dimethyl(phenyl)silylcyclohexanols (1.70 g) and acetic anhydride (20 cm^3) were stirred at room temperature for 3.75 h, after which the mixture was evaporated and the residue chromatographed [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:8] to give the *acetates* (1.58 g, 89%); R_F[EtOAc, light petroleum (b.p. 60–80 °C), 1:8] 0.41; ν_{max}(film)/cm^{-1} 1730 (C=O) 1255 (SiMe); $\delta(CCl_4$, 90 MHz) 7.6–7.3 (5 H, m, Ph), 4.8–4.4 (1 H, m, C*H*OAc), 2.0 (3 H, s, OAc), 2.1–0.9 (9 H, m, ring) and 0.35 (6 H, s, $SiMe_2$); *m*/*z* 276 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 276.1545. $C_{16}H_{24}O_2Si$ requires *M*, 276.1546).

(1RS,3RS,5SR)- *and* (1SR,3RS,5SR)-3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohexanol* **22b**.—A mixutre of the ketone (4.2 g, 13.6 mmol) and sodium borohydride (0.28 g, 7.4 mmol) in ethanol (150 cm^3) was stirred at room temperature for 2 h, after which it was poured into water and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated to give a *ca.* 1:1 mixture of the alcohols (4.2 g, 99%), which were used without further purification or separation; ν_{max}(film)/cm^{-1} 3375 (OH), 1610 (Ph), 1495 (Ph) and 1255 ($SiMe_2$); $\delta(CDCl_3$, 60 MHz), 7.7–7.05 (10 H, m, SiPh and Ph), 3.82 (1 H, m, C*H*OH), 3.38 (0.5 H, m, PhC*H cis* to OH), 2.85–1.2 (8.5 H, m, PhC*H trans* to OH, CH_2, SiCH and OH), 0.63 (3 H, s, $SiMe_AMe_B$) and 0.52 (3 H, s, $SiMe_AMe_B$).

(1RS,3RS,5SR)- *and* (1SR,3RS,5SR)-3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohexyl Acetate* **22c**.—Dry triethylamine (1.3 cm^3), DMAP (0.1 g) and acetic anhydride (3 cm^3) were stirred with the alcohols **22b** (4.2 g, 13.5 mmol) in dry dichloromethane (50 cm^3) at room temperature overnight. After dilution of the mixture with light petroleum (b.p. 60–80 °C), the solution was washed with hydrochloric acid solution (5%) and with aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and evaporated. The residue was chromatographed (SiO_2, hexane–EtOAc, 10:1) to give the *acetate* (4.4 g, 92%) as a *ca.* 1:1 mixture of isomers, R_F(hexane–EtOAc) 0.35; $\nu_{max}(CCl_4)/cm^{-1}$ 1735 (C=O), 1605 (Ph), 1495 (Ph) and 1245 ($SiMe_2$ and C–O); $\delta(CCl_4$, 90 MHz), 7.75–7.1 (10 H, m, SiPh and Ph), 4.97 (1 H, m, C*H*OAc), 3.35 (0.5 H, m, $w_{\frac{1}{2}}$ 11, C*H*Ph *cis* to OAc), 2.05 (3 H, s, MeCO), 1.98 (3 H, s, MeCO), 2.8–1.05 (7.5 H, m, C*H*Ph *trans* to OAc, CH_2 and SiCH), 0.55 (3 H, s, $SiMe_AMe_B$) and 0.52 (3 H, s, $SiMe_AMe_B$), 0.37 (3 H, s, $SiMe_AMe_B$) and 0.34 (3 H, s, $SiMe_AMe_B$); *m*/*z* 309 (0.4%, M – Ac) 308 (0.5, M – C_2H_4O), 214 (0.5, M – C_6H_6/AcOH), 135 (78, $SiMe_2$Ph), 117 (100) and 105 (82) (Found: M – C_2H_4O, 308.1596. $C_{22}H_{28}O_2Si$ requires *M* – C_2H_4O, 308.1597).

(1RS,3RS,5SR)- *and* (1SR,3RS,5SR)-3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohexyl Benzoate* **22d**.—The alcohols **22b** (0.95 g, 3.1 mmol) in dry dichloromethane (20 cm^3) were stirred with pyridine (0.65 cm^3) and benzoyl chloride (0.41 cm^3) at room temperature overnight. Work-up of the reaction mixture and chromatography of the residue gave the *benzoates* (1.23 g, 98%) as a *ca.* 1:1 mixture of isomers; R_F(hexane–EtOAc, 5:1) 0.56; $\nu_{max}(CCl_4)/cm^{-1}$ 1725 (C=O), 1610 (Ph), 1595 (Ph), 1495 (Ph) and 1280 (C–O); $\delta(CCl_4$, 90 MHz) 8.15–7.0 (15 H, m, PhCO, SiPh and Ph), 5.13 (1 H, m, CHOCO), 3.32 (0.5 H, m, $w_{\frac{1}{2}}$ 12, C*H*Ph *cis* to OCOPh), 2.9–0.85 (7.5 H, m, C*H*Ph *trans* to OCOPh, CH_2 and SiCH), 0.49, 0.45, 0.27 and 0.24 (6 H, 4 × s, $SiMe_2$); *m*/*z* 292 (1.3%, M – PhCOOH), 214 (2, M – PhCOOH/C_6H_6), 135 (100, $SiMe_2$Ph), 117 (57) and 105 (53) (Found: M – PhCOOH, 292.1645. $C_{27}H_{30}O_2Si$ requires *M* – PhCOOH, 292.1647).

(1RS,3RS,5SR)- *and* (1RS,3SR,5RS)-N-[3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohexyl*]-N-*isopropylamine*.—Following Borch and his co-workers,[64] isopropylamine (1.6 cm^3, 18.8 mmol), dry hydrogen chloride in dry methanol (2 mol dm^{-3}; 3.3 cm^3, 6.6 mmol) and sodium cyanoborohydride (0.10 g, 1.6 mmol) were stirred at room temperature with the ketone **16** (0.50 g, 1.6 mmol) in dry methanol (10 cm^3) and 4 Å molecular sieves under nitrogen for 4 d. The mixture was acidified to pH 1–2 with hydrochloric acid and extracted with light petroleum (b.p. 40–60 °C). The aqueous phase was adjusted to pH 12 with solid potassium hydroxide and extracted with dichloromethane and the combined extracts were dried (Na_2SO_4) and evaporated to give the crude amine (0.46 g) as a *ca.* 2:1 mixture of isomers; $\nu_{max}(CHCl_3)/cm^{-1}$ 3275 (NH), 1600 (Ph), 1490 (Ph) and 1255 ($SiMe_2$); $\delta(CDCl_3$, 90 MHz) 7.8–7.2 (10 H, m, SiPh and Ph), 3.35–2.4 (2 H, m, CH_2CHN and PhCH), 3.00 (1 H, septet, *J* 6, MeC*H*N), 2.4–1.0 (8 H, m, NH, CH_2 and SiCH), 1.10 (6 H, d, *J* 6, Me_2CHN), 0.49 (3 H, s, $SiMe_AMe_B$) and 0.34 (3 H, s, $SiMe_AMe_B$).

(1RS,3RS,5SR)- *and* (1RS,3SR,5RS)-N-[3-*Dimethyl(phenyl)silyl*-5-*phenylcyclohexyl*]-N-*isopropylacetamide* **22e**.—Pyridine (0.16 cm^3) and acetyl chloride (0.14 cm^3) were stirred with the crude amine (0.45 g, 1.3 mmol) in dry dichloromethane (10 cm^3) under nitrogen for 3 h. Work-up of the mixture and chromatography (SiO_2, EtOAc–hexane, 3:2) of the residue gave the *amide* (0.29 g, 45% from ketone) as a mixture of isomers; R_F(EtOAc–hexane, 3:2) 0.45; $\nu_{max}(CHCl_3)/cm^{-1}$ 1625 (C=O), 1490 (Ph) and 1255 ($SiMe_2$); $\delta(CDCl_3$, 90 MHz) 7.75–7.15 (10 H, m, SiPh and Ph), 4.1–3.15 (m, MeC*H*N, CH_2CHN and PhC*H cis* to NCO) and 2.85–0.95 (m, PhC*H trans* to NCO, MeCO, CH_2, Me_2CHN and SiCH; together 19 H), 0.45 (3 H, s, $SiMe_AMe_B$) and 0.30 (3 H, s, $SiMe_AMe_B$); *m/z* 393 (0.15%, M^+), 378 (0.1, M – Me), 292 (38, M – $MeCO/C_3H_8N$) and 135 (100, $SiMe_2Ph$) (Found: M^+, 393.2485. $C_{25}H_{35}NOSi$ requires *M*, 393.2488).

trans-2-[*Dimethyl(phenyl)silylmethyl*]*cyclohexanol*.—Copper(I) iodide (0.43 g) in THF (10 cm^3) was stirred at −30 °C for 10 min with dimethyl(phenyl)silylmethylmagnesium chloride, prepared from the chloride[65] (4.24 g) and magnesium (0.55 g) in THF (10 cm^3) by heating at 65 °C for 40 min. Cyclohexene oxide (1.47 g) in THF (2 cm^3) was added at 0 °C over 5 min to the mixture which was then stirred for a further 6.5 h. The mixture was quenched at 0 °C with basic aqueous ammonium chloride and extracted with light petroleum (b.p. 60–80 °C) and the extracts were washed with basic aqueous ammonium chloride until no further blue colour appeared, dried (Na_2SO_4) and evaporated. The residue was distilled (Kugelrohr) to give the *alcohol* (2.87 g, 77%), b.p. 130–140 °C/0.5 mmHg; R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:10] 0.14; ν_{max}(film)/cm^{-1} 3400 (OH), 1250 (SiMe) and 1115 (SiPh); $\delta(CCl_4$, 90 MHz) 7.7–7.3 (5 H, m, SiPh), 3.1 (1 H, m, C*H*OH), 2.2–1.0 (10 H, m, ring and OH), 0.8–0.5 (2 H, m, CH_2Si) and 0.4 (6 H, s, $SiMe_2$); *m/z* 233 (9%, M – Me) and 137 (100, PhMeSiOH) (Found: M – Me, 233.1364. $C_{15}H_{24}OSi$ requires *M* – Me, 233.1362).

trans-2-[*Dimethyl(phenyl)silylmethyl*]*cyclohexyl Acetate* **24a**.—A mixture of the alcohol (1.5 g), acetic anhydride (25 cm^3) and pyridine (30 cm^3) were stirred at room temperature for 2 h, after which work-up and chromatography [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:12] gave the *acetate* (1.26 g, 70%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:12] 0.40; ν_{max}(film)/cm^{-1} 1735 (C=O), 1240 (SiMe) and 1110 (SiPh); $\delta(CCl_4$, 90 MHz) 7.6–7.3 (5 H, m, Ph), 4.4 (1 H, m, C*H*OAc), 2.0 (3 H, s, OMe), 2.1–0.9 (10 H, m, ring), 0.6 (1 H, dd, *J* 10 and 15, $SiCH_AH_B$) and 0.4 (6 H, s, $SiMe_2$); *m/z* 275 (2%, M – Me) and 179 (100, $PhMe_2SiC_3H_8$) (Found: M – Me, 275.1477. $C_{17}H_{26}O_2Si$ requires *M* – Me, 275.1467).

3-*Dimethyl(phenyl)silylpropan*-1-*ol*.—Dimethyl(phenyl)silyllithium (1.0 mol dm^{-3} solution in THF; 58 cm^3) was added dropwise to oxetane (3.7 g) under nitrogen at 0 °C. The mixture was warmed to room temperature and stirred for 23 h after which it was diluted with ether. The organic layer was separated, washed with water and with brine, dried (Na_2SO_4), and evaporated. The residue was distilled and passed down a short column of silica gel eluting with light petroleum (b.p. 60–80 °C) to give the alcohol (5.2 g, 46%), b.p. 160 °C/0.3 mmHg (lit.,[66] 98–99 °C/0.2 mmHg); $\delta(CCl_4$, 60 MHz) 7.7–7.2 (5 H, m, Ph), 3.6 (2 H, t, *J* 7, CH_2OH), 3.0 (1 H, br s, OH), 1.9–1.3 (2 H, m, CCH_2C), 1.1–0.7 (2 H, m, CH_2Si) and 0.5 (6 H, s, $SiMe_2$).

1-*Chloro*-3-*dimethyl(phenyl)silylpropane*.—The alcohol (3.1 g) and triphenylphosphine (5.5 g) were refluxed in carbon tetrachloride (15 cm^3) for 1.5 h, after which the mixture was cooled, diluted with pentane, filtered and evaporated and the residue distilled (Kugelrohr) to give the chloride[67] (3.0 g, 89%); $\delta(CCl_4$, 60 MHz) 7.7–7.3 (5 H, m, Ph), 3.6 (2 H, t, *J* 7, CH_2Cl), 2.2–1.7 (2 H, m, CCH_2C), 1.3–0.9 (2 H, m, CH_2Si) and 0.5 (6 H, s, $SiMe_2$).

trans-2-[3′-*Dimethyl(phenyl)silylpropyl*]*cyclohexanol*.—Copper(I) iodide (0.09 g) in THF (2 cm^3) was stirred at −30 °C for 10 min with 3-[dimethyl(phenyl)silyl]propylmagnesium chloride, prepared from the chloride (1.0 g) and magnesium (0.12 g) in THF (2 cm^3) initiated with an ultrasound bath and refluxed for 1.5 h. Cyclohexene oxide (0.30 g) in THF (0.5 cm^3) was added to the mixture which was then warmed to 0 °C and stirred for a further 4 h. Work-up of the mixture and chromatography [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:5] of the residue gave the *alcohol* (0.23 g, 27%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.32; ν_{max}(film)/cm^{-1} 3350 (OH), 1250 (SiMe) and 1120 (SiPh); $\delta(CCl_4$, 90 MHz) 7.7–7.3 (5 H, m, Ph), 3.2 (1 H, m, C*H*OH), 2.3 (1 H, br s, OH), 2.1–0.7 (15 H, m, ring-$CH_2CH_2CH_2Si$) and 0.4 (6 H, s, $SiMe_2$); *m/z* 261 (4%, M – Me), 243 (5, M – Me – H_2O) and 135 (100, $PhMe_2Si$) (Found: M – Me, 261.1695. $C_{18}H_{28}OSi$ requires *M* – Me, 261.1675).

trans-2-[3-*Dimethyl(phenyl)silylpropyl*]*cyclohexyl Acetate* **24b**.—The alcohol (0.23 g), acetic anhydride (4 cm^3) and pyridine (5 cm^3) were stirred at room temperature for 2.25 h. Work-up of the mixture and chromatography [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:10] of the residue gave the *acetate* (0.11 g, 42%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:10] 0.44; ν_{max}(film)/cm^{-1} 1735 (C=O) and 1250 (SiMe); $\delta(CCl_4$, 90 MHz) 7.6–7.3 (5 H, m, Ph), 4.5 (1 H, m, C*H*OAc), 2.0 (3 H, s, MeCO), 2.1–0.6 (15 H, m, ring-$CH_2CH_2CH_2Si$) and 0.3 (6 H, s, $SiMe_2$); *m/z* 303 (7%, M – Me), 135 (95, $PhMe_2Si$) and 117 (100, $MeCO_2C_4H_{10}$) (Found: M – Me, 303.1761. $C_{10}H_{30}O_2Si$ requires *M* – Me, 303.1780).

1-*Dimethyl(phenyl)silyl*-5-*phenylpent*-1-*yn*-3-*ol*.—Dimethyl(phenyl)silylethyne was prepared [75%, b.p. 54 °C/3 mmHg, lit.,[68] 45–50 °C/0.01 mmHg; $\delta(CCl_4$, 60 MHz), 7.98–7.34 (2 H, m, Ph), 2.96 (1 H, s, C≡CH) and 0.85 (6 H, s, $SiMe_2$)] by adaptation of the method of Holmes and Sporikou.[69] Butyllithium (1.6 mol dm^{-3} solution in hexane; 0.7 cm^3, 1.12 mmol) was added to dimethyl(phenyl)silylethyne (0.18 g, 1.12 mmol) in ether (1 cm^3) at −78 °C under nitrogen. THF (3 cm^3) and 3-phenylpropanal (0.134 g, 1 mmol) were then added at room temperature to the mixture which was then kept for 10 min. Aqueous work-up of the mixture and chromatography of

the residue gave the *alcohol* (0.17 g, 51%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.26; ν_{max}(film)/cm^{-1} 3600 (OH), 2225 (C≡C), 1600 and 1500 (Ph); δ($CDCl_3$, 80 MHz) 7.89–7.55 (2 H, m, Ph), 7.50–7.30 (3 H, m, Ph), 7.25 (5 H, s, Ph), 4.42 (1 H, t, *J* 6, C*H*OH), 2.85 (2 H, m, PhCH_2), 2.25 (2 H, m, CH_2CH_2Ph), 1.95 (1 H, br s, OH) and 0.38 (6 H, s, $SiMe_2$); *m*/*z* 276 (10%, M − H_2O), 261 (12, M − H_2O − Me), 216 (30, M − Ph), 135 (60, $PhMe_2Si$), 91 (100, $PhCH_2$) and 77 (70, Ph) (Found: M − H_2O, 276.1316. $C_{19}H_{22}OSi$ requires *M* − H_2O, 276.1334).

1-*Dimethyl*(*phenyl*)*silyl*-5-*phenylpentan*-3-*ol*.—The prop-2-ynyl alcohol (0.67 g, 2.28 mmol) was hydrogenated in ethanol (25 cm^3) over palladium on charcoal (10%; 0.67 g) for 0.5 h. Filtration (Celite) and evaporation of the reaction mixture gave the crude alcohol (0.68 g, '100%'), which was used directly in the next step. Chromatography of another sample gave the pure *alcohol*; R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.15; ν_{max}(film)/cm^{-1} 3360 (OH), 1600 and 1500 (Ph), 1250 ($SiMe_2$) and 1120 (SiPh); δ($CDCl_3$, 80 MHz) 7.58–7.25 (5 H, m, Ph), 7.24–7.15 (5 H, s, Ph), 3.55 (1 H, quintet, *J* 6, C*H*OH), 2.72 (2 H, m, PhCH_2), 1.92–1.23 (4 H, m, CH_2CHCH_2), 1.60 (1 H, br s, OH), 0.80 (2 H, m, CH_2Si) and 0.26 (6 H, s, $SiMe_2$); *m*/*z* 283 (1%, M − Me), 265 (12, M − H_2O − Me), 137 (100, $PhMe_2SiH_2$), 135 (72, $PhMe_2Si$), 104 (20, $PhCH_2CH_2$), 91 (38, $PhCH_2$) and 77 (29, Ph) (Found: M − Me, 283.1525. $C_{19}H_{26}OSi$ requires *M* − Me, 283.1518).

1-*Dimethyl*(*phenyl*)*silyl*-5-*phenylpentan*-3-*yl Benzoate* **26a**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 0.624 cm^3, 1 mmol) was added to the alcohol (0.3 g, 1 mmol) in ether (5 cm^3) at 0 °C. After 5 min, benzoyl chloride (0.13 cm^3) was added to the mixture which was then warmed to room temperature and kept for 20 h. Aqueous work-up and chromatography gave the *benzoate* (0.14 g, 35%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.45; ν_{max}(film)/cm^{-1} 1720 (C=O), 1280 ($SiMe_2$) and 1115 (SiPh); δ(CCl_4, 90 MHz) 8.14 (2 H, m, *o*-PhCO), 7.67–7.30 (8 H, m, *m*- and *p*-Ph and SiPh), 7.25 (5 H, s, Ph), 5.17 (1 H, quintet, *J* 6, C*H*OCO), 3.66 (2 H, m, PhCH_2), 2.15–1.55 (4 H, m, CH_2CHCH_2), 1.00–0.65 (2 H, m, CH_2Si) and 0.22 (6 H, s, $SiMe_2$); *m*/*z* 135 (100%, $PhMe_2Si$), 105 (95, PhCO) and 91 (35, $PhCH_2$) (Found: M − Ph, 325.1626. $C_{26}H_{30}O_2Si$ requires *M* − Ph, 325.1624).

6-*Dimethyl*(*phenyl*)*silyl*-1-*phenylhexan*-3-*ol*.—3-Dimethyl(phenyl)silylpropan-1-ol (5.1 g) and toluene-*p*-sulfonyl chloride were kept at room temperature in pyridine (15 cm^3) for 2.5 h. The mixture was extracted with ether, and the ether was washed with hydrochloric acid solution and with aqueous sodium hydrogen carbonate. The solvent was removed at reduced pressure to give the crude tosylate (8.3 g); δ(CCl_4, 60 MHz) 7.9–7.2 (9 H, m, Ar), 4.0 (2 H, t, *J* 7, CH_2O), 2.6 (3 H, s, Me), 2.1–1.4 (2 H, m, CCH_2C), 1.1–0.7 (2 H, m, CH_2Si) and 0.5 (6 H, s, $SiMe_2$), which was stirred with lithium bromide (4.2 g) in acetone (50 cm^3) at room temperature for 18 h and at 38 °C for 5 h. The solvent was evaporated at reduced pressure, the residue dissolved in ether and the solution washed with water, dried (Na_2SO_4) and concentrated. The residue was distilled (Kugelrohr) to give the 3-*dimethyl*(*phenyl*)*silylpropyl bromide* (5.7 g, 83%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.75; δ(CCl_4, 60 MHz) 7.7–7.2 (5 H, m, Ph), 3.4 (2 H, t, *J* 7, CH_2Br), 2.2–1.7 (2 H, m, CCH_2C), 1.2–0.8 (2 H, m, CH_2Si) and 0.4 (6 H, s, $SiMe_2$). The bromide (0.257 g, 1 mmol) was refluxed with magnesium (0.03 g, 1.25 mmol) in THF (2 cm^3) for 1 h, after which 3-phenylpropanal (0.134 g, 1 mmol) was added to the mixture which was then refluxed for 5 h. An aqueous work-up of the mixture and chromatography (PLC) of the residue gave the *alcohol* (0.04 g, 13%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:10] 0.07; ν_{max}(film)/cm^{-1} 3350 (OH), 1600 and 1500 (Ph), 1250 ($SiMe_2$) and 1120 (SiPh); δ(CCl_4, 60 MHz), 7.75–7.25 (5 H, m, Ph), 7.25 (5 H, s, Ph), 3.6 (1 H, m, C*H*OH), 2.75 (2 H, m, PhCH_2), 2.00–1.27 (7 H, m, CCH_2C and OH), 0.90 (2 H, m, CH_2Si) and 0.40 (6 H, s, $SiMe_2$); *m*/*z* 297 (12%, M − Me), 279 (32, M − Me − OH), 135 (100, $PhMe_2Si$) and 91 (60, $PhCH_2$) (Found: M − Me, 297.1667. $C_{20}H_{28}OSi$ requires *M* − Me, 297.1674).

6-*Dimethyl*(*phenyl*)*silyl*-1-*phenylhexan*-3-*yl Benzoate* **26b**.—The alcohol (0.30 g, 1 mmol), benzoic anhydride (0.34 g, 1.5 mmol) and DMAP (0.01 g, 0.1 mmol) were kept in triethylamine (3 cm^3) under nitrogen for 1 h. Aqueous work-up of the mixture and chromatography (PLC) of the residue gave the *benzoate* (0.3 g, 75%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.66; ν_{max}(film)/cm^{-1} 1710 (C=O), 1600 and 1500 (Ph), 1250 ($SiMe_2$) and 1120 (SiPh); δ(CCl_4, 90 MHz), 8.0 (2 H, m, *o*-Ph), 7.45 (3 H, *m*- and *p*-Ph), 7.25 (5 H, s, Ph), 7.15 (5 H, br s, Ph), 5.15 (1 H, m, C*H*OCO), 2.62 (2 H, m, PhCH_2), 2.10–1.22 (6 H, m, CCH_2C), 0.70 (2 H, m, CH_2Si) and 0.30 (6 H, s, $SiMe_2$); *m*/*z* 295 (16%, M − $PhCO_2$), 135 (100, $PhMe_2Si$), 105 (63, PhCO), 91 (390, $PhCH_2$) and 77 (30, Ph) (Found: M − $PhCO_2$, 295.1855. $C_{27}H_{32}O_2Si$ requires *M* − $PhCO_2$, 295.1882).

4-*Dimethyl*(*phenyl*)*silylbutan*-1-*ol*.—Dimethyl(phenyl)silyllithium (100 cm^3 in THF) was heated at 125 °C in a sealed tube for 40 h, after which cold water was added to it. The aqueous layer was extracted with ether and the combined extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed [SiO_2, light petroleum (b.p. 60–80 °C)] and distilled to give the alcohol (2.0 g), b.p. 150 °C/0.01 mmHg (lit.,[70] 92 °C/0.002 mmHg); δ(CCl_4, 60 MHz) 7.6–7.2 (5 H, m, Ph), 3.8–3.4 (2 H, m, CH_2OH), 2.8 (1 H, br s, OH), 1.9–1.3 (4 H, m, CCH_2CH_2C), 1.2–0.7 (2 H, m, $SiCH_2$) and 0.5 (6 H, s, $SiMe_2$).

4-*Dimethyl*(*phenyl*)*silylbutyl Bromide*.—Toluene-*p*-sulfonyl chloride (2.0 g) and the alcohol (1.9 g) were kept in pyridine (5 cm^3) at room temperature for 2.5 h, after which the mixture was diluted with ether, washed with hydrochloric acid solution (0.5%), aqueous sodium hydrogen carbonate and brine, dried (Na_2SO_4) and evaporated to give the tosylate (3.0 g, 92%); δ(CCl_4, 60 MHz) 7.9–7.2 (9 H, m, Ph), 4.0 (2 H, t, *J* 6, CH_2O), 2.6 (3 H, s, Me), 2.0–1.2 (4 H, m, CCH_2CH_2C), 1.1–0.6 (2 H, m, CH_2Si) and 0.4 (6 H, s, $SiMe_2$). Lithium bromide (1.7 g) and the tosylate (3.0 g) in acetone (20 cm^3) were stirred at room temperature for 14 h. Work-up of the mixture and distillation of the product gave the bromide (2.1 g, 85% overall), b.p. 100 °C/0.01 mmHg (lit.,[66] 123–125 °C/2.8 mmHg); δ(CCl_4, 60 MHz) 7.7–7.2 (5 H, m, Ph), 3.4 (2 H, t, *J* 7, CH_2Br), 2.3–1.2 (4 H, m, CCH_2CH_2C), 1.1–0.6 (2 H, m, CH_2Si) and 0.4 (6 H, s, $SiMe_2$).

7-*Dimethyl*(*phenyl*)*silyl*-1-*phenylheptan*-3-*ol*.—3-Phenylpropanal (1.0 g) in ether (1 cm^3) was refluxed for 3 h with 4-[dimethyl(phenyl)silyl]butylmagnesium bromide, prepared from the bromide (2.0 g) and magnesium (0.2 g) in dry ether (5 cm^3) by refluxing for 1.25 h and stirred at room temperature for 18 h. Work-up of the mixture and chromatography [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1.5] of the residue gave the *alcohol* (0.56 g, 23%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.31; ν_{max}(film)/cm^{-1} 3400 (OH), 1250 (SiMe) and 1120 (SiPh); δ(CCl_4, 90 MHz) 7.7–7.1 (10 H, m, SiPh and Ph), 3.8–3.4 (1 H, m, C*H*OH), 3.0–2.7 (2 H, m, CH_2Ph), 2.0–1.2 (8 H, m, chain), 1.4 (1 H, br s, OH), 1.0–0.6 (2 H, m, CH_2Si) and 0.4 (6 H, s, $SiMe_2$); *m*/*z* 311 (0.5%, M − H_2O) and 135 (100, $PhMe_2Si$) (Found: M − Me, 311.1827. $C_{21}H_{30}OSi$ requires *M* − Me, 311.1831).

7-*Dimethyl*(*phenyl*)*silyl*-1-*phenylheptan*-3-*yl Acetate* **26c**.—The alcohol (0.10 g), acetic anhydride (1 cm^3) and pyridine

($2\ cm^3$) were stirred at room temperature for 3 h. Work-up of the mixture and chromatography [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:3] of the residue gave the *ester* (0.06 g, 53%); R_F[SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:4] 0.49; ν_{max}(film)/cm^{-1} 1745 (C=O) and 1250 (SiMe); δ(CCl_4, 90 MHz) 7.7–7.1 (10 H, m, Ph and SiPh), 4.9 (1 H, m, C*H*OAc), 2.7 (2 H, m, CH_2Ph), 2.0 (3 H, s, OAc), 1.9–1.2 (8 H, m, $CH_2COAcCH_2CH_2CH_2$), 1.8 (2 H, m, CH_2Si) and 0.3 (6 H, s, $SiMe_2$); *m*/*z* 308 (5%, M − AcOH) and 135 (100, $PhMe_2Si$) (Found: M − AcOH, 308.1971. $C_{23}H_{32}O_2Si$ requires *M* − AcOH, 308.1961).

(2RS,3RS)- *and* (2RS,3SR)-4-*Dimethyl*(*phenyl*)*silyl*-2-*methyl*-3,4-*diphenylbutan*-2-*ol* **36**.—A mixture of the esters **35** (0.80 g) in ether ($4\ cm^3$) was refluxed for 22 h with methylmagnesium iodide, prepared from methyl iodide (1.0 g) and magnesium (0.12 g) in dry ether ($3\ cm^3$). The mixture was cooled, quenched with aqueous ammonium chloride and extracted with ether. The combined extracts were washed with water and with brine, dried (Na_2SO_4) and evaporated and the residue was chromatographed [TLC, EtOAc–light petroleum (b.p. 60–80 °C), 1:8] to give the alcohols, largely the (2*RS*,3*SR*), isomer) (0.49 g, 61%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:8] 0.35; ν_{max}(CH_2Cl_2)/cm^{-1} 3570 and 3450 (OH), 1600 and 1495 (Ph), 1250 (SiMe) and 1115 (SiPh); δ(CCl_4, 90 MHz) 7.5–7.0 (15 H, m, Ph and SiPh), 3.5 (1 H, d, *J* 12, C*H*COH), 3.2 (1 H, d, *J* 12, SiCH), 1.2 (3 H, s, C*Me*$_A$Me$_B$), 1.1 (1 H, br s, OH), 0.8 (3 H, s, CMe$_A$*Me*$_B$), 0.0 (3 H, s, Si*Me*$_A$Me$_B$) and −0.1 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 316 (0.8%, M − Me_2CO) and 135 (100, $PhMe_2Si$) (Found: M − Me_2CO, 316.1644. $C_{25}H_{30}OSi$ requires *M* − Me_2CO, 316.1647).

3-*Methyl*-1,3-*diphenylbut*-1-*ene* **31**.—*Method A.* The ketone **30**[2] (0.10 g) and tetrafluoroboric acid–diethyl ether complex (0.12 g) in dichloromethane ($1\ cm^3$) were stirred for 70 min at room temperature under nitrogen. Water and chloroform were added to the mixture, the organic layer was washed with brine, dried (Na_2SO_4) and evaporated and the residue was chromatographed [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:10] to give a mixture of products (0.06 g), R_F[SiO_2, EtOAc–light petroleum (b.p. 60–80 °C), 1:10] 0.60. The product mixture (0.06 g) was refluxed in THF ($20\ cm^3$) with aqueous sodium hydroxide ($30\ cm^3$) for 90 min after which the reaction mixture was allowed to cool and then diluted with ether. The aqueous layer was salted out and extracted with ether and the combined extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed (TLC, EtOAc–light petroleum (b.p. 60–80 °C), 1:10] to give the alkene[71] (0.02 g, 27%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:10] 0.55; ν_{max}(film)/cm^{-1} 1600 and 1500 (Ph); δ($CDCl_3$, 250 MHz), 7.5–7.2 (10 H, m, Ph), 6.4 (2 H, s, HC=CH) and 1.5 (6 H, s, CMe_2); *m*/*z* 222 (40%, M^+), 207 (50, M − Me) and 129 (100, $PhCH{=}CHC_2H_2$).

Method B. Boron trifluoride–acetic acid complex ($1\ cm^3$) was stirred with the mixed alcohols **36** (0.11 g) in dichloromethane ($2\ cm^3$) at 0 °C under nitrogen for 80 min, after which the mixture was quenched with aqueous sodium hydroxide (10%) at 0 °C and extracted with ether. The extracts were washed with water and with brine, dried (Na_2SO_4) and evaporated. The residue was dissolved in THF ($20\ cm^3$) and the solution refluxed with aqueous sodium hydroxide ($30\ cm^3$) for 90 min. After this the mixture was cooled and diluted with ether and the aqueous layer salted out. This was extracted with ether and the extract dried (Na_2SO_4) and evaporated. The residue was chromatographed [TLC, EtOAc–light petroleum (b.p. 60–80 °C), 1:10] to give the alkene **31** (0.02 g, 31%), identical (TLC, ^{1}H NMR) with the earlier sample.

5-*Dimethyl*(*phenyl*)*silylhex*-2-*ene* **39**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 1.75 cm^3, 2.8 mmol) was added dropwise to a stirred solution of ethyltriphenylphosphonium bromide (0.90 g, 2.4 mmol) in a mixture of dry THF ($15\ cm^3$) and dry DMSO ($5\ cm^3$) under nitrogen at 0 °C and the orange–red mixture stirred at room temperature for a further 15 min. The mixture was cooled to 0 °C and the silyl aldehyde (0.75 g, 3.6 mmol) in dry THF ($5\ cm^3$) was added to it; the resulting cloudy mixture was stirred for 35 min while reaching room temperature. The mixture was poured into water and extracted with light petroleum (b.p. 30–40 °C) and the combined extracts were washed with water, dried ($MgSO_4$) and evaporated. The residue was chromatographed [SiO_2, light petroleum (b.p. 30–40 °C)] to give the *alkene* (0.16 g, 30%); R_F[light petroleum (b.p. 30–40 °C)] 0.46; δ($CDCl_3$, 60 MHz) 7.48 (5 H, m, Ph), 5.53 (2 H, m, CH=CH), 2.55–2.05 (2 H, m, $CH_2C{=}C$), 1.78 (3 H, *J* 5, MeC=C), 1.46 (1 H, m, CHSi) and 0.55 (6 H, s, $SiMe_2$).

Reaction of the Alkene **39** *with Acid.*—The alkene (0.15 g, 0.7 mmol) was stirred with tetrafluoroboric acid–diethyl ether complex (0.13 cm^3, *ca.* 1.1 mmol) in dry dichloromethane ($2\ cm^3$) at 0 °C for 2.25 h, after which work-up gave a mixture (0.124 g) containing fluorodimethyl(phenyl)silane; δ($CDCl_3$, 60 MHz) 7.5 (m, Ph) and 0.7 (d, *J* 7, Ph*Me*$_2$SiF).

(2RS,3RS,4SR)- *and* (2RS,3SR,4RS)-N-[4-*Dimethyl*(*phenyl*)*silyl*-3-*methyl*-4-*phenylbutan*-2-*yl*]*pyrrolidine* **42**.—Following Borch,[64] a mixture of pyrrolidine ($1.35\ cm^3$, 16 mmol), dry hydrogen chloride in dry methanol (2 mol dm^{-3}; 2.7 cm^3, 5.4 mmol) and sodium cyanoborohydride (0.125 g, 2 mmol) was stirred at room temperature under nitrogen for 1 day with the ketone[31] **30** (0.80 g, 2.7 mmol) in dry methanol ($10\ cm^3$) containing 4 Å molecular sieves. Work-up as before gave the *amine* (0.85 g, 90%); ν_{max}(CCl_4)/cm^{-1} 2785 (N–CH_2), 1595 (Ph), 1490 (Ph) and 1255 ($SiMe_2$); δ(CCl_4, 90 MHz) 7.65–7.1 (10 H, m, SiPh and Ph), 2.79 (1 H, d, *J* 4, PhC*H*), 2.55–2.05 (6 H, m, CHN, CH_2N and SiCCHCN), 1.68 (4 H, m, CH_2CH_2N), 1.08 (3 H, d, *J* 7, *Me*CHN), 0.79 (3 H, d, *J* 6.5, *Me*CHCSi), 0.41 (3 H, s, Si*Me*$_A$Me$_B$) and 0.18 (3 H, SiMe$_A$*Me*$_B$); *m*/*z* 351 (0.3%, M^+), 336 (1, M − Me), 135 (12, $SiMe_2Ph$) and 98 (100, $C_6H_{12}N$) (Found: M^+, 351.2377. $C_{23}H_{33}NSi$ requires *M*, 351.2382).

(RS,RS)-1-*Dimethyl*(*phenyl*)*silyl*-1,2-*epoxypropane* **56**.—*m*-Chloroperbenzoic acid (*ca.* 80% peracid; 6.30 g, 29.2 mmol) was stirred with (*E*)-1-dimethyl(phenyl)silylpropene[8] (3.43 g, 19.5 mmol) in dry dichloromethane ($30\ cm^3$) over anhydrous disodium hydrogen phosphate (4.15 g, 29.2 mmol) at room temperature for 20 h after which the mixture was diluted with ether ($200\ cm^3$), washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was taken up in hexane and the solution filtered and evaporated under reduced pressure. The resulting oil was chromatographed (SiO_2, hexane–EtOAc, 10:1) to give the *epoxide* (3.29 g, 88%); R_F(hexane–EtOAc, 6:1) 0.5; ν_{max}(film)/cm^{-1} 1240 (SiMe) and 1110 (SiPh); δ($CDCl_3$) 7.3–7.8 (5 H, m, Ph), 2.9 (1 H, qd, *J* 5 and 4, C*H*Me), 2.2 (1 H, d, *J* 4, SiCHO), 1.45 (3 H, d, *J* 5, CH*Me*), 0.5 (3 H, s, Si*Me*$_A$Me$_B$) and 0.4 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 177 (28%, M − Me), 135 (100, $SiMe_2Ph$) and 121 (43, SiHMePh) (Found: M^+ − Me, 177.0739. $C_{11}H_{16}OSi$ requires *M* − Me, 177.0736).

(2RS,3RS)-3-*Dimethyl*(*phenyl*)*silylbutan*-2-*ol*.—Following Hudrlik,[72] a mixture of methyllithium (1.5 mol dm^{-3} solution in Et_2O; 18.7 cm^3, 28.0 mmol) was added dropwise to a stirred suspension of copper(I) iodide (2.67 g, 14.0 mmol) in dry ether ($15\ cm^3$) at −10 °C under nitrogen. The silyl epoxide **56** (1.92 g, 10.0 mmol) in dry ether ($10\ cm^3$) was added at −78 °C to the mixture which was then warmed to −40 °C, and finally to room temperature. After quenching of the reaction by addition of

basic aqueous ammonium chloride to the mixture, the organic layer was separated, washed with basic aqueous ammonium chloride and brine, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was passed through a short silica plug (hexane–EtOAc, 3:1) to give the β-*hydroxysilane* (1.94 g, 93%); R_F(hexane–EtOAc, 3:1) 0.4; ν_{max}(film)/cm^{-1} 3560 and 3360 (OH), 1245 (SiMe) and 1105 (SiPh); δ($CDCl_3$) 7.49–7.56 (2 H, m, Ph, *o*-Ph), 7.32–7.38 (3 H, m, *m*- and *p*-Ph), 3.85 (1 H, quintet, *J* 6.2, C*H*OH), 1.58 (1 H, br s, OH), 1.20 (1 H, m, SiC*H*Me), 1.12 (3 H, d, *J* 6.2, CHOH*Me*), 0.94 (3 H, d, *J* 7.3, *Me*CHSi) and 0.32 (6 H, s, $SiMe_2$); *m*/*z* 226 (15%, M + NH_4) and 152 (100, $SiMe_2OHPh$) [Found: (M + NH_4)$^+$, 226.1630. $C_{12}H_{20}OSi$ requires *M* + NH_4, 226.1633].

(1RS,2RS)-2-[*Dimethyl*(*phenyl*)*silyl*]-1-*methylpropyl Benzoate* **48**.—Triethylamine (1.49 cm^3, 10.68 mmol), DMAP (104 mg, 0.854 mmol) and benzoic anhydride (1.93 g, 8.54 mmol) were stirred with the β-hydroxysilane (0.83 g, 0.399 mmol) in dry dichloromethane (20 cm^3) for 12 h at room temperature. Ether (100 cm^3) was added to the solution which was then washed with hydrochloric acid solution (1 mol dm^{-3}), aqueous sodium hydrogen carbonate and brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc, 20:1) to give the *benzoate* (1.11 g, 89%); R_F(hexane–EtOAc, 10:1) 0.45; ν_{max}(film)/cm^{-1} 1700 (C=O), 1240 (SiMe) and 1105 (SiPh); δ($CDCl_3$) 8.0–8.2 (2 H, m, *o*-PhCO), 7.35–7.8 (8 H, m, *m*- and *p*-PhCO and PhSi), 5.3–5.55 (1 H, br quintet, *J* 6, C*H*OBz), 1.7 (1 H, br quintet, *J* 8, MeC*H*Si), 1.35 (3 H, d, *J* 6, *Me*CHOBz), 1.2 (3 H, d, *J* 8, *Me*CHSi) and 0.5 (6 H, s, $SiMe_2$); *m*/*z* 330 (19%, M + NH_4), 196 (100, M + H − $SiMe_2Ph$), 179 (47, M − $SiMe_2OPh$) and 152 (87, $SiMe_2OHPh$) [Found: (M + NH_4)$^+$, 330.1888. $C_{19}H_{24}O_2Si$ requires *M* + NH_4, 330.1886].

(E)-3-*Dimethyl*(*phenyl*)*silylprop*-2-*en*-1-*ol*.—Prop-2-ynyl alcohol (1.12 g, 20.0 mmol) was added dropwise to a stirred solution of the silylcuprate reagent [24.0 mmol from copper(I) cyanide (2.15 g, 24.0 mmol) and dimethyl(phenyl)silyllithium (48.0 mmol)] at 0 °C under nitrogen. After 3 h, the mixture was diluted with ether (100 cm^3), washed with basic aqueous ammonium chloride and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was distilled, the fractions boiling in the range 60–120 °C/0.4 mmHg being collected and chromatographed (SiO_2, hexane–EtOAc, with gradient elution) to give the vinylsilane[73] (2.61 g, 68%); R_F(hexane–EtOAc, 3:1) 0.39; ν_{max}(film)/cm^{-1} 3300 (OH), 1615 (C=C), 1240 (SiMe) and 1110 (SiPh); δ($CDCl_3$) 7.3–7.7 (5 H, m, Ph), 6.2 (1 H, dt, *J* 19 and 3, SiCH=C), 6.1 (1 H, d, *J* 19, C*H*CH_2OH), 4.2 (2 H, d, *J* 3, C*H*$_2$OH), 1.9 (1 H, br s, OH) and 0.4 (6 H, s, $SiMe_2$); *m*/*z* 193 (16%, M + H), 177 (20, M − Me), 159 (12, M − Me − H_2O), 137 (100, SiMeOHPh), 135 (90, $SiMe_2Ph$), 121 (25, SiHMePh) and 77 (98, Ph) [Found: (M + H)$^+$, 193.1040. $C_{11}H_{16}OSi$ requires *M* + H, 193.1048].

(2RS,3RS)-3-*Dimethyl*(*phenyl*)*silyl*-2,3-*epoxypropan*-1-*ol* **57**.—MCPBA (*ca.* 80% peracid; 1.09 g, 5.07 mmol) was stirred with the vinylsilane (0.649 g, 3.38 mmol) in dry dichloromethane (10 cm^3) over anhydrous disodium hydrogen phosphate (0.90 g, 6.34 mmol) at room temperature for 2 h. The mixture was then diluted with ether (50 cm^3), washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc, using gradient elution) to give the *epoxide* (0.636 g, 90%); R_F(hexane–EtOAc, 1:1) 0.4; ν_{max}(film)/cm^{-1} 3380 (OH), 1580 (Ph), 1260 (SiMe) and 1130 (SiPh); δ($CDCl_3$) 7.2–7.7 (5 H, m, Ph), 3.4–4.1 (2 H, m, CH_2), 2.9–3.1 (1 H, m, C*H*CH_2OH), 2.4 (1 H, d, *J* 4, SiCH), 2.1 (1 H, br t, *J* 6, OH) and 0.4 (6 H, s, $SiMe_2$); *m*/*z* 208 (1%, M), 137 (100, SiMeOHPh) and 135 (99, $SiMe_2Ph$) (Found: M$^+$, 208.0903. $C_{11}H_{16}O_2Si$ requires *M*, 208.0920).

(2RS,3RS)-3-*Dimethyl*(*phenyl*)*silylbutane*-1,2-*diol*.—Following Hudrlik,[72] methyllithium (1.5 mol dm^{-3} solution in ether; 20 cm^3, 30.6 mmol) was added dropwise to a stirred suspension of copper(I) iodide (2.91 g, 15.3 mmol) in dry ether (10 cm^3) at −10 °C under nitrogen. The epoxide **57** (1.10 g, 5.29 mmol) in dry ether was added to the resulting solution at −78 °C which was then warmed to −40 °C over 1 h and finally to room temperature. After this the mixture was quenched with aqueous ammonium chloride and the organic layer separated, washed with basic aqueous ammonium chloride and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was passed through a short silica plug (Et_2O) to give the *diol* (1.12 g, 95%); R_F(hexane–EtOAc, 1:1) 0.33; ν_{max}(film)/cm^{-1} 3360 (OH), 1240 (SiMe) and 1105 (SiPh); δ($CDCl_3$) 7.2–7.6 (5 H, m, Ph), 3.15–3.7 (3 H, m, C*H*OHCH_2OH), 2.4 (2 H, br s, 2 OH), 1.1 (1 H, m, SiC*H*Me) 0.8 (3 H, d, *J* 7, *Me*CHSi) and 0.3 (6 H, s, $SiMe_2$); *m*/*z* 209 (1%, M − Me), 191 (16, M − Me, H_2O), 137 (100, SiMeOHPh) and 135 (85, $SiMe_2Ph$) (Found: M$^+$ − Me, 209.1016. $C_{12}H_{20}O_2Si$ requires *M* − Me, 209.0998).

(2RS,3RS)-3-*Dimethyl*(*phenyl*)*silylbutane*-1,2-*diol Diacetate* **50**.—Triethylamine (0.55 cm^3, 3.95 mmol), DMAP (44 mg, 0.36 mmol) and acetic anhydride (0.37 cm^3, 3.92 mmol) were stirred with the diol (0.403 g, 1.80 mmol) in dry dichloromethane (20 cm^3) at room temperature for 5 h. After this, the mixture was diluted with ether (100 cm^3), and washed with hydrochloric acid solution (1 mol dm^{-3}), aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was passed through a short silica plug (hexane–EtOAc, 4:1) to give the *diacetate* (0.522 g, 95%); R_F(hexane–EtOAc, 1:1) 0.6; ν_{max}(film)/cm^{-1} 1730 (C=O) and 1105 (SiPh); δ($CDCl_3$) 7.48–7.51 (2 H, m, *o*-Ph), 7.33–7.36 (3 H, m, *m*- and *p*-Ph), 5.10 (1 H, td, *J* 7.5 and 2.7, C*H*OAcCH_2OAc), 4.18 (1 H, dd, *J* 12.0 and 2.7, C$H_A$$H_B$OAc), 3.96 (1 H, dd, *J* 12.0 and 7.5, C$H_A$$H_B$OAc), 2.01 (3 H, s, MeCO), 1.88 (3 H, s, MeCO), 1.46 (1 H, quintet, *J* 7.5, MeC*H*Si), 0.99 (3 H, d, *J* 7.5, *Me*CHSi), 0.33 (3 H, s, Si*Me*$_A$Me$_B$) and 0.34 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 326 (100%, M + NH_4), 249 (34, M + H) and 152 (22, $SiMe_2OHPh$) [Found: (M + NH_4)$^+$, 326.1788. $C_{16}H_{24}O_4Si$ requires *M* + NH_4, 326.1788].

Methyl (2RS,3SR)-3-*Dimethyl*(*phenyl*)*silyl*-2-*hydroxybutanoate* **54**.—Based on the methods of Davis *et al.*[74] and Evans *et al.*,[75] dry hexane (5 cm^3) was added to potassium hydride (35% suspension in mineral oil; 2 cm^3) under nitrogen, and the flask was swirled to mix the liquids. The supernatant was removed by syringe and the process was repeated (3 × 5 cm^3). The residual hexane was evaporated under reduced pressure (0.2 mmHg) to give potassium hydride (0.64 g) as a fine powder. Dry THF (12 cm^3) was added to the powder, followed, with stirring, by freshly distilled hexamethyldisilazane (2.70 cm^3, 12.8 mmol), the reaction mixture being cooled with a water bath at room temperature. The evolution of hydrogen was complete in 15 min, and the resulting solution was stored at 0 °C overnight. This solution[76] (4.60 cm^3, *ca.* 4.00 mmol) was added dropwise to a stirred solution of the β-silyl ester **58** (472 mg, 2.00 mmol) in dry THF (6 cm^3) at −78 °C under nitrogen. After 10 min, 2-phenylsulfonyl-3-phenyloxaziridine[77] (1.04 g, 4.00 mmol) in dry THF (6 cm^3) was added dropwise to the mixture, followed immediately by camphor-10-sulfonic acid (1.86 g, 8.01 mmol) in dry THF (10 cm^3) and basic aqueous ammonium chloride (4 cm^3). After the mixture had been warmed to room temperature it was diluted with ether (100 cm^3) and the organic layer separated. This was washed with aqueous sodium

thiosulfate, aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–CH_2Cl_2, using gradient elution) to give the *alcohol* (390 mg, 83%); R_F(CH_2Cl_2) 0.38; ν_{max}(film)/cm^{-1} 3500 (OH), 1725 (C=O), 1240 (SiMe) and 1105 (SiPh); δ($CDCl_3$) 7.28–7.64 (5 H, m, Ph), 4.29 (1 H, d, *J* 2.6, C*H*OH), 3.73 (3 H, s, OMe), 1.39 (1 H, br s, OH), 1.43 (1 H, qd, *J* 7.2 and 2.6, MeC*H*Si), 0.88 (3 H, d, *J* 7.2, *Me*CHSi), 0.35 (3 H, s, Si*Me*$_A$Me$_B$) and 0.38 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 237 (7%, M – Me), 152 (20, $SiMe_2OHPh$), 137 (100, SiMeOHPh) and 135 (82, $SiMe_2Ph$) (Found: M$^+$ – Me, 252.0941. $C_{13}H_{20}O_3Si$ requires *M* – Me, 237.0947).

(2RS,3RS)-3-*Dimethyl*(*phenyl*)*silylbutane*-1,2-*diol Carbonate* **52**.—Following Plattner *et al.*,[78] phosgene (63% by mass solution in toluene; 2.5 cm^3) was stirred with (2*RS*,3*RS*)-3-dimethyl(phenyl)silylbutane-1,2-diol (221 mg, 0.99 mmol), in dry chloroform (20 cm^3) and dry pyridine (5 cm^3) at 0 °C under nitrogen for 3 h after which it was warmed to room temperature and evaporated under reduced pressure. The residue was taken up in ether and the solution was washed with hydrochloric acid solution (1 mol dm^{-3}), aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (PLC, hexane–EtOAc, 1:1) to give the *carbonate* (144.5 mg, 59%); R_F(hexane–EtOAc, 2:1) 0.33; ν_{max}(film)/cm^{-1} 1800 (C=O), 1580 (Ph), 1250 (SiMe) and 1110 (SiPh); δ($CDCl_3$) 7.4–7.7 (5 H, m, Ph), 4.8 (1 H, q, *J* 8, SiCHC*H*O), 4.3 (1 H, t, *J* 8, C*H*$_A$CH$_B$O), 4.0 (1 H, t, *J* 8, CH$_A$*H*$_B$O), 1.6 (1 H, dq, *J* 8 and 7, MeC*H*Si), 1.1 (3 H, d, *J* 7, *Me*CHSi), 0.5 (3 H, s, Si*Me*$_A$Me$_B$) and 0.45 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 268 (100%, M + NH_4) and 152 (8, $SiMe_2OHPh$) [Found: (M + NH_4)$^+$, 268.1375. $C_{13}H_{18}O_3Si$ requires *M* + NH_4, 268.1381].

Protodesilylation of Phenylsilanes.—Chloro(*dimethyl*)(2-*phenylethyl*)*silane* 7. Following Kumada,[23] dry hydrogen chloride was bubbled gently through a solution of dimethyl(phenethyl)phenylsilane (3.72 g) in dry chloroform (20 cm^3) for 22.5 h at room temperature. The solvent was evaporated under reduced pressure and the residue distilled to give the chlorosilane (2.15 g, 70%), b.p. 47–49 °C/0.15 mmHg (lit.,[79] 283 °C/760 mmHg); δ(CCl_4, 60 MHz) 7.30 (5 H, br s, Ph), 2.80 (2 H, m, C*H*$_2$Ph), 1.25 (2 H, m, CH_2Si) and 0.50 (6 H, s, $SiMe_2$).

Conversion of Phenylsilanes into Fluorosilanes

Method A.—Typically, the phenylsilane (5.6 mmol) and tetrafluoroboric acid–diethyl ether complex (1.0 g) in dichloromethane (10 cm^3) was stirred at room temperature for 1–11 h, quenched with water or cold aqueous potassium hydroxide and extracted with dichloromethane. The extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure to give the fluorosilane. The following compounds, not all of which were fully characterised, were prepared by this method.

Fluoro(*dimethyl*)(3-*phenylpropyl*)*silane* **10a** (70 min) (78%), b.p. 63–64 °C/0.13 mmHg; ν_{max}(film)/cm^{-1} 1605 and 1500 (Ph) and 1265 (SiMe); δ(CCl_4, 90 MHz) 8.6–7.2 (5 H, m, Ph), 2.8 (2 H, t, *J* 7, C*H*$_2$Ph), 2.1–1.7 (2 H, m, CCH_2C), 1.0–0.7 (2 H, m, CH_2Si) and 0.3 (6 H, d, *J* 8, $SiMe_2$); *m*/*z* 196 (5%, M$^+$) and 77 (100, Ph) (Found: M$^+$, 196.1086. $C_{11}H_{17}FSi$ requires *M*, 196.1084).

Fluoro(*dimethyl*)(4-*phenylbutan*-2-*yl*)*silane* **10b** (1 h) (88%), b.p. 80 °C/0.06 mmHg; ν_{max}(film)/cm^{-1} 1605 and 1500 (Ph) and 1265 (SiMe); δ(CCl_4, 90 MHz) 7.5–7.2 (5 H, m, Ph), 3.1–2.5 (2 H, m, C*H*$_2$Ph), 2.2–1.4 (2 H, m, C*H*$_2$CMe) 1.2 (3 H, d, *J* 6, *Me*CH), 1.1–0.8 (1 H, m, MeC*H*) and 0.3 (6 H, d, *J* 8, $SiMe_2$); *m*/*z* 210 (0.7%, M$^+$), 195 (0.5, M – Me) and 77 (100, Ph) (Found: M$^+$, 210.1234. $C_{12}H_{19}FSi$ requires *M*, 210.1240).

Fluoro(*dimethyl*)(2-*methyl*-4-*phenylbutan*-2-*yl*)*silane* **10c** (1.5 h) (98% without distillation); δ(CCl_4, 90 MHz) 7.25 (5 H, m, Ph), 2.65 (2 H, m, PhC*H*$_2$), 1.66 (2 H, m, Me_2CCH_2), 1.07 (6 H, s, Me_2C) and 0.30 (6 H, d, *J* 8, $SiMe_2$); *m*/*z* 224 (1%, M$^+$), 209 (5, M – Me), 113 (15, M – $PhCH_2CH_2$) and 77 (100, Ph) (Found: M$^+$, 224.1042. $C_{13}H_{21}FSi$ requires *M*, 224.0933).

Methyl (2RS,3RS) 3-*fluoro*(*dimethyl*)*silyl*-2-*methyl*-3-*phenylpropionate* (2 h) (98%), b.p. 93–95 °C/0.05 mmHg; ν_{max}(film)/cm^{-1} 1735 (C=O), 1600 (Ph) and 1500 (Ph); δ(CCl_4, 90 MHz) 7.5–7.1 (5 H, m, Ph), 3.75 (3 H, s, OMe), 3.1 (1 H, dq, *J* 8 and 11, MeC*H*), 2.5 (1 H, dd, *J* 6 and 11, PhC*H*), 1.1 (3 H, d, *J* 8, *Me*CH), 0.2 (3 H, d, *J* 8, Si*Me*$_A$Me$_B$) and 0.1 (3 H, d, *J* 8, SiMe$_A$*Me*$_B$); *m*/*z* 254 (12%, M$^+$), 239 (25, M – Me), 195 (10, M – CO_2Me) and 131 (100, PhCHSiCH) (Found: M$^+$, 254.1127. $C_{13}H_{19}FO_2Si$ requires *M*, 254.1138).

Methyl (2RS,3SR)-3-*fluoro*(*dimethyl*)*silyl*-2-*methyl*-3-*phenylpropionate* (2 h) (87%), b.p. 100 °C/0.25 mmHg; ν_{max}(CCl_4)/cm^{-1} 1735 (C=O); δ(CCl_4, 90 MHz) 7.4–7.0 (5 H, m, Ph), 3.4 (3 H, s, OMe), 3.1 (1 H, dq, *J* 5 and 7, CHCO), 2.5 (1 H, dd, *J* 4 and 7, PhC*H*), 1.3 (3 H, dd, *J* 1 and 5, Me), 0.2 (3 H, d, *J* 6, Si*Me*$_A$Me$_B$) and 0.1 (3 H, d, *J* 6, SiMe$_A$*Me*$_B$); *m*/*z* 254 (23%, M$^+$), 239 (30, M – Me) and 135 (100, $PhMe_2Si$) (Found: M$^+$, 254.1143. $C_{13}H_{19}FO_2Si$ requires *M*, 254.1138).

trans-3-*Fluoro*(*dimethyl*)*silyl*-5-*phenylcyclohexanone* (8 h in $CHCl_3$) (87%); δ(CCl_4, 60 MHz), 7.30 (5 H, m, Ph), 3.56 (1 H, m, PhCH), 2.85–2.05 (6 H, m, CH_2), 1.49 (1 H, m, SiCH) and 0.38 (6 H, d, *J* 7.5, $SiMe_2$).

(2RS,3RS)-3-*Fluoro*(*dimethyl*)*silyl*-2-*methyl*-1,3-*diphenylpropan*-1-*one* (2.25 h) (78%); δ(CCl_4, 90 MHz) 8.2–6.9 (10 H, m, Ph), 4.2 (1 H, quintet, *J* 8, MeC*H*), 2.8 (1 H, t, *J* 8, PhC*H*), 1.4 (3 H, d, *J* 8, Me), and 0.35 (3 H, d, *J* 7, Si*Me*$_A$Me$_B$) and 0.15 (3 H, d, *J* 7, SiMe$_A$*Me*$_B$).

(2RS,3RS)-3-*Fluoro*(*dimethyl*)*silyl*-2-*methyl*-3-*phenylpropionic acid* (3 h) (96%) as prisms, m.p. 96–101 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3300–2500 (CO_2H), 1705 (C=O), 1600 (Ph), 1595 (Ph), 1490 (Ph) and 1260 ($SiMe_2$); δ($CDCl_3$, 90 MHz) 11.54 (1 H, br s, CO_2H), 7.5–7.1 (5 H, m, Ph), 3.14 (1 H, qd, *J* 6.5 and 10.5, MeC*H*), 2.57 (1 H, dd, *J* 5.5 and 10.5, CHSiF), 1.17 (3 H, d, *J* 6.5, *Me*CH) and 0.21 (6 H, d, *J* 7.5, $SiMe_2F$); *m*/*z* 220 (20%, M – HF), 205 (98, M – HF – Me), 161 (100, M – HF – Me – CO_2), 117 (86), 115 (60), 77 (50, $SiMe_2F$/Ph) and 75 (85, Me_2SiOH) (Found: C, 60.5; H, 7.2%; M$^+$ – HF, 220.0920. $C_{12}H_{17}FO_2Si$ requires C, 60.0; H, 7.15%; *M* – HF, 220.0920).

(2RS,3RS)-3-*Fluoro*(*dimethyl*)*silyl*-2-*methyl*-3-*phenylpropionamide* (8.5 h) (95%) as needles, m.p. 121–123 °C (from CCl_4–hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 (NH_2), 3400 (NH_2), 3340 (NH_2), 3180 (NH_2), 1675 (amide I), 1600 (Ph), 1590 (amide II), 1495 (Ph) and 1265 ($SiMe_2$); δ($CDCl_3$, 90 MHz) 7.45–7.1 (5 H, m, Ph), 6.3 and 6.0 (2 H, br s, NH_2), 2.92 (1 H, quintet, *J* 7.5, MeC*H*), 2.44 (1 H, dd, *J* 7.5 and 9, CHSiF), 1.14 (3 H, d, *J* 7, *Me*CH), 0.18 (3 H, d, *J* 7.5, Si*Me*$_A$Me$_B$) and 0.15 (3 H, d, *J* 7.5, SiMe$_A$*Me*$_B$); *m*/*z* 239 (10%, M$^+$), 224 (100, M – Me), 131 (100) and 77 (72, $SiMe_2F$/Ph) (Found: C, 60.6; H, 7.50; N, 5.7%; M$^+$, 239.1142. $C_{12}H_{18}FNOSi$ requires C, 60.2; H, 7.60; N, 5.8%; *M*, 239.1142).

(2RS,3RS)-N,N-*Diethyl*-3-*fluoro*(*dimethyl*)*silyl*-2-*methyl*-3-*phenylpropionamide* (5 h) (98%) as prisms, m.p. 76–78 °C [from light petroleum (b.p. 40–60 °C)]; ν_{max}($CHCl_3$)/cm^{-1} 1615 (C=O), 1490 (Ph) and 1260 ($SiMe_2$); δ($CDCl_3$, 90 MHz) 7.45–7.0 (5 H, m, Ph), 3.47 (4 H, m, CH_2N), 3.15 (1 H, m, CHCON), 2.49 (1 H, br t, *J* 4, CHSiF), 1.27 (3 H, t, *J* 7, CH_2Me_A), 1.20 (3 H, t, *J* 7, CH_2Me_B), 1.23 (3 H, d, *J* 7, *Me*CH), 0.29 (3 H, d, *J* 6.5, Si*Me*$_A$Me$_B$) and 0.03 (3 H, d, *J* 6.5, SiMe$_A$*Me*$_B$); *m*/*z* 295 (14%, M$^+$), 280 (57, M – Me), 266 (15, M – Et), 204 (33) and 77 (100, $SiMe_2F$/Ph) (Found: C, 64.8; H, 8.9; N, 4.8%; M$^+$, 295.1771. $C_{16}H_{26}FNOSi$ requires C, 65.0 H, 8.90; N, 4.7%; *M*, 295.1768).

(2RS,3RS)-3-*Fluoro(dimethyl)silyl*-2-*methyl*-3-*phenylpropionitrile* (17 h) (96%); $\nu_{max}(CCl_4)/cm^{-1}$ 2250 (CN), 1600 (Ph), 1495 (Ph) and 1265 ($SiMe_2$); $\delta(CCl_4$, 90 MHz) 7.5–7.1 (5 H, m, Ph), 3.11 (1 H, qd, *J* 7 and 9, MeC*H*), 2.36 (1 H, dd, *J* 7 and 9, CHSiF), 1.30 (3 H, d, *J* 7, *Me*CH), 0.37 (3 H, d, *J* 7.5, $SiMe_AMe_B$) and 0.24 (3 H, d, *J* 7.5, $SiMe_A\mathit{Me}_B$); *m/z* 206 (2%, M − Me), 118 (100, M − $SiMe_2F$ − CN) and 77 (17, $SiMe_2F$/Ph) (Found: M^+ − Me, 206.0809. $C_{12}H_{16}FNSi$ requires *M* − Me, 206.0801).

cis- *and* trans-3-(*Fluorodimethylsilyl*)*cyclohexyl acetate* (2 h) (76%); ν_{max}(film)/cm^{-1} 1735 (C=O); $\delta(CCl_4$, 90 MHz) 5.0–4.7 (1 H, 2 × m, $w_{\frac{1}{2}}$ 9 and 24, *trans*- and *cis*-C*H*OAc respectively), 2.1 and 2.0 (3 H, 2 × s, *trans*- and *cis*-OAc respectively), 2.2–0.8 (9 H, m, ring) and 0.5 and 0.2 (6 H, 2 × d, *J* 7, *trans*- and *cis*-$SiMe_2$, respectively); *m/z* 158 (13%, M − AcOH) and 80 (100, C_6H_8) (Found: M − AcOH, 158.0923. $C_{10}H_{19}FO_2Si$ requires *M* − AcOH, 158.0927).

(1RS,3SR,5SR)- *and* (1RS,3RS,5RS)-N-3-*Fluoro(dimethyl)silyl*-5-*phenylcyclohexyl*-N-*isopropylacetamide* (11 h) (100%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1625 (C=O), 1495 (Ph) and 1265 ($SiMe_2$); $\delta(CDCl_3$, 90 MHz) 7.55–7.15 (5 H, m, Ph), 4.15–3.25 (m, MeC*H*N, CH_2CHN and PhC*H cis* to NCO) and 3.0–1.0 (19 H, m, PhC*H trans* to NCO, MeCO, CH_2, *Me*CHN and SiCH), 0.35 (3 H, d, *J* 7.5, $SiMe_AMe_B$) and 0.26 (3 H, d, *J* 7.5, $SiMe_A\mathit{Me}_B$); *m/z* 335 (5%, M^+), 234 (23, M − MeCO/C_3H_8N), 156 (36) and 102 (100).

trans-2-[3-*Fluoro(dimethyl)silylpropyl*]*cyclohexyl acetate* (2 h) (78%); ν_{max}(film)/cm^{-1} 1735 (C=O) and 1250 (SiMe); $\delta(CCl_4$, 90 MHz) 4.5 (1 H, m, C*H*OAc), 2.0 (3 H, s, MeCO), 2.1–0.4 (15 H, m, ring and $CH_2CH_2CH_2Si$) and 0.2 (6 H, d, *J* 7, $SiMe_2$); *m/z* 200 (7%, M − AcOH) and 77 (100, Ph) (Found: M − AcOH, 200.1408. $C_{13}H_{21}FO_2Si$ requires *M* − AcOH, 200.1396).

7-*Fluorodimethylsilyl*-1-*phenylhept*-3-*yl acetate* (2 h) (97%); $\delta(CCl_4$, 60 MHz) 7.2 (5 H, br s, Ph), 5.0–4.6 (1 H, m, C*H*OAc), 3.0–2.5 (2 H, m, CH_2Ph), 2.1 (3 H, s, MeCO), 2.2–1.2 (8 H, m, chain), 1.1–0.5 (2 H, m, CH_2Si) and 0.3 (6 H, d, *J* 7, $SiMe_2$).

Methyl (2RS,3SR)-3-(*fluorodimethylsilyl*)-2,3-*diphenylpropionate* (2.25 h) (100%); $\delta(CCl_4$, 90 MHz) 7.7–7.1 (10 H, m, Ph), 4.2 (1 H, d, *J* 13, CHCO), 3.4 (3 H, s, OMe), 3.0 (1 H, dd, *J* 10 and 13, SiCH), −0.25 (3 H, d, *J* 7, $SiMe_AMe_B$) and −0.35 (3 H, d, *J* 7, $SiMe_A\mathit{Me}_B$).

Method B.—Typically, the boron trifluoride–acetic acid complex (0.30 cm^3, 2.4 mmol) was added in one portion to a stirred solution of the phenylsilane (1.3 mmol) in dry dichloromethane (7 cm^3) at room temperature. After being stirred for 1–7 h, the orange coloured solution was poured into aqueous sodium hydrogen carbonate and extracted with dichloromethane. The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the fluorosilane usually as a pale yellow oil. The following compounds, not all of which were fully characterised, were prepared by this method. When both method A and method B were used on the same phenylsilane, method B gave cleaner products.

cis-3-*Fluoro(dimethyl)silyl*-5-*phenylcyclohexanone* (7 h) (92%); $\nu_{max}(CCl_4)/cm^{-1}$ 1720 (C=O), 1605 (Ph), 1495 (Ph) and 1260 ($SiMe_2$); $\delta(CCl_4$, 90 MHz) 7.30 (5 H, m, Ph), 3.05 (1 H, m, PhCH), 2.6–1.15 (7 H, m, CH_2 and SiCH) and 0.29 (6 H, d, *J* 7.5, $SiMe_2F$); *m/z* 250 (17%, M^+), 104 (100) and 77 (77, $SiMe_2F$/Ph) (Found: M^+, 250.1182. $C_{14}H_{19}FOSi$ requires *M*, 250.1189).

(2RS,3RS)-3-*Fluoro(dimethyl)silyl*-2-*methyl*-3-*phenylpropionitrile* (10 h) (100%) identical with the earlier sample.

(2RS,3RS)-4-*Fluoro(dimethyl)silyl*-3-*methyl*-4-*phenylbutanonitrile* (3.5 h) (93%); ν_{max}(film)/cm^{-1} 2500 (CN) and 1265 ($SiMe_2$); $\delta(CCl_4$, 90 MHz) 7.55–7.05 (5 H, m, Ph), 2.73–2.10 (4 H, m, $CHCHCH_2CN$), 1.08 (3 H, d, *J* 6, *Me*CH) and 0.22 (6 H, s, $SiMe_2$).

(2RS,3RS,4RS)-4-*Fluoro(dimethyl)silyl*-3-*methyl*-4-*phenylbutan*-2-*yl acetate* (3.5 h) (91%); $\nu_{max}(CCl_4)/cm^{-1}$ 1740 (C=O), 1605 (Ph), 1495 (Ph) and 1250 ($SiMe_2$/C–O); $\delta(CCl_4$, 90 MHz) 7.5–7.15 (5 H, m, Ph), 5.15 (1 H, m, C*H*OAc), 2.55 (1 H, m, SiCC*H*COAc), 2.19 (1 H, m, SiCH), 2.11 (3 H, s, AcO), 1.25 (3 H, d, *J* 7, $CHMe_A$), 0.92 (3 H, d, *J* 7, $CH\mathit{Me}_B$), 0.44 (3 H, d, *J* 8, $SiMe_AMe_B$) and 0.10 (3 H, d, *J* 8, $SiMe_A\mathit{Me}_B$); *m/z* 222 (9%, M − AcOH), 146 (86, M − $SiMe_2F$/OAc), 131 (100) and 77 (89, $SiMe_2F$).

(3RS,4RS,5SR)-4,5-*Dimethyl*-2-*dimethylsila*-3-*phenyl*-1-*oxacyclopentane* from the alcohol **20h** (with a trace of the silyl fluoride detectable) (0 °C, 2 h, room temperature, 1 h) (97%); R_F(hexane–EtOAc, 10:1) 0.34; $\nu_{max}(CCl_4)/cm^{-1}$ 1600 (Ph), 1495 (Ph) and 1260 ($SiMe_2$); $\delta(CCl_4$, 90 MHz) 7.45–7.05 (5 H, m, Ph), 4.43 (1 H, quintet, *J* 6.5, CHOSi), 2.75 (1 H, quintet d, *J* 6.5 and 13, PhCC*H*CO), 2.27 (1 H, d, *J* 13, PhC*H*), 1.18 (3 H, d, *J* 6.5, $CHMe_A$), 1.00 (3 H, d, *J* 6.5, $CH\mathit{Me}_B$), 0.34 (3 H, s, $SiMe_AMe_B$) and −0.02 (3 H, s, $SiMe_A\mathit{Me}_B$); *m/z* 220 (36%, M^+), 205 (100, M − Me), 161 (50, M − C_3H_7O) and 75 (56, Me_2SiOH) (Found: M^+, 220.1266. $C_{13}H_{20}OSi$ requires *M*, 220.1283).

(1RS,3RS,5SR)- *and* (1RS,3SR,5SR)-3-*Fluoro(dimethyl)silyl*-5-*phenylcyclohexanol* (0 °C, 2 h, room temperature, 0.5 h) (100%); $\nu_{max}(CCl_4)/cm^{-1}$ 3610 (OH), 3350 (OH), 1600 (Ph), 1495 (Ph) and 1260 ($SiMe_2$); $\delta(CCl_4$, 90 MHz) 7.55–7.1 (5 H, m, Ph), 3.89 (1 H, m, C*H*OH), 3.35 (0.5 H, m, PhC*H cis* to OH), 3.18 (1 H, s, OH), 2.9–1.0 (7.5 H, m, PhC*H trans* to OH, CH_2 and SiCH) and 0.50–0.27 (6 H, m, $SiMe_2F$); *m/z* 252 (6%, M^+), 234 (23, M − H_2O), 117 (59), 104 (79), 91 (60) and 77 (100, $SiMe_2F$) (Found: M^+, 252.1353. $C_{14}H_{21}FOSi$ requires *M*, 252.1346).

(1RS,3RS,5SR)- *and* (1RS,3SR,5RS)-3-*Fluoro(dimethyl)silyl*-5-*phenylcyclohexyl acetate* (4 h) (97%); $\nu_{max}(CCl_4)/cm^{-1}$ 1740 (C=O), 1610 (Ph), 1495 (Ph) and 1250 ($SiMe_2$/C–O); $\delta(CCl_4$, 90 MHz), 7.4–7.15 (5 H, m, Ph), 4.97 (1 H, m, C*H*OAc), 3.29 (0.5 H, m, $w_{\frac{1}{2}}$ 15, PhC*H cis* to OAc), 2.04 (1.5 H, s, MeCO), 1.98 (1.5 H, s, MeCO), 3.0–0.9 (7.5 H, m, PhC*H trans* to OAc, CH_2 and SiCH) and 0.43–0.18 (6 H, m, $SiMe_2F$); *m/z* 234 (60%, M − AcOH), 156 (34, M − AcOH − C_6H_6), 104 (80), 91 (41) and 77 (100, $SiMe_2F$ and/or Ph) (Found: M − AcOH, 234.1241. $C_{16}H_{23}FO_2Si$ requires *M* − AcOH, 234.1240).

(1RS,3SR,5SR *and* 1RS,3RS,5RS)-3-*Fluoro(dimethyl)silyl*-5-*phenylcyclohexyl acetate* (3.2 h) (95%); $\nu_{max}(CCl_4)/cm^{-1}$ 1735 (C=O), 1600 (Ph), 1495 (Ph) and 1250 ($SiMe_2$/C–O); $\delta(CCl_4$, 90 MHz), 7.24 (5 H, m, Ph), 5.24 (0.5 H, m, $w_{\frac{1}{2}}$ 11, C*H-trans*-OAc), 4.85 (0.5 H, m, $w_{\frac{1}{2}}$ 24, C*H-cis*-OAc), 2.69 (1 H, m, PhC*H*), 2.0 (3 H, s, MeCO), 2.35–1.0 (7 H, m, CH_2 and SiCH) and 0.21 (6 H, d, *J* 7.5, $SiMe_2F$); *m/z* 294 (4%, M^+), 234 (54, M − AcOH), 117 (61), 104 (100) and 77 (76, $SiMe_2F$ and/or Ph) (Found: M^+, 294.1453. $C_{16}H_{23}FO_2Si$ requires *M*, 294.1451).

(1RS,3RS,5SR)- *and* (1RS,3SR,5RS)-3-*Fluoro(dimethyl)silyl*-5-*phenylcyclohexyl benzoate* (3.5 h) (98%); $\nu_{max}(CCl_4)/cm^{-1}$ 1725 (C=O), 1610 (Ph), 1595 (Ph), 1500 (Ph) and 1275 ($SiMe_2$/C–O); $\delta(CCl_4$, 90 MHz) 8.15–7.0 (10 H, m, PhCO and Ph), 5.17 (1 H, m, CHOCO), 3.35 (0.5 H, m, $w_{\frac{1}{2}}$ 12, PhC*H cis* to OCOPh), 3.1–0.9 (7.5 H, m, PhC*H trans* to OCOPh, CH_2 and SiCH) and 0.46–0.13 (6 H, m, $SiMe_2F$); *m/z* 234 (95%, M − PhCOOH), 158 (70, M − PhCOOH–C_6H_4), 143 (100), 105 (77), 104 (90) and 77 (36, $SiMe_2F$ and/or Ph) (Found: M − PhCOOH, 234.1239. $C_{21}H_{25}FO_2Si$ requires *M* − PhCOOH, 234.1240).

trans-2-[*Fluoro(dimethyl)silylmethyl*]*cyclohexyl acetate* (4 h) (100%); ν_{max}(film)/cm^{-1} 1720 (C=O) and 1260 (SiMe); $\delta(CCl_4$, 90 MHz) 4.4 (1 H, m, C*H*OAc), 2.0 (3 H, s, MeCO), 2.1–1.1 (9 H, m, ring), 1.0–0.3 (2 H, m, CH_2Si), 0.25 (3 H, d, *J* 8, CMe_AMe_BSi) and 0.2 (3 H, d, *J* 8, $CMe_A\mathit{Me}_BSi$); *m/z* 172 (37%, M − AcOH) and 77 (100, Ph) (Found: M − AcOH, 172.1082. $C_{11}H_{21}FO_2Si$ requires *M* − AcOH, 172.1084).

1-*Fluoro(dimethyl)silyl*-5-*phenylpent*-3-*yl benzoate* (3.5 h) (100%); δ($CDCl_3$, 60 MHz) 8.2 (2 H, m, *o*-PhCO), 7.65 (3 H, m, *m*- and *p*-PhCO), 7.25 (5 H, s, Ph), 5.25 (1 H, m, CHOCO), 2.82 (2 H, m, PhCH_2), 2.25–1.45 (**4** H, m, CH_2CHCH_2), 1.05 (2 H, m, CH_2Si) and 0.45 (6 H, d, *J* 7, $SiMe_2F$).

6-*Fluoro(dimethyl)silyl*-1-*phenylhexan*-3-*yl benzoate* (2 h) (100%); δ($CDCl_3$, 60 MHz) 8.2 (2 H, m, *o*-PhCO), 7.65 (3 H, m, *m*- and *p*-PhCO), 7.25 (5 H, s, Ph), 5.25 (1 H, m, CHOCO), 2.82 (2 H, m, PhCH_2), 2.25–1.45 (6 H, m, CH_2CH_2CHCH_2), 1.05 (2 H, m, CH_2Si) and 0.45 (6 H, d, *J* 7, $SiMe_2F$).

(RS,SR)-*Methyl* 3-*fluoro(dimethyl)silyl*-2-*methyl*-3-*phenyl*-2-(*prop*-3′-*enyl*)*propionate* (3 h) (100%) as an 80:20 mixture of diasteroisomers; δ(CCl_4, 60 MHz) 7.20–6.65 (5 H, m, Ph), 5.4 (1 H, m, C*H*=CH_2), 4.90 (1 H, m, CH=CH_AH_B), 4.70 (1 H, m, CH=CH_AH_B), 4.40 (3 H, s, OMe), 2.35 (3 H, m, CH_2 and CHSi), 1.25 (3 H, s, Me), 0.20 (3 H, d, *J* 7, Si$Me_A$$Me_B$) and 0.05 (3 H, d, *J* 7, $SiMe_A$$Me_B$).

(RS,RS)-*Methyl* 3-*fluoro(dimethyl)silyl*-2-*methyl*-3-*phenyl*-2-(*prop*-3′-*enyl*)*propionate* (3 h) (87%) as an 83:17 mixture of diastereoisomers; δ(CCl_4, 60 MHz) 6.90 (5 H, br s, Ph), 5.40 (1 H, m, C*H*=CH_2), 4.90 (1 H, m, CH=CH_AH_B), 4.75 (1 H, m, CH=CH_AH_B), 3.52 (3 H, s, OMe), 2.42 (1 H, d, *J* 8, CHSi), 2.50–1.65 (2 H, m, CH_2), 1.12 (3 H, s, Me), 0.30 (3 H, d, *J* 7, Si$Me_A$$Me_B$) and 0.05 (3 H, d, *J* 7, $SiMe_A$$Me_B$).

N-[1-*Fluoro(dimethyl)silyl*-2-*methyl*-1-*phenylbutan*-3-*yl*]-*pyrrolidine* (17 h) (96%); ν_{max}(CCl_4)/cm^{-1} 2800 (N–CH_2), 1595 (Ph), 1490 (Ph) and 1260 ($SiMe_2$); δ(CCl_4, 90 MHz) 7.23 (5 H, m, Ph), 2.9–1.65 (11 H, m, CHN, CH_2N, PhC*H*, CH_2CH_2N and SiCC*H*CN), 1.25–0.75 (6 H, m, *Me*CH) and 0.24 to −0.01 (6 H, m, $SiMe_2F$).

Oxidations of Silanes

Preparation of Alcohols from the Chlorosilane 7.—This preparation was adapted from the method of Buncel and Davies.[24] Dry ammonia was gently bubbled through chloro(dimethyl)phenethylsilane **7** (1.40 g, 7 mmol) and dry *m*-chloroperoxybenzoic acid (85% material; 7.50 g, 41 mmol) in dry ether (90 cm^3) at 0 °C for 2.5 h. After the mixture had been stirred for 16 h at room temperature it was extracted with ether (175 cm^3) and the extract washed with aqueous sodium carbonate and brine (125 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give crude product (1.25 g). This was dissolved in THF (25 cm^3) and the solution stirred with dry caesium fluoride (5.0 g) for 21 h at room temperature. The mixture was then extracted with ether (25 cm^3) and the extract washed with aqueous sodium carbonate and brine (25 cm^3), dried (Na_2SO_4), evaporated under reduced pressure and the residue distilled to give 2-phenylethanol **8** (0.32 g, 37%), b.p. 73–75 °C/0.7 mmHg (lit.,[80] 102–107 °C/14 mmHg); δ(CCl_4, 60 MHz) 7.35 (5 H, br s, Ph), 3.90 (2 H, t, *J* 6, CH_2O), 3.40 (1 H, br s, OH) and 3.00 (2 H, t, *J* 6, CH_2Ph) identical with a commercial sample.

Preparation of Alcohols from Fluorosilanes

Method A.—Typically, triethylamine (0.62 g, 6 mmol) in ether (5 cm^3) was added dropwise to a stirred solution of fluorosilane (5.1 mmol) and *m*-chloroperoxybenzoic acid (95% material; 3.24 g, 20 mmol) in ether (10 cm^3) under nitrogen at 0 °C. The mixture was warmed to room temperature, stirred for 2.25 h and then quenched with aqueous sodium thiosulfate. The organic layer was washed with aqueous sodium thiosulfate and with 0.5% aqueous hydrochloric acid and then evaporated under reduced pressure. The product was dissolved in methanol to which a few drops of concentrated hydrochloric acid were added and, after 15 min, was evaporated under reduced pressure. The product was redissolved in ether and the solution washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4) and evaporated under reduced pressure and the residue chromatographed [SiO_2, EtOAc–light petroleum (b.p. 60–80 °C)] to give the alcohol. In some cases, silyl ether cleavage with tetrabutylammonium fluoride (0.2 mol dm^{-3} in THF) for 45 min at 0 °C was used in place of acidic methanol. The following compounds were prepared by this method.

3-Phenylpropanol[18] **11a** (74%); δ($CDCl_3$, 60 MHz) 7.1 (5 H, s, Ph), 3.5 (2 H, t, *J* 6, CH_2OH), 2.65 (2 H, m, CH_2Ph), 2.3 (1 H, br s, OH) and 2.1–1.6 (2 H, m, CCH_2C).

4-Phenylbutan-2-ol[82] **11b** (70%); δ($CDCl_3$, 60 MHz) 7.2 (5 H, br s, Ph), 3.7 (1 H, tq, *J* 7 and 7, C*H*OH), 2.9–2.5 (2 H, m, CH_2Ph), 2.0–1.5 (2 H, m, CH_2CMe), 1.8 (1 H, br s, OH) and 1.25 (3 H, d, *J* 7, *Me*CH), identical with an authentic sample.

Methyl (2*RS*,3*SR*)-3-hydroxy-2-methyl-3-phenylpropionate **13** (76%) as needles, m.p. 49–51 °C [from Et_2O–light petroleum (b.p. 60–80 °C)] (lit.,[83] 50.5–51.5 °C); ν_{max}($CHCl_3$) 3500 (OH) and 1730 (C=O); δ($CDCl_3$, 90 MHz) 7.4 (5 H, br s, Ph), 4.8 (1 H, d, *J* 9, C*H*OH), 3.8 (3 H, s, OMe), 2.8 (1 H, dq, *J* 8 and 9, CHCO), 2.8 (1, br s, OH) and 1.0 (3 H, d, *J* 8, CMe); *m*/*z* 194 (4%, M^+) and 88 (100, $MeCH_2CO_2Me$) (Found: M^+, 194.0936. $C_{11}H_{14}O_3$ requires *M*, 194.0943).

Methyl (2*RS*,3*RS*)-3-hydroxy-2-methyl-3-phenylpropionate[83] **15** (72%); b.p. 100 °C/0.2 mmHg; ν_{max}(film)/cm^{-1} 3480 (OH) and 1730 (C=O); ν_{max}(CCl_4, 90 MHz) 7.4 (5 H, br s, Ph), 5.1 (1 H, d, *J* 5, C*H*OH), 3.7 (3 H, s, OMe), 3.0 (1 H, br s, OH), 2.7 (1 H, dq, *J* 5 and 9, C*H*Me) and 1.1 (3 H, d, *J* 9, CH*Me*); *m*/*z* 194 (12%, M^+) and 88 (100, $MeCH_2CO_2Me$) (Found: M^+, 194.0940. $C_{11}H_{14}O_3$ requires *M*, 194.0943).

trans-3-*Hydroxy*-5-*phenylcyclohexanone* **17** (64%) as plates, m.p. 157–158 °C (from $CHCl_3$–hexane); R_F(EtOAc–hexane, 1:1) 0.15; ν_{max}($CHCl_3$)/cm^{-1} 3600 (OH), 3420 (OH), 1710 (C=O) and 1605 (Ph); δ($CDCl_3$, 250 MHz), 7.36–7.21 (5 H, m, Ph), 4.59 (1 H, quintet, *J* 2.5, CHOH), 3.56 (1 H, tt, *J* 4 and 12, C*H*Ph), 2.70–2.48 (4 H, m, CH_2C=O), 2.21 (1 H, m, PhCHCH_{eq}CHOH), 2.06 (1 H, dt, *J* 2 and 12, PhCHCH_{ax}-CHOH) and 1.71 (1 H, br s, OH); *m*/*z* 190 (7%, M^+), 172 (54, M − H_2O), 144 (37), 130 (38), 107 (43) and 104 (100) (Found: M^+, 190.0992. $C_{12}H_{14}O_2$ requires *M*, 190.0994).

(2*RS*,3*SR*)-3-*Hydroxy*-2-*methyl*-1,3-*diphenylpropan*-1-*one*[84] **21a** (63%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.28; ν_{max}(CCl_4)/cm^{-1} 3620 and 3500 (OH), 1680 (C=O) 1600 (Ph), 1575 (Ph) and 1495 (Ph); δ($CDCl_3$, 90 MHz) 8.2–7.2 (10 H, m, Ph), 5.0 (1 H, d, *J* 8, C*H*OH), 3.8 (1 H, quintet, *J* 8, CHCO), 3.2 (1 H, br s, OH) and 1.0 (3 H, d, *J* 8, Me); *m*/*z* 240 (3%, M^+) and 105 (100, PhCO) (Found: M^+, 240.1160. $C_{16}H_{16}O_2$ requires *M*, 240.1150).

cis- *and* trans-3-*Hydroxycyclohexyl acetate*[85] **23a** (55%); R_F-[EtOAc–light petroleum (b.p. 60–80 °C), 1:1] 0.28; ν_{max}-(CCl_4)/cm^{-1} 3400 (OH) and 1740 (C=O); δ(CCl_4, 90 MHz) 5.1 and 4.6 (1 H, 2 × m, $w_{\frac{1}{2}}$ 11 and 20, *trans*- and *cis*-C*H*OAc, respectively), 4.0 and 3.6 (1 H, 2 × m, $w_{\frac{1}{2}}$ 12 and 20, *trans*- and *cis*-C*H*OH, respectively), 2.0 (3 H, s, MeCO) and 2.2–1.0 (9 H, m, ring and OH); *m*/*z* 115 (0.4%, M − Ac) and 64 (100, C_5H_4) (Found: M − Ac, 115.0766. $C_8H_{14}O_3$ requires *M* − Ac, 115.0759).

trans-2-(3-*Hydroxypropyl*)*cyclohexyl acetate*[86] **25b** (56%); ν_{max}(film)/cm^{-1} 3400 (OH) and 1740 (C=O); δ(CCl_4, 60 MHz) 4.4 (1 H, m, C*H*OAc), 3.6 (1 H, m, CH_2OH), 2.8 (1 H, br s, OH), 2.1 (3 H, s, MeCO) and 2.2–0.7 (13 H, m, ring-CH_2CH_2); *m*/*z* 200 (2%, M^+) and 122 (100, C_6H_{10}=CHCH=CH_2) (Found: M^+, 200.1413. $C_{11}H_{20}O_3$ requires *M*, 200.1412).

7-*Hydroxy*-1-*phenylheptan*-3-*yl acetate* **27c** (69%); R_F[EtOAc–light petroleum (b.p. 60–80 °C) 1:33] 0.16; ν_{max}-(film)/cm^{-1} 3420 (OH) and 1730 (C=O); δ($CDCl_3$, 90 MHz) 7.4–7.2 (5 H, m, Ph), 4.9 (1 H, quintet, *J* 7, C*H*OAc), 3.6 (2 H, m, CH_2OH), 2.6 (2 H, m, PhCH_2), 2.0 (3 H, s, MeCO) and 2.1–1.1 (9 H, m, CH_2CH_2CH_2COAcCH_2 and OH); *m*/*z* 190 (24%, M − AcOH) and 104 (100, $PhCH_2CH_2$) (Found: M − AcOH, 190.1364. $C_{15}H_{22}O_3$ requires *M* − AcOH, 190.1358).

Methyl (2*RS*,3*RS*)-3-hydroxy-2,3-diphenylpropionate **29** (73%), as needles, m.p. 84–85 °C (lit.,[87] 87–88 °C); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.25; δ($CDCl_3$, 90 MHz) 7.5–7.2 (10 H, m, Ph), 5.3 (1 H, d, *J* 7, C*H*OH), 3.9 (1 H, d, *J* 7, CHCO), 3.6 (3 H, s, OMe) and 2.6 (1 H, br s, OH).

Method B.—Typically, *m*-chloroperoxybenzoic acid (0.83 g, 85%, 4.1 mmol) in dry DMF (7 cm^3) was added dropwise to a stirred solution of the fluorosilane (1.3 mmol) and anhydrous potassium fluoride (0.16 g, 2.8 mmol) in dry DMF (5 cm^3) at room temperature (there was a slightly exothermic reaction). The resulting solution was stirred for 4 h at room temperature, diluted with dichloromethane and washed successively with aqueous sodium thiosulfate, aqueous sodium carbonate and brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the alcohols, which were chromatographed. The following alcohols were prepared by this method.

2-Methyl-4-phenylbutan-2-ol **11c** (62%) [untypically using dimethylacetamide as the solvent, a large excess (16 mmol) of peracid, 3-*tert*-butyl-4-hydroxy-5-methylphenylsulfide,[30] and adding it in small portions at 15 min intervals over 4 h, followed by heating at 60 °C overnight]; R_F(EtOAc) 0.5; ν_{max}(film)/cm^{-1} 3400 (OH), 1600 (Ph) and 1500 (Ph); δ($CDCl_3$, 60 MHz) 7.25 (5 H, s, Ph), 2.8 (2 H, m, CH_2CH$_2$), 2.0 (1 H, br s, OH), 1.95 (2 H, m, CH$_2$CH_2) and 1.35 (6 H, s, CMe_2), identical (TLC, IR, ^{1}H NMR) with an authentic sample made from phenethylmagnesium bromide and acetone.

cis-3-*Hydroxy*-5-*phenylcyclohexanone* **19** (65% crude) as needles, m.p. 89–91 °C [from Et_2O–light petroleum (b.p. 30–40 °C]: R_F(EtOAc–hexane, 2:1) 0.28; ν_{max}($CHCl_3$)/cm^{-1} 3610 (OH), 3425 (OH), 1715 (C=O), 1605 (Ph) and 1495 (Ph); δ($CDCl_3$, 250 MHz) 7.38–7.20 (5 H, m, Ph), 4.08 (1 H, tt, *J* 4 and 11, C*H*OH), 2.93–2.79 (2 H, m, PhC*H* and CH_AH_BC=O), 2.60–2.33 (4 H, m, 3 H of CH_AH_BC=O, $COCH_2$ and PhCHC$H_{eq}H_{ax}$CHOH), 1.93 (1 H, td, *J* 11 and 12, PhCHCH$_{eq}H_{ax}$CHOH) and 1.90 (1 H, br s, OH); *m*/*z* 190 (84%, M^+), 172 (5, M − H_2O), 149 (36), 130 (34), 107 (98) and 104 (100) (Found: M^+, 190.0991. $C_{12}H_{14}O_2$ requires *M*, 190.0994). This compound is unstable to chromatography, and the spectroscopically pure sample was obtained in only 15% yield (UGI alumina, EtOAc–hexane, 3:1).

(2RS,3SR)-3-*Hydroxy*-2-*methyl*-3-*phenylpropionamide* **21c** (85%) as rhombs, m.p. 134–136 °C [from $CHCl_3$–Me_2CO–light petroleum (b.p. 40–60 °C)]; R_F(CH_2Cl_2–MeOH, 20:1) 0.08; ν_{max}(KBr)/cm^{-1} 3350 (OH/NH_2), 3180 (NH_2), 1670 (amide I), 1620 (amide II), 1590 (Ph) and 1490 (Ph); δ(CD_3OD + CD_3COCD_3, 90 MHz) 7.19 (5 H, m, Ph), 4.51 (1 H, d, *J* 7.5, PhC*H*), 3.78 (3 H, br s, OH and NH_2), 2.51 (1 H, br quintet, *J* 7.5, MeC*H*) and 0.76 (3 H, d, *J* 7, *Me*CH); *m*/*z* 179 (4%, M^+), 164 (6, M − Me), 105 (20), 77 (35, Ph) and 73 (100, retro-aldol) (Found: M^+, 179.0950. $C_{10}H_{13}NO_2$ requires *M*, 179.0946).

(2RS,3SR)-N,N-*Diethyl*-3-*hydroxy*-2-*methyl*-3-*phenylpropanamide* **21d** (90%); R_F(EtOAc–hexane, 3:1) 0.38; ν_{max}($CHCl_3$)/cm^{-1} 3360 (OH), 1610 (C=O) and 1490 (Ph); δ($CDCl_3$, 90 MHz) 7.38 (5 H, m, Ph), 4.85 (1 H, br s, OH), 4.80 (1 H, d, *J* 5, PhC*H*OH), 3.45–2.8 (5 H, m, CH_2N and CHCON), 1.28 (3 H, d, *J* 6.5, *Me*CH) and 1.01 (3 H, t, *J* 7, Me_ACH_2N) and 0.93 (3 H, t, *J* 7, Me_BCH_2N); *m*/*z* 235 (14%, M^+), 220 (26, M − Me), 202 (5, M − H_2O/Me), 129 (100, retro-aldol) and 58 (66) (Found: M^+, 235.1573. $C_{14}H_{21}NO_2$ requires *M*, 235.1573).

(2RS,3RS)-4-*Hydroxy*-3-*methyl*-4-*phenylbutanonitrile* (64% based on the phenylsilane); R_F[EtOAc–light petroleum (b.p. 60–80 °C). 1:5] 0.08; ν_{max}(film)/cm^{-1} 3450 (OH), 2275 (CN) and 1500 (Ph); δ(CCl_4, 90 MHz) 7.40 (5 H, s, Ph), 4.45 (1 H, d, *J* 8, PhC*H*), 2.53 (2 H, d, *J* 6, CH_2CN), 2.40 (1 H, br s, OH), 2.15 (1 H, m, MeC*H*) and 0.92 (3 H, d, *J* 7, *Me*CH); *m*/*z* 175 (10%, M^+), 107 (100, $PhCH_2O$), 79 (40) and 77 (22, Ph) (Found: M^+, 175.0981. $C_{14}H_{21}NO_2$ requires *M*, 175.0997).

(2RS,3SR,4RS)-4-*Hydroxy*-3-*methyl*-4-*phenylbutan*-2-*yl acetate* **21g** and (1RS,2RS,3RS)-3-*hydroxy*-2-*methyl*-1-*phenylbutyl acetate* (3:2, 71%); mixture: ν_{max}($CHCl_3$)/cm^{-1} 3620 (OH), 3460 (OH), 1730 (C=O), 1495 (Ph) and 1260 (C–O ester); *m*/*z* 222 (0.4%, M^+), 204 (0.2, M − H_2O), 162 (0.2, M − AcOH) and 107 (100, C_7H_7O) (Found: M^+, 222.1255. $C_{13}H_{18}O_3$ requires *M*, 222.1256); the isomers could be partly separated by PLC: major isomer **21g**: R_F(EtOAc–hexane, 3:2) 0.53; δ($CDCl_3$, 90 MHz) 7.38 (5 H, m, Ph), 5.29 (1 H, quintet, *J* 6, C*H*OAc), 4.49 (1 H, d, *J* 9, PhC*H*OH), 2.13 (2 H, m, OH and PhCC*H*COAc), 2.00 (3 H, s, MeCOO), 1.24 (3 H, d, *J* 6, *Me*CHOAc) and 0.71 (3 H, d, *J* 8, *Me*CHCPh); minor isomer: R_F(EtOAc–hexane, 3:2) 0.42; δ($CDCl_3$, 90 MHz) 7.38 (5 H, m, Ph), 5.84 (1 H, d, *J* 8, PhC*H*OAc), 3.81 (1 H, quintet, *J* 6, C*H*OH), 2.13 (2 H, m, OH and PhCC*H*COH), 2.06 (3 H, s, MeCOO), 1.17 (3 H, d, *J* 6, *Me*CHOH) and 0.71 (3 H, d, *J* 8, *Me*CHCPh). The regioisomeric hydroxyacetates interconverted on storage in $CDCl_3$.

(1RS,2RS,3SR)-2-*Methyl*-1-*phenylbutane*-1,3-*diol* **21h** (53%); R_F(CH_2Cl_2–MeOH, 30:1) 0.20; ν_{max}($CHCl_3$)/cm^{-1} 3590 (OH), 3375 (OH), 1600 (Ph) and 1490 (Ph); δ($CDCl_3$, 90 MHz), 7.40 (5 H, m, Ph), 4.68 (1 H, d, *J* 7, PhC*H*OH), 4.26 (1 H, br s, OH), 4.04 (1 H, dq, *J* 2.5 and 6.5, MeC*H*OH), 3.78 (1 H, br s, OH), 1.91 (1 H, d quintet, *J* 2.5 and 7, HOCC*H*COH), 1.18 (3 H, d, *J* 6.5, *Me*CHOH) and 0.79 (3 H, d, *J* 7, *Me*CHCPh); *m*/*z* 180 (1%, M^+), 162 (7, M − H_2O), 107 (100, C_7H_7O) and 57 (56) (Found: M^+, 180.1144. $C_{11}H_{16}O_2$ requires *M*, 180.1150).

(1RS,3SR,5RS)-5-*Phenylcyclohexane*-1,3-*diol* **23b** (34%) as plates, m.p. 133–135 °C (from CCl_4) (lit.,[88] 132–134 °C); R_F(CH_2Cl_2–MeOH, 20:1) 0.25; ν_{max}($CHCl_3$)/cm^{-1} 3590 (OH), 3400 (OH), 1600 (Ph), 1490 (Ph) and 1115 (C–O); δ($CDCl_3$, 90 MHz) 7.32 (5 H, m, Ph), 4.30 (2 H, m, $w_{\frac{1}{2}}$ 9, C*H*OH), 3.76 (2 H, br s, OH), 3.46 (1 H, tt, *J* 3.5 and 12.5, PhC*H*) and 2.25–1.5 (6 H, m, CH_2); *m*/*z* 192 (2%, M^+), 174 (15, M − H_2O), 156 (100, M − 2 × H_2O), 104 (31), 91 (44) and 78 (32) (Found: M^+, 192.1144. $C_{12}H_{16}O_2$ requires *M*, 192.1150); and (1*RS*,3*RS*,5*SR*)-5-phenylcyclohexane-1,3-diol **23b** (14%) as plates, m.p. 130–132 °C (from $CHCl_3$–hexane) (lit.,[88] 131–133 °C); R_F(CH_2Cl_2–MeOH, 20:1) 0.13; ν_{max}(KBr)/cm^{-1} 3300 (OH), 1600 (Ph), 1495 (Ph) and 1055 (C–O); δ($CDCl_3$ + CD_3OD, 90 MHz) 7.33 (5 H, m, Ph), 4.55 (2 H, s, OH), 4.34 (1 H, quintet, *J* 3, CH_{eq}OH), 4.16 (1 H, tt, *J* 4.5 and 12, CH_{ax}OH), 3.13 (1 H, tt, *J* 3.5 and 12.5, PhC*H*) and 2.3–1.25 (6 H, m, CH_2); *m*/*z* 192 (6%, M^+), 174 (10, M − H_2O), 156 (100, M − 2H_2O), 104 (39), 91 (32) and 78 (19) (Found: M^+, 192.1150. $C_{12}H_{16}O_2$ requires *M*, 192.1150); together with one isomer of the starting material (28%); R_F(CH_2Cl_2–MeOH, 20:1) 0.61; δ(CCl_4, 90 MHz), 7.75–7.1 (10 H, m, SiPh and Ph), 3.77 (1 H, tt, *J* 4.5 and 10, C*H*OH) 2.59 (1 H, tt, *J* 3 and 12, PhC*H*), 2.35–1.35 (8 H, m, CH_2, OH and SiCH) and 0.48 (6 H, s, $SiMe_2$).

(1RS,3RS,5RS)-3-*Hydroxy*-5-*phenylcyclohexyl acetate* **23c** (40%); R_F(hexane–EtOAc, 1:1) 0.27; ν_{max}(CCl_4)/cm^{-1} 3640 (OH), 3460 (OH), 1730 (C=O), 1610 (Ph), 1500 (Ph) and 1250 (C–O ester); δ($CDCl_3$, 90 MHz) 7.30 (5 H, m, Ph), 5.31 (1 H, tt, *J* 4.5 and 12, C*H*OAc), 4.41 (1 H, quintet, *J* 3, C*H*OH), 3.24 (1 H, tt, *J* 3.5 and 13, PhC*H*), 2.03 (3 H, s, MeCO) and 2.35–1.3 (7 H, m, CH_2 and OH); *m*/*z* 234 (9%, M^+), 174 (18, M − AcOH), 156 (98, M − AcOH/H_2O), 104 (100) and 91 (88) (Found: M^+, 234.1260. $C_{14}H_{18}O_3$ requires *M*, 234.1255); and (1RS,3SR,5SR)-3-*hydroxy*-5-*phenylcyclohexyl acetate* **23c** (28%) as plates, m.p. 83–85 °C (from $CHCl_3$–hexane); R_F(EtOAc–hexane, 1:1) 0.19; ν_{max}($CHCl_3$)/cm^{-1} 3610 (OH), 3450 (OH), 1740 (C=O), 1610 (Ph), 1500 (Ph) and 1250 (C–O ester); δ($CDCl_3$, 90 MHz) 7.32 (5 H, m, Ph), 5.34 (1 H, quintet, *J* 3, C*H*OAc), 4.17 (1 H, quintet, *J* 3, C*H*OH), 3.31 (1 H, tt, *J* 3.5 and 12, PhC*H*), 2.61 (1 H, br s, OH), 2.11 (3 H, s, MeCO) and 2.25–1.5 (6 H, m, CH_2); *m*/*z* 174 (15%, M − AcOH), 156 (100, M − AcOH/H_2O), 104 (14) and 91 (19) (Found:

M – AcOH, 174.1041. $C_{14}H_{18}O_3$ requires *M* – AcOH, 174.1045).

(1RS,3SR,5RS)- *and* (1RS,3RS,5SR)-3-*Hydroxy*-5-*phenylcyclohexyl acetates* (73%) (*ca.* 7:1 mixture of isomers) as needles, m.p. 106–110 °C [from Et_2O–light petroleum (b.p. 40–60 °C)]; R_F(EtOAc–hexane, 1:1) 0.26; $\nu_{max}(CCl_4)/cm^{-1}$ 3610 (OH), 3400 (OH), 1730 (C=O), 1600 (Ph), 1490 (Ph) and 1240 (C–O ester); $\delta(CDCl_3$, 90 MHz) 7.27 (5 H, m, Ph), 5.33 (1 H, m, $w_{\frac{1}{2}}$ 9, C*H*-*trans*-OAc), 4.88 (1 H, tt, *J* 4 and 12, C*H*-*cis*-OAc), 3.84 (1 H, tt, *J* 4 and 11, C*H*OH), 2.65 (1 H, tt, *J* 3 and 12, PhC*H*), 2.38 (1 H, s, OH), 2.03 (3 H, s, MeCO), 2.5–1.95 (3 H, m, *eq*-CHs) and 1.7–1.2 (3 H, m, *ax*-CHs); *m/z* 234 (19%, M^+), 174 (14, M – AcOH), 156 (100, M – AcOH – H_2O), 104 (48) and 91 (32) (Found: M^+, 234.1259. $C_{14}H_{18}O_3$ requires *M*, 234.1256).

(1RS,3RS,5RS)- *and* (1RS,3SR,5SR)-3-*Hydroxy*-5-*phenylcyclohexyl benzoate* **23d** (70%) (as a *ca.* 1.5:1 mixture of isomers); R_F(EtOAc–hexane, 4:5) 0.36; $\nu_{max}(CCl_4)/cm^{-1}$ 3620 (OH), 3460 (OH), 1720 (C=O), 1605 (Ph), 1590 (Ph), 1490 (Ph) and 1275 (C–O ester); $\delta(CCl_4$, 90 MHz) 8.15–7.95 and 7.55–7.1 (10 H, m, PhCO and Ph), 5.50 (1 H, m, CHOCO), 4.39 (1 H, quintet, *J* 3, C*H*OH), 4.19 (1 H, quintet, *J* 3.5, C*H*OH), 3.32 (1 H, tt, *J* 3.5 and 12, PhC*H*), 2.94 (1 H, br s, OH) and 2.5–1.4 (6 H, m, CH_2); *m/z* 174 (24%, M – PhCOOH), 156 (57, M – PhCOOH/H_2O), 128 (47), 105 (100), 91 (49) and 77 (85, Ph) (Found: M – PhCOOH, 174.1052. $C_{19}H_{20}O_3$ requires *M* – PhCOOH, 174.1045).

(1RS,3SR,5SR)-N-3-*Hydroxy*-5-*phenylcyclohexyl*-N-*isopropylacetamide* **23e** (43%); R_F(EtOAc–hexane 2:1) 0.10; $\nu_{max}(CHCl_3)/cm^{-1}$ 3590 (OH), 3375 (OH), 1625 (C=O) and 1495 (Ph); $\delta(CDCl_3$, 90 MHz), 7.36 (5 H, m, Ph), 4.5–2.4 (7 H, m, C*H*OH, MeC*H*N, CH_2CHN, C*H*Ph, OH and 1 × CH_2), 2.2–1.55 (4 H, m, 2 × CH_2), 2.12 (3 H, s, MeCO) and 1.45–1.0 (6 H, m, Me_2CHN); *m/z* 275 (35%, M^+), 257 (8, M – H_2O), 232 (29, M – MeCO or C_3H_7), 174 (24, M – MeCO/C_3H_8N), 156 (96, M – H_2O/MeCO/C_3H_8N), 126 (60), 102 (100) and 91 (67) (Found: M^+, 275.1883. $C_{17}H_{25}NO_2$ requires *M*, 275.1885); together with one isomer of the starting material **22e** (31%); R_F(EtOAc–hexane, 2:1) 0.50; $\delta(CDCl_3$, 90 MHz) 7.75–7.15 (10 H, m, SiPh and Ph), 4.1–3.2 (2 H, m, MeC*H*N and CH_2CHN), 3.0–1.1 (17 H, m, C*H*Ph, MeCO, CH_2, SiCH and Me_2CHN) and 0.52 (6 H, s, $SiMe_2$).

trans-2-*Hydroxymethylcyclohexyl acetate* **25a** (34%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:3] 0.28; ν_{max}(film)/cm^{-1} 3450 (OH) and 1735 (C=O); $\delta(CDCl_3$, 60 MHz) 4.6 (1 H, m, C*H*OAc), 3.4 (2 H, m, CH_2OH), 2.4 (1 H, br s, OH), 2.1 (3 H, s, MeCO) and 2.2–1.1 (9 H, m, ring); *m/z* 112 (20%, M – AcOH) and 64 (100, C_5H_4) (Found: M – AcOH, 112.0883. $C_9H_{16}O_3$ requires M – AcOH, 112.0888). On storage **25a** rearranged to the regioisomeric hydroxyacetate;[89] ν_{max}(film)/cm^{-1} 3400 (OH) and 1735 (C=O); $\delta(CDCl_3$, 90 MHz) 4.3 (1 H, dd, *J* 6 and 10, CH_AH_BOAc), 4.1 (1 H, dd, *J* 5 and 10, CH_AH_BOAc), 3.4 (1 H, m, C*H*OH), 2.8 (1 H, br s, OH), 2.1 (3 H, s, MeCO) and 2.2–1.1 (9 H, m, ring); *m/z* 112 (35%, M – AcOH), 94 (95, M – AcOH – H_2O) and 68 (100, C_5H_8) (Found: M – AcOH, 112.0888. $C_9H_{16}O_3$ requires *M* – AcOH, 112.0888).

1-*Hydroxy*-5-*phenylpentan*-3-*yl benzoate* **27a** (71%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:10] 0.13; ν_{max}(film)/cm^{-1} 3450 (OH), 1710 (C=O), 1600 (Ph) and 1580 (Ph); $\delta(CDCl_3$, 90 MHz), 8.10 (2 H, dd, *J* 9 and 2, *o*-PhCO), 7.69–7.28 (3 H, m, *m*- and *p*-PhCO), 7.20 (5 H, br s, Ph), 4.15 (1 H, br s, OH), 3.60 (2 H, t, *J* 6, CH_2OH), 2.75 (2 H, m, PhCH_2) and 2.25–1.35 (4 H, m, CH_2CHCH_2); *m/z* 266 (18%, M – H_2O), 162 (69), 144 (83), 105 (100, PhCO), 91 (57, $PhCH_2$) and 77 (58, Ph) (Found: M – H_2O, 266.1325. $C_{18}H_{18}O_3$ requires *M* – H_2O, 266.1307).

6-*Hydroxy*-1-*phenylhexan*-3-*yl benzoate* **27b** (72%); ν_{max}(film)/cm^{-1} 3400 (OH), 1710 (C=O) and 1600 (Ph); $\delta(CDCl_3$, 90 MHz) 8.15 (2 H, dd, *J* 9 and 3, *o*-PhCO), 7.70–7.37 (3 H, m, *m*- and *p*-PhCO), 7.28 (5 H, s, Ph), 5.28 (1 H, m, CHOCO), 3.80 (2 H, t, *J* 6, CH_2OH), 2.77 (2 H, m, PhCH_2), 2.20–1.45 (7 H, m, OH and $CH_2CH_2CHCH_2$); *m/z* 176 (7%, M – $PhCO_2H$), 162 (69), 105 (100, PhCO), 91 (95, $PhCH_2$) and 77 (87, Ph) (Found: M – $PhCO_2H$, 176.1205. $C_{19}H_{22}O_3$ requires *M* – $PhCO_2H$, 176.1201).

Methyl (2RS,3SR)-3-*hydroxy*-2-*methyl*-3-*phenyl*-2-(*prop*-3′-*enyl*)*propionate* **41a** (67%) (as an 83:17 mixture of **41a** and **41b**); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.19; ν_{max}(film)/cm^{-1} 3500 (OH), 1720 (CO) and 1620 (C=C); $\delta(CDCl_3$, 90 MHz) 7.37 (5 H, s, Ph), 5.82 (1 H, m, C*H*=CH_2), 5.15 (1 H, m, CH=CH_AH_B), 5.00 (1 H, m, CH=CH_AH_B), 4.97 (1 H, s, C*H*OH), 3.67 (3 H, s, OMe), 3.00 (1 H, br s, OH), 2.70 (1 H, dd, *J* 8 and 15, CH_AH_B), 2.50 (1 H, dd, *J* 8 and 15, CH_AH_B) and 1.05 (3 H, s, Me); full characterisation was carried out on the diastereoisomer **41b**, which was isolated pure.

Methyl (2RS,3RS)-3-*hydroxy*-2-*methyl*-3-*phenyl*-2-(*prop*-3′-*enyl*)*propionate* **41b** (52%) as a single diastereoisomer after PLC; R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5] 0.13; ν_{max}(film)/cm^{-1} 3495 (OH), 1725 (CO) and 1640 (C=C); $\delta(CDCl_3$, 90 MHz) 7.37 (5 H, s, Ph), 5.75 (1 H, m, C*H*=CH_2), 5.17 (1 H, m, CH=CH_AH_B), 5.00 (1 H, m, CH=CH_AH_B), 4.97 (1 H, s, C*H*OH), 3.70 (3 H, s, OMe), 3.10 (1 H, br s, OH), 2.55 (1 H, m, CH_AH_B), 2.05 (1 H, m, CH_AH_B) and 1.07 (3 H, s, Me); *m/z* 235 (10%, M^+ + H), 175 (31, M – HCO_2Me), 128 (100, M – PhCHO) and 107 (17, $PhCH_2O$) (Found: M + H, 235.1327. $C_{14}H_{18}O_3$ requires *M* + H, 235.1334).

(2RS,3SR,4RS)- *and* (2RS,3RS,4SR)-N-(4-*Hydroxy*-3-*methyl*-4-*phenylbutan*-2-*yl*)*pyrrolidine* N-*oxide* **43** (25%); R_F(CH_2Cl_2–MeOH, 7:1) 0.29; $\nu_{max}(CHCl_3)/cm^{-1}$ 3300–2300 (br, OH), 1600 (Ph) and 920 (N^+–O^-); $\delta(CDCl_3$, 90 MHz) 7.88 (1 H, br s, OH), 7.36 (5 H, m, Ph), 4.37 (1 H, d, *J* 9, PhC*H*OH), 3.93 (1 H, m, CHN^+) and 3.7–3.05 (4 H, m, CH_2N^+), 2.65–1.85 (5 H, m, $CH_2CH_2N^+$ and PhCC*H*CN^+), 1.60 (3 H, d, *J* 7, *Me*CHN^+) and 0.63 (3 H, d, *J* 7, *Me*CHPh); *m/z* (EI) 231 (13%, M – H_2O), 216 (3, M – H_2O/Me), 125 (56, $C_8H_{15}N$), 118 (59), 98 (45, $C_6H_{12}N$) and 70 (100, C_4H_8N); *m/z* (FAB) 250 (M + H), 234 ([M + H] – O) and 232 ([M + H] – H_2O).

Method C for a Larger Scale.—Triethylamine (7.4 cm^3, 53 mmol) was added carefully to the fluorosilane derived from the acid **20b** (11.6 g, 48 mmol) in peracetic acid in acetic acid (40%; 72 cm^3) at 0 °C under nitrogen and the mixture was stirred for 3.25 h. It was then added to aqueous potassium hydroxide (2 mol dm^{-3}; 250 cm^3), the pH adjusted to 11 by adding potassium hydroxide pellets, and the mixture extracted with ether (2 × 100 cm^3). The aqueous layer was acidified with concentrated sulfuric acid to pH 1, and the product extracted with ether (4 × 100 cm^3). The combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure and the residue was crystallised from light petroleum (b.p. 60–80 °C)–acetone (3:1), to give the acid as prisms (7.7 g, 89%), m.p. 92–94 °C (lit.,[90] 96.5–97 °C); ν_{max}(film)/cm^{-1} 3200 (OH), 1700 (C=O) and 1500 (Ph); $\delta(CCl_4$, 90 MHz) 7.9 (2 H, br s, OH), 7.32 (5 H, s, Ph), 4.71 (1 H, d, *J* 9, C*H*OH), 2.80 (1 H, m, CHCO) and 0.95 (3 H, d, *J* 7, CMe); *m/z* 180 (3%, M^+), 162 (25, M – H_2O), 107 (100, $PhCH_2O$), 79 (62) and 71 (40, $C_3H_3O_2$) (Found: M^+, 180.0774. $C_{10}H_{12}O_3$ requires *M*, 180.0787). The following compound was also made by this method.

(2RS,3SR)-3-*Hydroxy*-2-*methyl*-3-*phenylpropionitrile* **21e** (75%); R_F[EtOAc–light petroleum (b.p. 60–80 °C), 1:5) 0.01; ν_{max}(film)/cm^{-1} 3475 (OH), 2230 (CN) and 1500 (Ph); $\delta(CDCl_3$, 90 MHz) 7.40 (5 H, s, Ph), 4.67 (1 H, d, *J* 7, PhC*H*),

2.89 (1 H, quintet, *J* 7, MeC*H*), 2.85 (1 H, br s, OH) and 1.20 (3 H, d, *J* 7, *Me*CH).

Preparation of Alcohols from Dimethyl(phenyl)silanes in One Pot

Method A.—Typically, mercuric acetate (133 mg, 0.417 mmol) was stirred with the dimethyl(phenyl)silane (0.4 mmol) in peracetic acid (4 cm^3) at room temperature for 5 h. Ether (50 cm^3) was added to the solution which was then washed with aqueous sodium thiosulfate, water, aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc) to give the alcohol. The following compounds were prepared by this method.

Methyl (2*RS*,3*SR*)-3-hydroxy-2-methyl-3-phenylpropionate **13** (74%) as needles, m.p. 50–51 °C, identical (TLC, IR, ^1H NMR) with the earlier sample.

(3RS,4SR)-4-*Hydroxy*-3-*methyl*-4-*phenylbutan*-2-*one*[91] **46** (88%); R_F(hexane–EtOAc, 1:1) 0.5; ν_{max}(film)/cm^{-1} 3410 (OH) and 1700 (C=O); δ($CDCl_3$) 7.30 (5 H, m, Ph), 4.72 (1 H, d, *J* 8.6, C*H*OH), 3.10 (1 H, br s, OH), 2.90 (1 H, dq, *J* 8.6 and 7.2, C*H*Me), 2.20 (3 H, s, COMe) and 0.91 (3 H, d, *J* 7.2, CH*Me*); *m*/*z* 196 (100%, M^+), 178 (90, M − H_2O) and 106 (17, PhCHO) [Found: $(M + NH_4)^+$, 196.1341. $C_{11}H_{14}O_2$ requires *M* + NH_4, 196.1344].

(2*RS*,3*RS*)-Butane-2,3-diol monobenzoate[92] **49** (10%); R_F(hexane–EtOAc, 1:1) 0.45; ν_{max}(film)/cm^{-1} 3440 (OH), and 1700 (C=O); δ($CDCl_3$) 8.1–8.3 (2 H, m, *o*-PhCO), 7.3–7.8 (3 H, m, *m*- and *p*-PhCO), 5.1 (1 H, quintet, *J* 7, C*H*OBz), 3.95 (1 H, quintet, *J* 7, C*H*OH), 2.4 (1 H, br s, OH), 1.45 (3 H, d, *J* 7, *Me*CHOBz) and 1.3 (3 H, d, *J* 7, *Me*CHOH); *m*/*z* 150 (22%, M − C_2H_4O), 105 (100, PhCO) and 77 (30, Ph). This compound was further characterised as its dibenzoate (89%), prepared with benzoic anhydride, triethylamine and DMAP in dichloromethane at room temperature for 24 h; R_F(hexane–EtOAc, 3:1) 0.5; ν_{max}(film)/cm^{-1} 1710 (C=O), 1595 (Ph) and 1580 (Ph); δ($CDCl_3$) 7.95–8.09 (4 H, m, *o*-Ph), 7.24–7.61 (6 H, m, *m*- and *p*-Ph), 5.26–5.45 (2 H, m, 2 C*H*OBz) and 1.41 (6 H, d, *J* 6.3, 2 Me); *m*/*z* 298 (4%, M^+), 254 (9, M − C_2H_4O), 210 (17, M − $C_4H_8O_2$), 149 (4, $PhCO_2CHMe$), 105 (100, PhCO) and 77 (35, Ph) (Found: M^+, 298.1206. $C_{18}H_{18}O_4$ requires *M*, 298.1205), identical with an authentic sample prepared by benzoylation of (*R*,*R*)-butane-2,3-diol (Fluka).

(2*RS*,3*RS*)-Butane-1,2,3-triol triacetate[93] **51** (39%) by acetylation of the triol diacetate using acetic anhydride (0.17 cm^3, 1.80 mmol), triethylamine (0.25 cm^3, 1.79 mmol) and DMAP (27 mg, 0.22 mmol) in dichloromethane (2 cm^3) at room temperature for 16 h, followed by chromatography (PLC, hexane–EtOAc, 1:1); R_F(hexane–EtOAc, 1:1) 0.42; ν_{max}(film)/cm^{-1} 1740 (C=O); δ($CDCl_3$) 5.07–5.19 (2 H, m, MeC*H*OAcC*H*OAc), 4.28 (1 H, dd, *J* 11.9 and 3.8, CH_AH_BOAc), 4.05 (1 H, dd, *J* 11.9 and 6.4, CH_AH_BOAc), 2.04 2.05 and 2.09 (9 H, 3 s, 3 OAc) and 1.22 (3 H, d, *J* 6.3, *Me*CHOAc); *m*/*z* 188 (2%, M − C_2H_4O), 159 (7, M − CH_2OCOMe) and 145 (100, M − C_2H_4OCOMe).

Method B.—Typically, mercuric acetate (28 mg, 0.088 mmol) and palladium acetate (7 mg, 0.031 mmol) were added to a stirred solution of the dimethyl(phenyl)silane (0.35 mmol) in peracetic acid (2 cm^3). A gas (presumably oxygen) is evolved shortly after the addition of the palladium acetate, and the solution became warm. After 1–3 h, ether was added to the solution which was then washed with aqueous sodium thiosulfate, water, aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed to give the alcohol. The following compounds were prepared by this method.

Methyl (2*RS*,3*SR*)-3-hydroxy-2-methyl-3-phenylpropionate **13** (78%), identical (TLC, IR, ^1H NMR) with the earlier sample.

(3*RS*,4*SR*)-4-Hydroxy-3-methyl-4-phenylbutan-2-one **46** (81%), identical (TLC, IR, ^1H NMR) with the earlier sample.

Method C.—Typically, bromine (1 mol dm^{-3} solution in acetic acid; 0.08 cm^3, 0.08 mmol) was added dropwise to a stirred solution of the dimethyl(phenyl)silane (0.163 mmol) in peracetic acid (1 cm^3) at 0 °C. The disappearance of the starting material was monitored by TLC, and more bromine in acetic acid was added until none remained. The resulting mixture was stirred for 5 h at room temperature. Ether was added to the solution which was then washed with aqueous sodium thiosulfate solution, aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (PLC, hexane–EtOAc) to give the alcohol. The following compounds were prepared by this method.

Methyl (2*RS*,3*SR*)-3-hydroxy-2-methyl-3-phenylpropionate **13** (84%), identical (TLC, IR, ^1H NMR) with the earlier sample.

(2*RS*,3*RS*)-Butane-1,2,3-triol triacetate **51** (72%), by acetylation of the triol diacetate using acetic anhydride as before, identical (TLC, IR, ^1H NMR) with the earlier sample.

(2RS,3RS)-3-*Acetoxybutane*-1,2-*diol carbonate* **53** (46 mg, 67%), by acetylation of the triol carbonate using acetic anhydride as in the conversion of the diacetate **50** into the triacetate **51** described above; R_F(EtOAc) 0.5; ν_{max}(film)/cm^{-1} 1800 (carbonate C=O) and 1730 (acetate C=O); δ($CDCl_3$) 5.15 (1 H, qd, *J* 7 and 3, C*H*OAc), 4.8 (1 H, m, AcOCHC*H*), 4.6 (1 H, t, *J* 8, CH_AH_BO), 4.3 (1 H, dd, *J* 8 and 5, CH_AH_BO), 2.15 (3 H, s, MeCO) and 1.4 (3 H, d, *J* 7, *Me*CHOAc); *m*/*z* 175 (5%, M + H), 130 (100, M − CO_2) and 87 (51, M − CO_2, MeCO) [Found: $(M + H)^+$, 175.0619. $C_7H_{10}O_5$ requires *M* + H, 175.0607].

Method D.—Typically, potassium bromide (0.14 g, 1.18 mmol) and anhydrous sodium acetate (0.25 g) were added to a stirred solution of the dimethyl(phenyl)silane (0.98 mmol) in glacial acetic acid (2.5 cm^3). Peracetic acid (2.5 cm^3) was then added dropwise to the mixture with ice cooling. More sodium acetate (0.75 g) and peracetic acid (7.5 cm^3) were added to the mixture and the resulting turbid solution was then stirred at room temperature for 18 h and at 35 °C for 1 h. After addition of ether (100 cm^3) and powdered sodium thiosulfate (10 g) to the mixture it was stirred vigorously for 0.5 h, filtered through Celite, and evaporated under reduced pressure. The residue was then taken up in ether and washed with aqueous sodium hydrogen carbonate and brine, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc, usually with gradient elution) to give the alcohol. The following compounds were prepared by this method.

Methyl (2*RS*,3*SR*)-3-hydroxy-2-methyl-3-phenylpropionate **13** (72%), identical (TLC, IR, ^1H NMR) with the earlier sample.

(3*RS*,4*SR*)-4-Hydroxy-3-methyl-4-phenylbutan-2-one **46** (36%), identical (TLC, IR, ^1H NMR) with the earlier sample.

(2*RS*,3*RS*)-Butane, 2,3-diol monobenzoate **49** (81%), identical (TLC, IR, ^1H NMR) with the earlier sample.

(2*RS*,3*RS*)-Butane-1,2,3-triol triacetate **51** (74%), by acetylation of the triol diacetate using acetic anhydride as before, identical (TLC, IR, ^1H NMR) with the earlier sample.

Methyl 2,2,4-trimethyl-1,3-dioxolane-5-carboxylate[94] **55** (74%), after conversion of the crude diol into the acetal by stirring it in dichloromethane with 2,2-dimethoxypropane and toluene-*p*-sulfonic acid for 16 h; R_F(hexane–EtOAc, 3:1) 0.3; ν_{max}(film)/cm^{-1} 1750 and 1730 (C=O); δ($CDCl_3$) 4.47 (1 H,

d, *J* 6.7, C*H*CO_2Me), 4.49 (1 H, quintet, *J* 6.7, MeC*H*), 3.74 (3 H, s, OMe), 1.6 (3 H, s, C*Me*$_A$Me$_B$), 1.37 (3 H, s, CMe$_A$*Me*$_B$) and 1.23 (3 H, d, *J* 6.7, *Me*CH); *m/z* 159 (100%, M − Me) and 115 (46, M − CO_2Me) (Found: M^+ − Me, 159.0657. $C_8H_{14}O_4$ requires *M* − Me, 159.0657).

Proof of Stereochemistry

(4RS,5RS,6RS)-2,2,4,5-*Tetramethyl*-6-*phenyl*-1,3-*dioxane* **44**.—The 1:1 mixture of hydroxyacetates containing **21g** (0.12 g, 0.54 mmol) in dry ether (5 cm^3) was added dropwise to a stirred suspension of lithium aluminium hydride (0.04 g) in dry ether (5 cm^3), and the mixture refluxed for 1.5 h. Aqueous work-up gave the diol[95] (0.10 g), which was heated with toluene-*p*-sulfonic acid (0.01 g) in 2,2-dimethoxypropane (5 cm^3) at 60 °C for 1.75 h. The solution was stirred with solid potassium carbonate for 30 min at room temperature and then evaporated. The residue was extracted several times with light petroleum (b.p. 30–40 °C) and the combined extracts were filtered, evaporated and the crude residue chromatographed (TLC, hexane–EtOAc, 5:1) to give the *acetal* (0.093 g, 78% from hydroxy acetates); R_F(hexane–EtOAc, 5:1) 0.49; $\nu_{max}(CCl_4)/cm^{-1}$ 1610 (Ph) and 1495 (Ph); $\delta(CDCl_3$, 90 MHz), 7.39 (5 H, m, Ph), 4.43 (1 H, d, *J* 10, PhC*H*O), 3.80 (1 H, qd, *J* 6 and 10, MeC*H*O), 1.56 (1 H, m, OCC*H*CO), 1.57 (3 H, s, C*Me*$_A$Me$_B$), 1.49 (3 H, s, CMe$_A$*Me*$_B$), 1.24 (3 H, d, *J* 6, *Me*CHO) and 0.64 (3 H, d, *J* 7, *Me*CHCPh); *m/z* 205 (5%, M − Me), 145 (26, M − $C_3H_7O_2$), 107 (100, C_7H_7O) and 59 (72) (Found: M − Me, 205.1223. $C_{14}H_{20}O_2$ requires *M* − Me, 205.1228).

(4RS,5SR,6SR)-2,2,4,5-*Tetramethyl*-6-*phenyl*-1,3-*dioxane* **45**.—The diol **21h** (0.11 g, 0.61 mmol) and toluene-*p*-sulfonic acid (0.01 g) in 2,2-dimethoxypropane (3 cm^3) were stirred at room temperature for 5.5 h. Work-up and chromatography as above gave the *acetal* (0.089 g, 66%); R_F(hexane–EtOAc, 5:1) 0.51; $\nu_{max}(CCl_4)/cm^{-1}$ 1605 (Ph) and 1495 (Ph); $\delta(CDCl_3$, 90 MHz) 7.38 (5 H, m, Ph), 4.30 (1 H, quintet, *J* 6.5, MeC*H*O), 4.27 (1 H, d, *J* 8, PhC*H*O), 2.03 (1 H, m, OCC*H*CO), 1.46 (6 H, s, CMe_2), 1.15 (3 H, d, *J* 6.5, *Me*CHO) and 0.85 (3 H, d, *J* 7, *Me*CHCPh); *m/z* 205 (1.5%, M − Me), 165 (13, M − C_4H_7), 145 (8, M − $C_3H_7O_2$), 107 (61), 59 (100) and 56 (56) (Found: M − Me, 205.1237. $C_{14}H_{20}O_2$ requires *M* − Me, 205.1228).

(2RS,3SR)-3-[*Dimethyl*(*phenyl*)*silyl*]*butane*-1,2-*diol*.—The α-hydroxy-β-silyl ester **54** (80 mg, 0.34 mmol) in dry ether (2 cm^3) was added dropwise to a stirred suspension of lithium aluminium hydride (26 mg, 0.68 mmol) in dry ether (1 cm^3) at 0 °C. After 1 h, aqueous ammonium chloride (0.06 cm^3) was added to the mixture which was then filtered through Celite, washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (PLC, hexane–EtOAc, 1:1) to give the *diol* (21 mg, 28%); R_F(hexane–EtOAc, 1:1) 0.33; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3580 and 3350 (OH) and 1105 (SiPh); $\delta(CDCl_3)$ 7.59–7.49 (2 H, m, *o*-Ph), 7.40–7.32 (3 H, m, *m*- and *p*-Ph), 3.75 (1 H, td, *J* 6.0 and 4.4, C*H*OHCH$_2$OH), 3.46 (2 H, d, *J* 6.0, CHOHC*H*$_2$OH), 2.11 (1 H, br s, OH), 1.06 (1 H, m, MeC*H*Si), 1.01 (3 H, d, *J* 5.8, *Me*CHSi), 0.32 (3 H, s, Si*Me*$_A$Me$_B$) and 0.34 (3 H, s, SiMe$_A$*Me*$_B$); *m/z* 242 (60%, M + NH_4), 166 (20, PhSiMe$_2$CH$_2$OH) and 152 (65, PhSiMe$_2$OH) [Found: (M + NH_4)$^+$, 242.1575. $C_{12}H_{20}O_2Si$ requires *M* + NH_4, 242.1573], recognisably different from the (2*RS*,3*RS*) diastereoisomer prepared from the epoxide **57** as described above.

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