

Carbonium Ion Rearrangements Controlled by the Presence of a Silyl Group†

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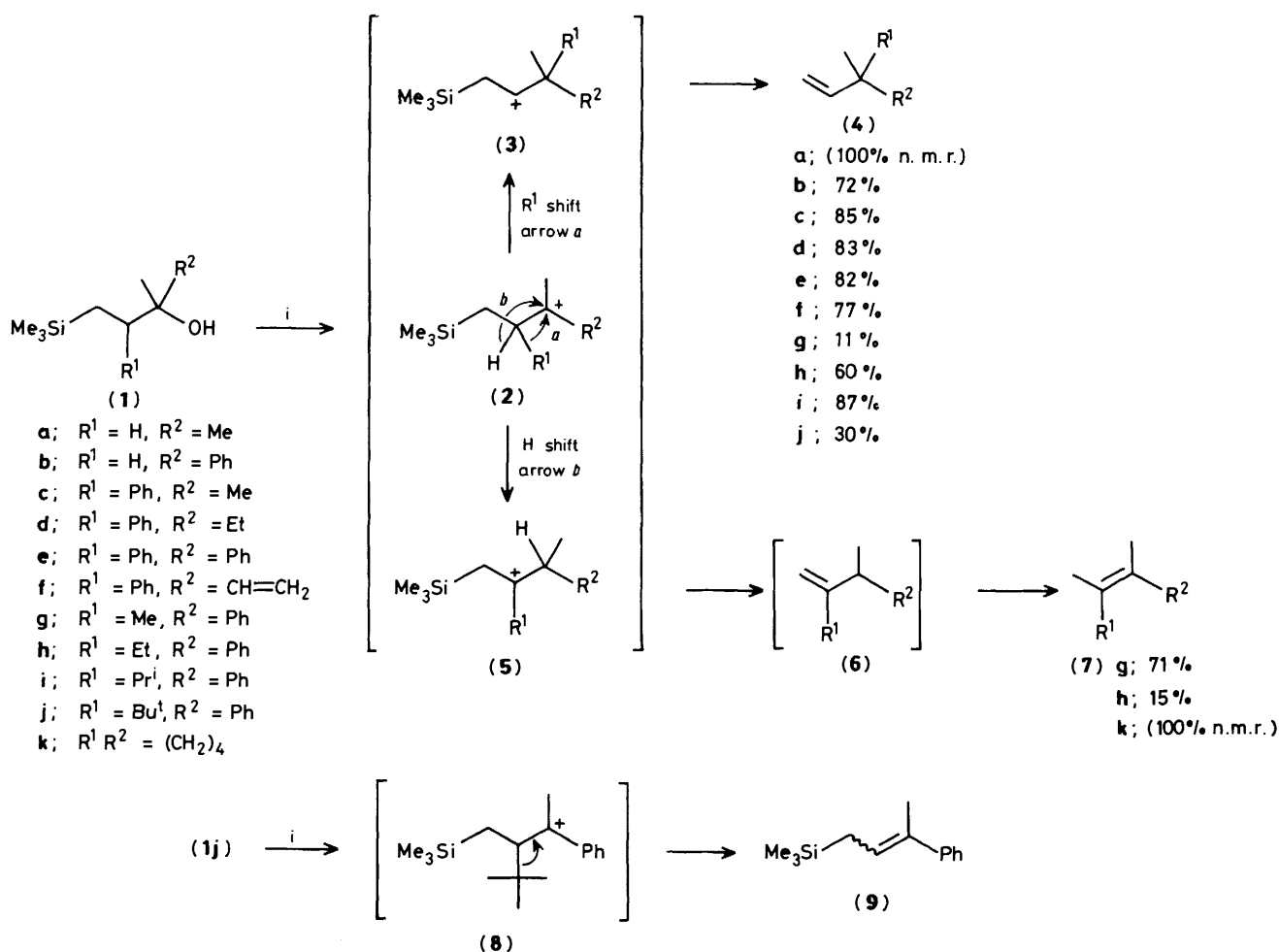
γ -Silyl tertiary alcohols rearrange in protic acid with 1,2-shift of hydride, phenyl, or alkyl groups, and loss of the silyl group to give alkenes. The placing of the silyl group thus controls the carbonium ion rearrangement in a preparatively useful way. Methoxycarbonyl groups do not migrate; instead, cyclopropanes are formed, except when the conformation suitable for cyclopropane formation is unattainable. When the alkene product is 2,2-disubstituted, it can be reprotonated under the reaction conditions and does not therefore always survive. This can be avoided by carrying out the reaction using a Lewis acid on the silyl ether. The starting γ -silyl alcohols are prepared by a variety of versatile methods.

In a preliminary communication,¹ we reported that a wide range of γ -silyl tertiary alcohols rearrange in acid in the general sense (1)→(4), in a process which is controlled by the presence of the silyl group. Rearrangement (2)→(3) is made favourable by the well-known stabilisation in the cation (3) from the neighbouring Si-C bond,² and the outcome is controlled by the ready loss of the silyl group (3)→(4).³ In this, our full paper, we give experimental details, and we add two further observations,

one on the only example we have yet come across of cyclopropane formation, and the other on how to prevent subsequent rearrangement of the first-formed product.

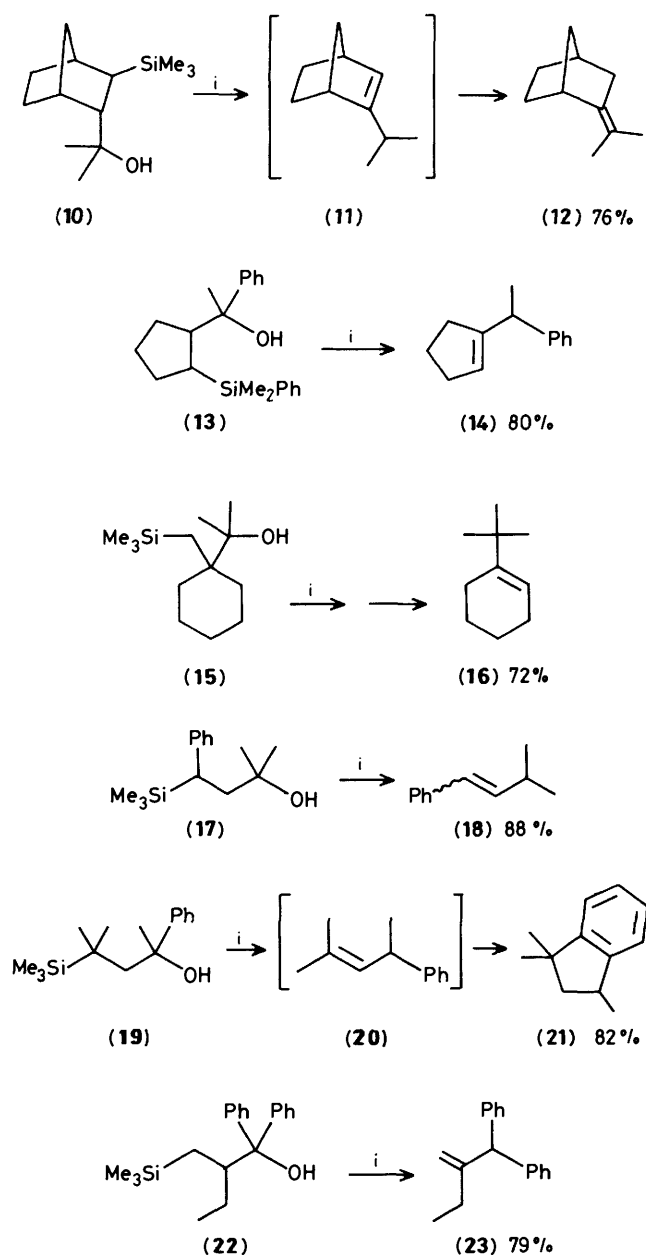
Discussion

Rearrangements (Schemes 1 and 2).—The results with the tertiary alcohols (1a–f) show that hydride shift, for which



Scheme 1. Reagent: i, $BF_3 \cdot 2AcOH, CH_2Cl_2$

† No reprints available.



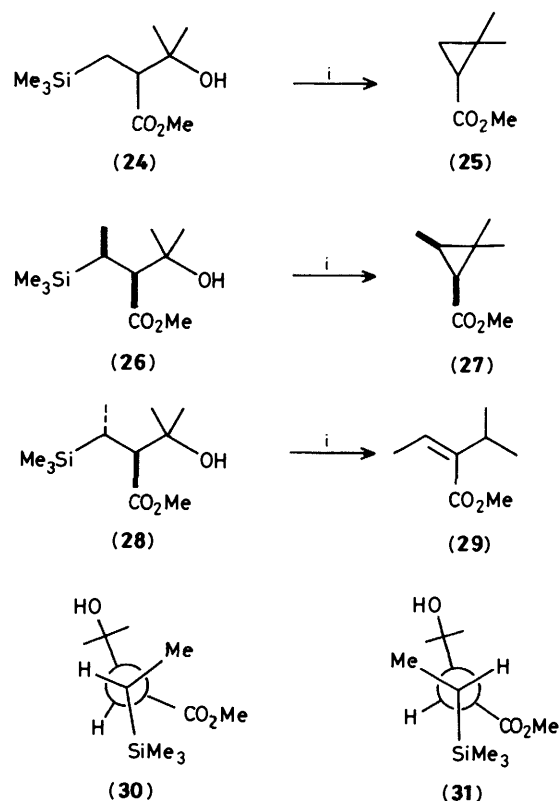
Scheme 2. Reagent: *i*, $\text{BF}_3 \cdot 2\text{AcOH}$, CH_2Cl_2

there was precedent,⁴ and phenyl shift are well-behaved reactions. Alkyl shift is a little more complicated in that hydride shift competes with it (**1g**–**1k**): when the migrating group R^1 is methyl (**1g**) or part of a cyclohexane ring (**1k**) (either stereoisomer), hydride shift (**2**) (arrow *b*) is the major reaction, but when R^1 is an ethyl or isopropyl group (**1h**) and (**1i**), alkyl shift (**2**) (arrow *a*) is the major reaction, exclusively so in the latter case. However, when R^1 is a *t*-butyl group (**1j**), fragmentation (**8**) \rightarrow (**9**) is the major pathway, and migration of the *t*-butyl group is only a minor pathway (30%). When hydride shift occurred (**1g**), (**1h**), and (**1k**), the alkene initially produced (**6**) was susceptible to reprotonation and the products actually isolated (**7g**), (**7h**), and (**7k**), were the result of such protonation, followed by proton loss to give the more highly substituted alkene.

The failure to get ring contraction in the cyclic system (**1k**) was surprising in view of our earlier results in the norbornyl series,

but in that case there had been no alternative group to migrate.⁵ We were equally unable to get ring expansions: the tertiary alcohols (**10**) and (**13**) gave the alkenes (**12**) and (**14**), both of which are products of hydride shift, the former having come from the first formed alkene (**11**). An attempt at ring-expansion in which hydride shift could not compete was also unsuccessful: the alcohol (**15**) gave initially a mixture of at least five products, which were converted fairly cleanly into one product (**16**) by longer treatment with acid. The most likely route from (**15**) to (**16**) is by initial shift of the trimethylsilylmethyl group, a pathway which would have been most unfavourable in all the other reactions we tried, but which is presumably very favourable here. We also examined two cases in which there were substituents on the silicon-bearing carbon: one (**17**) was uneventful, but the other (**19**) proceeded beyond the first-formed product (**20**) to give the indane (**21**). One other clean reaction was the hydride shift in the reaction (**22**) \rightarrow (**23**): here, the alkyl group did not migrate, presumably because the cationic centre is more hindered, nor did a prototropic shift disguise the nature of the first-formed product.

The pattern of our results bears a very close resemblance to the corresponding pinacol rearrangements. Thus hydride and phenyl shifts are well known,⁶ hydride migrates rather than alkyl when the alkyl group is methyl^{7,8} or when the migration terminus has two aryl groups,⁹ and larger alkyl groups migrate rather than hydride, except when they are ring residues.¹⁰ Synthetically the reaction is potentially useful, not only in controlling many rearrangements well, but in establishing quaternary centres in high yield, notably compounds (**4c**–**f**, *i*).



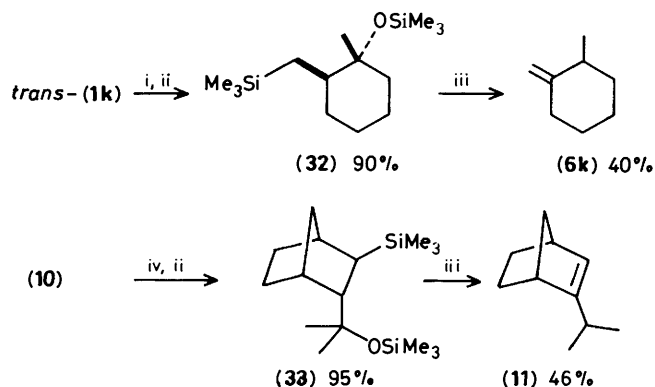
Scheme 3. Reagent: *i*, $\text{BF}_3 \cdot 2\text{AcOH}$, CDCl_3

Cyclopropane Formation (Scheme 3).—In none of this work did we see any sign of cyclopropanes, which could reasonably, and with precedent,^{4,11} have been formed by 1,3-elimination. It appears that, when the potential migration terminus is primary,¹¹ cyclopropane formation is normal, when it is

secondary, there is competition between rearrangement and cyclopropane formation,⁴ and, when it is tertiary, as in all our work, rearrangement is normal. However, we have found one case in which cyclopropanes are formed from a tertiary alcohol. Although we had been successful in encouraging the migration of a diphenylphosphinoyl group,¹² we were not successful in encouraging the migration of a methoxycarbonyl group: the alcohol (**24**) gave only the cyclopropane (**25**). In the hope of demonstrating the stereochemistry of this reaction at the silicon-bearing carbon (C-3), we prepared the diastereoisomers (**26**) and (**28**), stereochemically labelled at this site. We have not proved the relative configuration of these compounds, but one of them cleanly gave the cyclopropane (**27**). Since this was expected, by analogy with tin¹³ and boron¹⁴ chemistry, to go with inversion of configuration, we tentatively assign the stereochemistry to (**26**) appropriate for that event. This is in agreement with a simple conformational argument based on the coupling constant between the two methine hydrogens, which was smaller (2 Hz) for the isomer giving the cyclopropane (**27**) than for the other diastereoisomer (6 Hz). The latter, however, did not give a cyclopropane, but instead gave the alkene (**29**). This could have been formed either by hydride shift, or by dehydration followed by protodesilylation of the resultant allylsilane. The mystery in this bizarre pair of reactions is the ready formation of the more-hindered *cis* cyclopropane (**27**), and the avoidance of the less-hindered *trans* cyclopropane, which we had expected to get from the diastereoisomer (**28**). This isomer would appear, at first sight, to be ideally set up in what looks like the lowest-energy conformation, a conformation which also happens to be suitable for 1,3-elimination with inversion of configuration at C-3. However, such a conformation, if it is the best conformation, ought to have a much higher coupling constant between the methine hydrogens than 6 Hz; this suggests that the conformation (**28**) is not, in fact, a stable conformation. Instead, as with 1,1,2,2-tetra-*t*-butylethane,¹⁵ repulsion between the two large groups on C-2, and between the two large groups on C-3, flattens the tetrahedral angle between them on C-2 and on C-3. When this is allowed for in the diastereoisomer (**28**), the groups are forced more nearly to eclipse each other, as in the Newman projection (**31**). This conformation is therefore avoided, and cyclopropane formation does not occur. The diastereoisomer (**26**), on the other hand, is likely to find, again by analogy with the conformation of 1,1,2,2-tetra-*t*-butylethane,¹⁵ that the conformation (**30**) is the best possible. In this conformation, cyclopropane formation is favourable, and the coupling constant is likely to be very low, since the dihedral angle is close to 90°.

In any event, the failure of the isomer (**28**) to give a cyclopropane indicated that this was not a powerful new cyclopropane synthesis, and, in order to achieve that end, we turned to the corresponding tin series, as reported.¹³

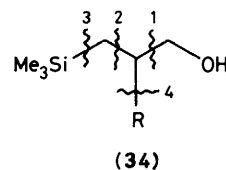
Avoiding Subsequent Rearrangement of the First-formed Product (Scheme 4).—In a few cases reported above, we found that the first-formed product had undergone either a prototropic shift, (**7g**), (**7h**), (**7k**), and (**12**), or a proton-initiated cyclisation (**20**)→(**21**), before we could isolate it. We thought that this problem might be avoidable, and have examined, with some success, two of the examples listed above, as models for how to stop the subsequent rearrangement of a first-formed product. The secret is to find reaction conditions that allow the initial cation to be formed in the complete absence of protons. This is easily managed by making two modifications: using the trimethylsilyl ether in place of the alcohol, and using Lewis acid in place of protic acid. The two examples upon which we tested this idea are the silyl ethers (**32**) and (**33**). On treatment with boron trifluoride-diethyl ether these gave the alkenes (**6k**) and (**11**), respectively. Each of these alkenes rearranged in protic



Scheme 4. Reagents: i, BuLi; ii, Me₃SiCl; iii, BF₃·OEt₂, CCl₄; iv, MeLi

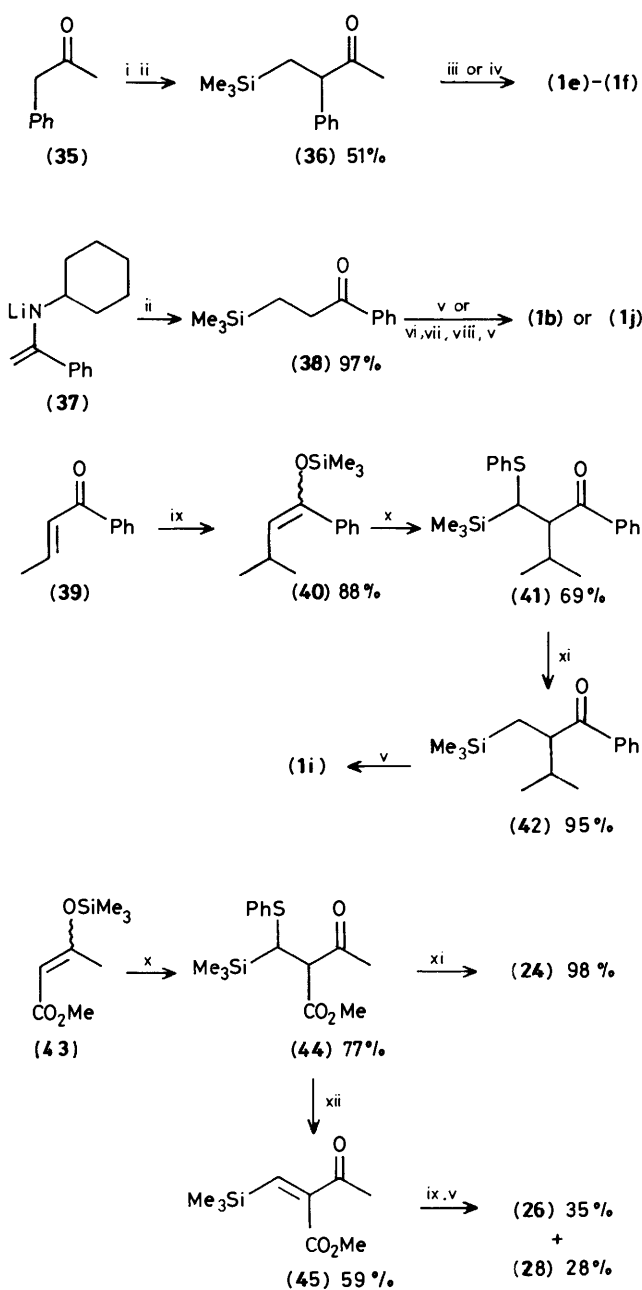
acid to give the more-substituted alkenes, (**7k**) and (**12**), respectively, substantiating our belief that they were true intermediates in the overall reactions (**1k**)→(**7k**) and (**10**)→(**12**). The yields were not high, but they were encouraging enough for us to believe that the method is, in principle, sound and that, with suitable care to ensure anhydrous reagents and conditions, it might be made preparatively useful. The kinetic products of pinacol-pinacolone rearrangements are also susceptible to further rearrangement in the presence of acid. In that series, however, the aldehyde or ketone products are not as stable to Lewis acid as the alkene products are in the present series.

The Synthesis of the γ -Silyl Alcohols (Schemes 5 and 6).—For silicon-controlled rearrangement to be synthetically useful it is essential to have a variety of easy ways in which to set up the γ -silyl alcohol starting materials. We find that γ -silyl alcohols may be assembled in many ways, with each of the disconnections 1—4 in (**34**) useful in one system or another.



Disconnection 2 (Scheme 5) is the most powerful, taking the form, at its most simple, in the reaction (**35**)→(**36**) used for the synthesis of the alcohols (**1c**—**f**). A closely similar reaction is the trimethylsilylmethylation of the lithium salt (**37**) of the cyclohexylimine of acetophenone, which gave 3-trimethylsilylpropionophenone (**38**), the precursor for the synthesis of the alcohols (**1b**) and (**1j**). Similarly, (**1a**) was prepared from 2-trimethylsilylpropionic acid derived by trimethylsilylmethylation of acetonitrile. However, trimethylsilylmethyl iodide is expensive and sometimes it is too unreactive to alkylate simple enolates and imines. We have therefore developed the reagent phenylthio(trimethylsilyl)methyl chloride, which we find reacts with silyl enol ethers in the presence of Lewis acids to give phenylthio(trimethylsilyl)methylated ketones. This sequence is exemplified by the reactions (**40**)→(**41**) and (**43**)→(**44**), in which the phenylthio group was removed reductively as part of the synthesis of the alcohols (**1i**) and (**24**).

Similar sequences were used to trimethylsilylmethylate the silyl enol ethers of propiophenone, butyrophenone, ethyl butyrate, cyclohexanone, and methyl cyclohexanecarboxylate, for the synthesis of the alcohols (**1g**), (**1h**), (**22**), *cis*-(**1k**), and (**15**), respectively. Phenylthioalkylation was pioneered by Pater-



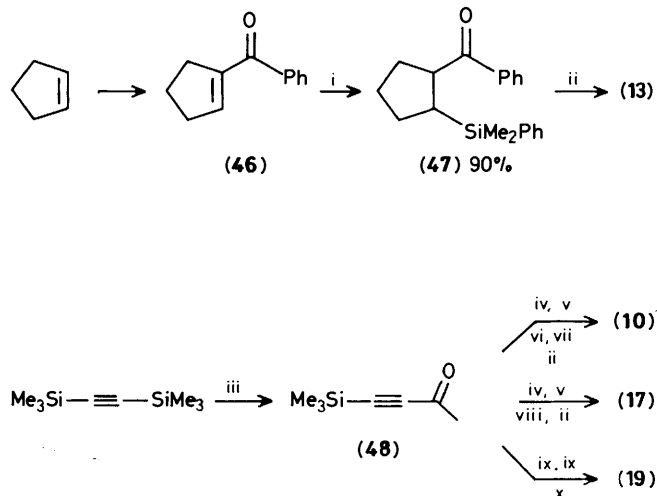
Scheme 5. Reagents: i, NaH; ii, $\text{Me}_3\text{SiCH}_2\text{I}$; iii, PhMgBr ; iv, $\text{CH}_2=\text{CHMgBr}$; v, MeLi; vi, LDA; vii, Me_3SiCl ; viii, Bu^tCl , TiCl_4 ; ix, Me_2CuLi ; x, $\text{Me}_3\text{SiCHClSiPh}$, ZnBr_2 ; xi, Raney Ni; xii, MCPBA

son^{16,17} but has only occasionally been used with a trimethylsilyl group present.^{17,18} Phenylthioalkylation in general can also lead to $\alpha\beta$ -unsaturated carbonyl compounds when the phenylthio group is removed oxidatively. Unfortunately, the presence of the silyl group deflects the sulphoxide into a sila-Pummerer rearrangement,¹⁹ and this present route is not usually a good way of preparing γ -silyl enones. However, it is a good way in the case of the products (44) derived from methyl acetoacetate. In this case, the oxidation gave directly the silyl enone (45). Evidently the β -cycloelimination, with two carbonyl groups activating the C-H bond, is much faster than the sila-Pummerer reaction. The enone (45) was used for the synthesis of the alcohols (26) and (28).

Disconnection 2 can also be used in an umpolung version. We

used a reaction corresponding to this disconnection in the synthesis of the cyclohexane *trans*-(1k), where the key reaction was the copper-catalysed nucleophilic opening of 1-methylcyclohexene oxide with the trimethylsilylmethyl Grignard reagent. The corresponding *cis* isomer was made stereospecifically²⁰ by the reaction of the methylcuprate reagent on 2-trimethylsilylmethylcyclohexanone.

Disconnections 1 and 3 are also powerful (Scheme 6). We



Scheme 6. Reagents: i, $(\text{PhMe}_2\text{Si})_2\text{CuLi-LiCN}$; ii, MeLi; iii, MeCOCl , AlCl_3 ; iv, LiAlH_4 ; v, PDC, CH_2Cl_2 ; vi, cyclopentadiene, ZnBr_2 ; vii, H_2 , Pd; viii, Ph_2CuLi ; ix, Me_2CuLi ; x, PhMgBr

used reactions corresponding to the former to prepare phenyl cyclopentenyl ketone (46), and to the latter to introduce the silyl group nucleophilically to give the ketone (47), from which we prepared the alcohol (13). These disconnections also correspond to the method²¹ that we used for the synthesis of 4-trimethylsilylbut-3-yn-2-one (48), the precursor of the alcohols (10), (17), and (19).

Finally, disconnection 4, is embedded (trivially) in the methods used for the synthesis of some of our starting materials, (1i) and (3g) for example. However, it is a key step in the synthesis of the alcohol (1j). The silyl enol ether of the ketone (38) and *t*-butyl chloride reacted in the presence of titanium tetrachloride to give the α -*t*-butylated ketone, which then gave the alcohol (1j) on treatment with methyl-lithium.

In conclusion, the power of all these synthetic methods is considerable. γ -Silyl tertiary alcohols can demonstrably be made in a wide variety of ways, and, once made, their behaviour in acid is reasonably predictable with controlled cationic rearrangement the major pathway.

Experimental

Acid-catalysed Rearrangements.—Typically the boron trifluoride-acetic acid complex (0.5 g) was added to a solution of the alcohol (2 mmol) in dichloromethane (10 ml) and kept at 0°C for 15 min. The mixture was diluted with ether (50 ml), washed with saturated aqueous sodium carbonate (2×10 ml), dried (MgSO_4), evaporated and the residue distilled (Kugelrohr) to give the alkenes. Except as noted, the following compounds were prepared in this way.

3-Methylbutene (4a) (no work up, experiment carried out in n.m.r. tube); $\delta(\text{CD}_2\text{Cl}_2)$ 5.75 (1 H, ddd, J 18, 10, and 7 Hz, $\text{CH}=\text{CH}_2$), 4.89 (2 H, m, $=\text{CH}_2$), 2.30 (1 H, m, CH), and 1.00 (6 H, d, J 7 Hz, CHMe_2).

3-Phenylbutene²² (**4b**) [a minor contaminant was the allylsilane (**9**); the mixture was therefore refluxed with the boron trifluoride-acetic acid complex in carbon tetrachloride for 15 min to protodesilylate the allylsilane, total yield 72%]; $\delta(\text{CCl}_4)$ 7.13 (5 H, s, Ph), 5.93 (1 H, ddd, J 17, 10, and 6 Hz, $\text{CH}=\text{CH}_2$), 5.96 (2 H, m, $=\text{CH}_2$), 3.40 (1 H, quintet, J 7 Hz), and 1.32 (3 H, d, J 7 Hz).

3-Methyl-3-phenylbutene²³ (**4c**) (85%); $\delta(\text{CDCl}_3)$ 7.22 (5 H, m, Ph), 5.98 (1 H, dd, J 18 and 10 Hz, CHCH_2), 5.00 (1 H, dd, J 18 and 2 Hz, CH_AH_B), 5.02 (1 H, dd, J 10 and 2 Hz, $=\text{CH}_A\text{H}_B$), and 1.41 (6 H, s, Me) (Found: M^+ , 146.1090 $\text{C}_{11}\text{H}_{14}$ requires M , 146.1094).

3-Methyl-3-phenylpentene²⁴ (**4d**) (83%); ν_{max} (film) 1 638 ($\text{C}=\text{C}$) and 808 cm^{-1} ($=\text{CH}_2$); $\delta(\text{CCl}_4)$ 7.21 (5 H, s, Ph), 5.97 (1 H, dd, J 17 and 11 Hz, $\text{CH}=\text{CH}_2$), 5.09 (1 H, dd, J 11 and 2 Hz, $=\text{CH}_A\text{H}_B$), 4.92 (1 H, dd, J 17 and 2 Hz, $=\text{CH}_A\text{H}_B$), 1.72 (2 H, q, J 7 Hz, CH_2), 1.33 (3 H, s, Me), and 0.73 (3 H, t, J 7 Hz, CH_2Me) (Found: M^+ , 160.1254. $\text{C}_{12}\text{H}_{16}$ requires M , 160.1252); m/z 160 (30%, M^+), and 145 (100, $M - \text{Me}$).

3,3-Diphenylbutene²⁵ (**4e**) (82%); ν_{max} (film) 1 640 ($\text{C}=\text{C}$) and 808 cm^{-1} ($=\text{CH}_2$); $\delta(\text{CCl}_4)$ 7.23 (10 H, s, Ph), 6.51 (1 H, dd, J 18 and 11 Hz, $\text{CH}=\text{CH}_2$), 5.12 (1 H, dd, J 11 and 2 Hz, $=\text{CH}_A\text{H}_B$), 4.85 (1 H, dd, J 18 and 2 Hz, $=\text{CH}_A\text{H}_B$), and 1.73 (3 H, s, Me) (Found: M^+ , 208.1252. $\text{C}_{16}\text{H}_{16}$ requires M , 208.1252); m/z 202 (25%, M^+), 193 (19, $M - \text{Me}$), and 131 (100, $M - \text{Ph}$).

3-Methyl-3-phenylpenta-1,4-diene²⁶ (**4f**) (77%); ν_{max} (film) 1 640 ($\text{C}=\text{C}$) and 808 cm^{-1} ($=\text{CH}_2$); $\delta(\text{CCl}_4)$ 7.18 (5 H, s, Ph), 6.03 (2 H, dd, J 17 and 13 Hz, $\text{CH}=\text{CH}_2$), 5.03 (2 H, dd, J 13 and 2 Hz, $=\text{CH}_A\text{H}_B$), 4.96 (2 H, dd, J 17 and 2 Hz, $=\text{CH}_A\text{H}_B$), and 1.46 (3 H, s, Me) (Found: M^+ 158.1090. $\text{C}_{12}\text{H}_{14}$ requires M , 158.1096); m/z 158 (11%, M^+), 143 (40, $M - \text{Me}$), 81 (10, $M - \text{Ph}$), and 77 (100, Ph).

A mixture of (**4g**) ($=\text{4c}$) and 2-methyl-3-phenylbut-2-ene²⁷ (**7g**) (82%) in a ratio (g.l.c.) of 13:87, the latter identified by signals in the ^1H n.m.r. spectrum of the mixture; $\delta(\text{CCl}_4)$ 7.20 (5 H, m, Ph), 1.93 (3 H, br s, Me), 1.78 (3 H, s, Me), and 1.56 (3 H, br s, Me).

A mixture of (**4h**) ($=\text{4d}$) and 3-methyl-2-phenylpent-2-ene²⁸ (**7h**) (as a mixture of geometrical isomers) in a ratio (g.l.c.) of 80:20, the latter identified by signals in the ^1H n.m.r. spectrum of the mixture, $\delta(\text{CCl}_4)$ 7.20 (5 H, m, Ph), 2.18 (q, J 7 Hz, CH_2 of one isomer), 1.65 (m, CH_2 of other isomer and 2 \times Me), and 1.11 (3 H, t, CH_2Me).

3,4-Dimethyl-3-phenylpentene (**4i**) (87%); ν_{max} (film) 1 638 ($\text{C}=\text{C}$) and 808 cm^{-1} ($=\text{CH}_2$); $\delta(\text{CCl}_4)$ 7.20 (5 H, m, Ph), 6.13 (1 H, dd, J 15 and 12 Hz, $\text{CH}=\text{CH}_2$), 5.15 (2 H, m, $=\text{CH}_2$), 2.16 (1 H, septet, J 7 Hz, CHMe_2), 1.30 (3 H, s, Me), and 0.86 and 0.77 (3 H each, d, J 7 Hz, CHMe_2) (Found: M^+ , 174.1408. $\text{C}_{13}\text{H}_{18}$ requires M , 174.1409).

A mixture of allylsilane (**9**) and 3,4,4-trimethyl-3-phenylpentene (**4j**) in a ratio (n.m.r.) of 70:30, the latter identified by signals in the ^1H n.m.r. spectrum of the mixture; $\delta(\text{CCl}_4)$ 7.10 (5 H, m, Ph), 5.74 (1 H, m, $\text{CH}=\text{CH}_2$), 5.11 (2 H, m, $=\text{CH}_2$), 1.25 (3 H, s, Me), and 0.71 (9 H, s, Bu^t).

1,2-Dimethylcyclohexene²⁷ (**7k**) (100%) from either isomer of (**1k**); $\delta(\text{CDCl}_3)$ 2.22—1.41 (8 H, m, CH_2 's) and 1.61 (6 H, br s, Me's).

2-(Diphenylmethyl)butene (**23**) (79%); $\delta(\text{CCl}_4)$ 7.10 (10 H, s, Ph's), 5.02 (1 H, s, $=\text{CH}_A\text{H}_B$), 4.67 (1 H, s, CHPh_2), 4.46 (1 H, s, $=\text{CH}_A\text{H}_B$), 2.03 (2 H, q, J 7 Hz, CH_2), and 1.03 (3 H, t, J 7 Hz, CH_2Me) (Found: M^+ , 222.1409. $\text{C}_{17}\text{H}_{18}$ requires M , 222.1409); m/z , 222 (9%, M^+), 221 (4, $M - \text{H}$), 145 (100, $M - \text{Ph}$), and 116 (19, $M - \text{Ph} - \text{Et}$).

2-Isopropylidenebicyclo[2.2.1]heptane²⁹ (**12**) (76%); δ_{H} (CCl_4) 2.85 and 2.35 (1 H each, m, bridgehead CH's), 2.21—0.81 (8 H, m), and 1.68 and 1.56 (3 H each, d, J 2 and 1 Hz respectively $=\text{CMe}_2$); δ_{C} (CDCl_3) 137.92, 117.67, 40.83, 39.32, 37.58, 36.75, 29.07, 28.52, 20.40, and 20.19 (Found: M^+ ,

136.1255. $\text{C}_{10}\text{H}_{16}$ requires M , 136.1252); m/z , 136 (14%, M^+), 121 (8, $M - \text{Me}$), and 107 (100, $M - \text{Et}$).

1-(1'-Phenylethyl)cyclopentene (**14**) (80%); $\delta(\text{CDCl}_3)$ 7.07 (5 H, s, Ph), 5.40 (1 H, m, $\text{CH}=\text{CH}_2$), 3.33 (1 H, m, PhCH), 2.45—1.41 (6 H, m, CH_2 's), and 1.33 (3 H, d, J 6 Hz, CHMe) (Found: M^+ , 172.1254. $\text{C}_{13}\text{H}_{16}$ requires M , 172.1252); m/z , 172 (16%, M^+), 157 (16, $M - \text{Me}$), 121 (100), and 105 (72, PhCHMe).

1-t-butylcyclohexene³⁰ (**16**) (72%); $\delta(\text{CCl}_4)$ 5.38 (1 H, br s, $=\text{CH}$), 2.10—1.8 (4 H, m, $\text{CH}_2\text{C}=\text{C}$), 1.71—1.32 (4 H, m, CH_2 's), and 0.98 (9 H, s, Bu^t).

3-Methyl-1-phenylbutene³¹ (**18**) [88%, after chromatography eluting with light petroleum (b.p. 30—40 °C)]; $\delta(\text{CCl}_4)$ 7.23 (5 H, s, Ph), 6.20 (2 H, m, $\text{CH}=\text{CH}$), 2.46 (1 H, m, CHMe_2), and 1.63 (6 H, d, J 6 Hz, CHMe_2) (Found: M^+ , 146.1094. $\text{C}_{11}\text{H}_{14}$ requires M , 146.1095); m/z 146 (40%, M^+), 131 (10, $M - \text{Me}$), and 130 (100, $M - \text{CH}_4$).

1,1,3-Trimethylindane³² (**21**) (82%); $\delta(\text{CDCl}_3)$ 7.10 (4 H, s, Ar), 3.20 (1 H ddq, J 2, 7 and 7 Hz, CHMe), 2.13 (1 H, dd, J 12 and 7 Hz, CH_AH_B), 1.5 (1 H, dd, J 12 and 2 Hz, CH_AH_B), 1.31 and 1.13 (3 H each, s, CMe_2), and 1.26 (3 H, d, J 7 Hz, CHMe) (Found: M^+ , 160.1242. $\text{C}_{12}\text{H}_{16}$ requires M , 160.1252); m/z 160 (25%, M^+), 159 (100, $M - \text{H}$), and 145 (70, $M - \text{Me}$).

Methyl 2,2-dimethylcyclopropanecarboxylate³³ (**25**) (100%, n.m.r.) (carried out in CDCl_3 at room temperature for 40 min); ν_{max} (CDCl_3) 1 722 cm^{-1} (CO); $\delta(\text{CDCl}_3)$ 3.66 (3 H, s, OMe), 1.47 (1 H, dd, J 5 and 8 Hz CHCO), 1.17 and 1.13 (3 H, each s, CMe_2), 1.1 (1 H, m, CH_AH_B), and 0.81 (1 H, m, CH_AH_B); m/z , 128 (86%, M^+), 113 (87, $M - \text{Me}$), 97 (100, $M - \text{OMe}$), 69 (64, $M - \text{CO}_2\text{Me}$), 59 (25, CO_2Me), and 55 (36, C_4H_7).

Methylcis-2,2,3-trimethylcyclopropylcarboxylate (**28**) (carried out at room temperature in CDCl_3 for 6 h); ν_{max} (CCl_4) 1 722 cm^{-1} (CO); $\delta(\text{CDCl}_3)$ 3.61 (3 H, s, OMe), 1.37 (1 H, m, CHCO), and 1.3—1.0 (10 H, m, CHMe and CMe_2) (Found: M^+ , 142.0981. $\text{C}_8\text{H}_{14}\text{O}_2$ requires M , 142.0994); m/z 142 (10%, M^+), 128 (26, $M - \text{CH}_2$), 127 (14, $M - \text{Me}$), 113 (28, $M - \text{Et}$), 111 (11, $M - \text{OMe}$), 84 (100, C_6H_{14}), 83 (64, $M - \text{CO}_2\text{Me}$), 69 (38, $\text{C}_4\text{H}_5\text{O}$), 67 (52, C_5H_7), 59 (57, CO_2Me), and 55 (80, C_4H_7).

Methyl(Z)-2-Isopropylbut-2-enoate (**29**) (carried out at room temperature in CDCl_3 for 6 h); ν_{max} (CCl_4) 1 720 cm^{-1} (CO); $\delta(\text{CDCl}_3)$ 5.81 (1 H, br q, J 7 Hz, $=\text{CH}$), 3.72 (3 H, s, OMe), 2.64 (1 H, br septet, J 7 Hz, CHMe_2), 1.81 (3 H, d, J 7 Hz, $=\text{CMe}$), and 1.12 (6 H, d, J 7 Hz, CMe_2) (Found: M^+ , 142.0988. $\text{C}_8\text{H}_{14}\text{O}_2$ requires M , 142.0994); m/z 142 (63%, M^+), 127 (48, $M - \text{Me}$), 111 (61, $M - \text{OMe}$), 110 (52, $M - \text{MeOH}$), 95 (79, $M - \text{O}_2\text{Me}$), 84 (53, C_6H_{14}), 83 (100, $M - \text{CO}_2\text{Me}$), 67 (83, C_5H_7), 59 (40, CO_2Me), and 55 (62, C_4H_7).

2-Methyl-1-methylenecyclohexane (**6k**).—Boron trifluoride-diethyl ether (0.517M solution in chloroform; 2.58 ml) was added to the silyl ether (**32**) (0.544 g, 2 mmol) in carbon tetrachloride (10 ml) under nitrogen. After 30 min, aqueous sodium hydroxide (5 ml) was added and the organic layer separated, dried (neutral alumina), and distilled to give the alkene³⁴ (40%); $\delta(\text{CCl}_4)$ 5.43 (2 H, br s, $=\text{CH}_2$), 2.1—0.7 (9 H, m), and 0.90 (3 H, d, J 7 Hz, Me).

2-Isopropylbicyclo[2.2.1]heptene (**11**).—Boron trifluoride-diethyl ether (0.8M solution in chloroform; 10 ml) and the silyl ether (**33**) (0.596 g, 2 mmol) were kept in carbon tetrachloride (10 ml) at 0 °C for 20 min and worked up as above to give the alkene³⁵ (46%); $\delta(\text{CCl}_4)$ 5.39 (1 H, br s, $=\text{CH}$), 2.8—2.6 (2 H, m, bridgeheads), 2.4—2.1 (1 H, m, CHMe_2), 1.7—0.8 (6 H, m), and 0.96 (6 H, d, J 6.5 Hz, CMe_2).

Trimethylsilylmethyl Iodide.—Trimethylsilylmethyl chloride (Petrarch Chemicals) (36 g) was stirred with sodium iodide (80 g) in acetone (300 ml) in the dark at room temperature for 24 h.

Distillation gave the iodide (56.5 g, 90%) b.p. 60 °C/40 mmHg (lit.,³⁶ b.p. 139 °C/144 mmHg).

3-Phenyl-4-trimethylsilylbutan-2-one (36).—Phenylacetone (6.7 ml, 50 mmol) was added dropwise with stirring to a suspension of sodium hydride (2.64 g, 55 mmol) in THF (60 ml) and the mixture refluxed for 10 min after the evolution of hydrogen ceased. Trimethylsilylmethyl iodide (8.5 ml, 55 mmol) was added and the mixture refluxed for 4 h. Aqueous work-up gave the ketone (5.15 g, 51%), b.p. 50–52 °C/0.03 mmHg (Found: C, 70.8; H, 9.0. C₁₃H₂₀OSi requires C, 71.0; H, 9.1%); ν_{\max} (film) 1 710 (C=O), 1 600 and 1 490 (Ph), and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 7.1–7.5 (5 H, m, Ph), 3.75 (1 H, dd, *J* 8.4 and 7 Hz, CH), 2.09 (3 H, s, COMe), 1.42 (1 H, dd, *J* 14.5 and 7 Hz, CH_AH_BSi), 1.09 (1 H, dd, *J* 14.5 and 8.4 Hz, CH_AH_BSi), and -0.03 (9 H, s, SiMe₃); *m/z* 202 (2%, *M*⁺), 205 (31, *M* - Me), 177 (100, *M* - COMe), and 73 (100, SiMe₃).

1-Phenyl-3-trimethylsilylpropan-1-one (38).—The cyclohexyl imine (37)³⁷ of acetophenone (10.05 g, 50 mmol) in THF (10 ml) and lithium di-isopropylamide, prepared from butyl-lithium (1.6M solution in hexane; 34.4 ml, 55 mmol) and di-isopropylamine (8 ml, 59 mmol) in THF (30 ml), were kept at 0 °C under nitrogen for 45 min, and trimethylsilylmethyl iodide (11.76 g, 55 mmol) added. After 45 min, the mixture was partitioned between a buffer prepared from acetic acid (25 ml), sodium acetate trihydrate (12.55 g), and water (25 ml), and ether (3 × 100 ml). The combined ether layers were washed with aqueous sodium carbonate, dried (MgSO₄), and distilled to give the ketone³⁸ (10.6 g, 97%), b.p. 75–78 °C/0.07 mmHg (Kugelrohr); ν_{\max} (film) 1 690 (CO), 1 600 (Ar), and 1 250 cm⁻¹ (SiMe₃); δ (CDCl₃) 7.94 (2 H, m, ArH), 7.51 (3 H, m, ArH), 2.95 (2 H, t, *J* 8 Hz, CH₂CO), 0.93 (2 H, t, *J* 8 Hz, CH₂Si), and 0.08 (9 H, s, SiMe₃) (Found: *M*⁺, 206.1093. C₁₂H₁₈OSi requires *M*, 206.1093); *m/z* 206 (10%, *M*⁺), 205 (23, *M* - H), 191 (23, *M* - Me), and 73 (100, SiMe₃).

Methyl 3-Trimethylsilylpropionate.—3-Trimethylsilylpropionic acid³⁶ (4.38 g) was refluxed in methanol (50 ml) with concentrated sulphuric acid (2 drops) for 5 h. An aqueous work-up gave the methyl ester³⁹ (4.08 g, 85%), b.p. 68 °C/18 mmHg, ν_{\max} (film) 1 735 (CO) and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 3.6 (3 H, s, OMe), 2.33 (2 H, t, *J* 8 Hz, CH₂CO), 0.82 (2 H, t, *J* 8 Hz, CH₂Si), and 0.0 (9 H, s, SiMe₃) (Found: *M*⁺ - Me, 145.0688. C₇H₁₆O₂Si requires *M* - Me, 145.0685); *m/z* 145 (15%, *M* - Me) and 73 (100, SiMe₃).

3-Methyl-1-phenyl-1-trimethylsilyloxybutene (40).—Methyl-lithium (1.4M solution in ether; 31.4 ml, 44 mmol) was stirred with copper(I) iodide (4.19 g, 22 mmol) suspended in ether at 0 °C under nitrogen for 10 min. Crotonophenone (2.92 g, 20 mmol) in ether (10 ml) was added at -78 °C over 5 min, and kept for 45 min before being warmed to -23 °C over 1 h. Triethylamine (8.36 ml, 60 mmol) and chlorotrimethylsilane (7.62 ml, 60 mmol) were added successively, and the mixture warmed to room temperature over 2 h, poured into saturated aqueous ammonium chloride (50 ml) at pH 8, and extracted with ether (3 × 100 ml). The combined ether layers were dried (MgSO₄) and distilled to give the silyl enol ether (4.12 g, 88%), b.p. 63–66 °C/0.2 mmHg; ν_{\max} (film) 1 640 (C=C) and 1 250 cm⁻¹ (SiMe₃); δ (CDCl₃) 7.45 (5 H, m, ArH), 5.16 (1 H, d, *J* 9 Hz, =CH), 3.12 (1 H, m, CHMe₂), 1.23 (6 H, d, *J* 6 Hz, CHMe₂), and 0.36 (9 H, s, SiMe₃) (Found: *M*⁺ - Me, 219.1205. C₁₄H₂₂O₂Si requires *M* - Me 219.1205); *m/z* 219 (0.3%, *M* - Me), 161 (10, *M* - SiMe₃), and 73 (100, SiMe₃).

Other Silyl Enol Ethers.—The other silyl enol ethers were prepared from propiophenone, butyrophenone, ethyl butyrate,

cyclohexanone, and methyl cyclohexanecarboxylate using lithium di-isopropylamide by the method of House.⁴⁰

Phenylthiotrimethylsilylmethyl Chloride.—Powdered *N*-chlorosuccinimide (6.67 g, 50 mmol) and phenylthiotrimethylsilylmethane⁴¹ (9.8 g, 50 mmol) were stirred in carbon tetrachloride (200 ml) for 18 h at room temperature. The mixture was filtered and evaporated to give the chloride (11.52 g, 100%); δ (CCl₄) 7.41–6.93 (5 H, m, Ar), 4.57 (1 H, s, CH), and 0.03 (9 H, s, SiMe₃), which was used directly, since distillation causes decomposition.

3-Methyl-1-phenyl-2-(phenylthiotrimethylsilylmethyl)butan-1-one (41).—The silyl enol ether (40) (2.34 g, 10 mmol) and phenylthiotrimethylsilylmethyl chloride (2.31 g, 10 mmol) were stirred with anhydrous zinc bromide (50 mg) in dichloromethane (20 ml) for 1 h at room temperature. The mixture was diluted with pentane (20 ml) filtered through neutral alumina (10 g), and the filtrate evaporated. Chromatography (SiO₂) of the residue eluting with ether–light petroleum (b.p. 30–40 °C; 5:95) gave the diastereoisomeric ketones (41) (2.45 g, 69%) (Found: *M*⁺ - Me, 341.1402. C₂₁H₂₈OSSi requires *M* - Me, 341.1408); *m/z* 341 (1%, *M* - Me), 247 (35, *M* - PhS), and 73 (100, Me₃Si). The diastereoisomers were separated: *R_F* (Et₂O–light petroleum) 0.31, ν_{\max} (film) 1 680 (CO) and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 7.83 (2 H, m, Ar), 7.40 (8 H, m, Ar), 3.67 (1 H, dd, *J* 1 and 4 Hz, CHCO), 3.07 (1 H, d, *J* 4 Hz, CHS), 2.25 (1 H, m, CHMe₂), 1.06 (3 H, d, *J* 6 Hz, CMe_AMe_B), 0.73 (3 H, d, *J* 6 Hz, CMe_AMe_B), and 0.33 (9 H, s, SiMe₃); and *R_F* 0.21; ν_{\max} (film) 1 680 and 1 250 cm⁻¹; δ (CCl₄) 7.39 (2 H, m), 7.36 (8 H, m), 3.80 (1 H, dd, *J* 6 and 8 Hz), 2.98 (1 H, d, *J* 8 Hz), 2.35 (1 H, m), 0.98 (6 H, d, *J* 6 Hz), and 0.16 (9 H, s).

Other Phenylthiotrimethylsilylmethylations.—The other silyl enol ethers were treated similarly to give the following ketones and esters.

2-Methyl-1-phenyl-3-phenylthio-3-trimethylsilylpropan-1-one (not characterised, but treated with Raney nickel directly, see below).

1-Phenyl-2-(phenylthiotrimethylsilylmethyl)butan-1-one (68%), ν_{\max} (film) 1 680 (CO) and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 7.85 (2 H, m, Ar), 7.45 (8 H, m, Ar), 3.75 (1 H, m, HCCO), 2.95 (1 H, 2 × d, two diastereoisomers, CHS), 2.12 (2 H, m, CH₂Me), 1.11 (3 H, m, CH₂Me), and 0.36 and 0.30 (9 H, 2 × s, SiMe₃) (Found: *M*⁺ - Me, 327.1234. C₂₀H₂₆OSSi requires *M* - Me, 327.1229); *m/z* 327 (4%, *M* - Me), 233 (68, *M* - PhS), and 73 (100, SiMe₃).

Ethyl 2-[phenylthio(trimethylsilyl)methyl]butyrate (79%) as a mixture of diastereoisomers ν_{\max} (film) 1 738 (CO) and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 7.35–7.15 (5 H, m, Ar), 4.13 and 3.88 (2 H, 2 × q, *J* 7 Hz, OCH₂), 2.86 (1 H, m, CHS), 2.54 (1 H, m, CHCO), 1.75 (2 H, m, CH₂Me), 1.30 and 1.18 (3 H, 2 × t, *J* 7 Hz, OCH₂Me), 0.90 (3 H, t, *J* 7 Hz, CCH₂Me), and 0.23 and 0.19 (9 H, 2 × s, SiMe₃) (Found: *M*⁺, 310.1422. C₁₆H₂₀O₂Si requires *M* 310.1422); *m/z* 310 (18%, *M*⁺), 295 (5, *M* - Me), 281 (40, *M* - Et), and 163 (100, PhSCH=CHCO).

2-[(Phenylthio)trimethylsilylmethyl]cyclohexanone (75%), ν_{\max} (film) 1 715 (CO) and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 7.56–7.10 (5 H, m, Ar), 3.38 and 3.15 (1 H, d, *J* 1.5 Hz and d, *J* 4.5 Hz, CHS), 2.8–1.4 (9 H, m), and 0.13 (9 H, s, SiMe₃) (Found: *M*⁺, 292, 1 320. C₁₆H₂₄OSSi requires *M*, 292.1323); *m/z* 292 (3%, *M*⁺), 277 (5, *M* - Me), and 183 (100, *M* - PhS).

Methyl 1-[(phenylthio)trimethylsilylmethyl]cyclohexanecarboxylate (71%), ν_{\max} (film) 1 738 (CO), 1 582 (Ar), and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 7.35 (5 H, m, Ar), 3.56 (3 H, s, OMe), 2.88 (1 H, s, CHS), 2.00–0.89 (10 H, m), and 0.24 (9 H, SiMe₃) (Found: *M*⁺ - Me, 321.1347. C₁₈H₂₈O₂SSi requires *M* - Me,

321.1345); m/z 231 (0.5%, $M - \text{Me}$), 227 (35, $M - \text{PhS}$), and 123 (100, $\text{C}_7\text{H}_{11}\text{CO}$).

Methyl 3-oxo-2-[(phenylthio)trimethylsilylmethyl]butyrate (**44**) (77%), v_{max} (film) 1 744 (CO_2Me), 1 725 (CO), 1 608, 1 585, and 1 482 (Ph), and 1 252 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 7.5–7.1 (5 H, m, Ph), 4.9–4.5 (1 H, m, CHS), 3.78 and 3.70 (3 H, 2 \times s, keto and enol OMe), 2.15 and 2.11 (0.6 H, 2 \times d, J 6 and 5 Hz, CHCO, two diastereoisomers), 2.21 and 2.12 (3 H, 2 \times s, enol and keto COMe), 1.40 (0.4 H, br s, enol OH), and 0.17 (9 H, s, SiMe_3) (Found: M^+ , 310.1060. $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Si}$ requires M , 310.1059); m/z 310 (3%, M^+), 295 (11, $M - \text{Me}$), 267 (31, $M - \text{COMe}$), 251 (33, $M - \text{CO}_2\text{Me}$), 201 (92, $M - \text{PhS}$), 185 (61, $M - \text{C}_7\text{H}_9\text{S}$), 163 (100, $\text{C}_9\text{H}_7\text{OS}$), 110 (55, PhSH), 89 (38, $\text{C}_2\text{H}_5\text{O}_2\text{Si}$), and 73 (97, SiMe_3).

3-Methyl-1-phenyl-2-trimethylsilylmethylbutan-1-one (**42**).—Raney nickel (9 g) and the ketone (**41**) (2.13 g, 6 mmol) were stirred in acetone (30 ml) for 3 h. The mixture was filtered and the solvent evaporated under reduced pressure to give the ketone (1.41 g, 95%); v_{max} (film) 1 684 (CO) and 1 250 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 7.95 (2 H, m, Ph), 7.55 (3 H, m, Ph), 3.44 (1 H, ddd, J 11, 5, and 4 Hz, CHCO), 2.06 (1 H, m, CHMe_2), 1.03 (3 H, d, J 6 Hz, CHMe_AMe_B), 0.95 (2 H, m, CH_2Si), 0.87 (3 H, d, J 6 Hz, CHMe_AMe_B), and 0.0 (9 H, s, SiMe_3) (Found: M^+ , 248.1594. $\text{C}_{15}\text{H}_{24}\text{OSi}$ requires M , 248.1597); m/z 248 (7%, M^+), 233 (25, $M - \text{Me}$), and 73 (100, SiMe_3).

Other Raney Nickel Desulphurisations.—The following ketones and esters were prepared similarly. Some were further purified by chromatography on silica gel.

2-Methyl-1-phenyl-3-trimethylsilylpropan-1-one (96%); v_{max} (film) 1 695 (CO) and 1 259 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 7.95 (2 H, m, Ph), 7.56 (3 H, m, Ph), 3.61 (1 H, sextet, J 7 Hz, CHCO), 1.32 (3 H, d, J 7 Hz, Me), 1.66 (1 H, dd, J 15 and 7 Hz, $\text{CH}_A\text{H}_B\text{Si}$), 0.85 (1 H, dd, J 15 and 7 Hz, $\text{CH}_A\text{H}_B\text{Si}$), and 0.16 (9 H, s, SiMe_3) (Found: M^+ , 220.1275. $\text{C}_{13}\text{H}_{20}\text{OSi}$ requires M , 220.1267); m/z 220 (3%, M^+), 205 (20, $M - \text{Me}$), and 73 (100, Me_3Si).

1-Phenyl-2-trimethylsilylmethylbutan-1-one (92%); v_{max} (film) 1 680 (CO) and 1 250 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 7.94 (2 H, m, Ph), 7.53 (3 H, m, Ph), 3.46 (1 H, quintet, J 7 Hz, CHCO), 1.72 (2 H, m, CH_2Me), 1.31–0.50 (5 H, m), and 0.02 (9 H, s, SiMe_3) (Found: M^+ , 234.1445. $\text{C}_{14}\text{H}_{22}\text{OSi}$ requires M , 234.1440); m/z 234 (2%, M^+), 219 (14, $M - \text{Me}$), and 73 (100, SiMe_3).

Ethyl 2-trimethylsilylmethylbutyrate (98%); v_{max} (film) 1 740 (CO) and 1 253 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 4.09 (2 H, q, J 7 Hz, OCH_2), 1.52 (1 H, m, CHCO), 1.26 (3 H, t, J 7 Hz, OCH_2Me), 1.00–0.54 (7 H, m), and 0.00 (9 H, s, SiMe_3) (Found: M^+ , 202.1388. $\text{C}_{10}\text{H}_{22}\text{O}_2\text{Si}$ requires M , 202.1389); m/z 202 (1%, M^+), 187 (5, $M - \text{Me}$), 173 (3, $M - \text{Et}$), and 73 (100, SiMe_3).

2-Trimethylsilylmethylcyclohexanone (99%).

Methyl 1-trimethylsilylmethylcyclohexanecarboxylate (98%); v_{max} (film) 1 738 (CO) and 1 250 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 3.70 (3 H, s, OMe), 2.15 (2 H, m), 1.8–1.05 (8 H, m), 0.76 (2 H, s, CH_2Si), and 0.06 (9 H, s, SiMe_3) (Found: M^+ , 228.1565. $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}$ requires M , 228.1585); m/z 228 (7%, M^+), 213 (18, $M - \text{Me}$), and 73 (100, SiMe_3).

Methyl 3-Oxo-2-trimethylsilylmethylbutyrate (98%).

Methyl 3-Oxo-2-trimethylsilylmethylidenbutyrate (**45**).—*m*-Chloroperbenzoic acid (2.7 g, 16 mmol) and methyl 3-oxo-2-[phenylthio(trimethylsilylmethyl)]butyrate (4.1 g, 13.2 mmol) were stirred in dichloromethane (30 ml) at -78°C under nitrogen for 5 min and poured into aqueous sodium carbonate. The aqueous layer was extracted with dichloromethane and the combined extracts were dried (MgSO_4), evaporated under reduced pressure, and distilled (Kugelrohr, $200^\circ\text{C}/20$ mmHg). Chromatography of the residue on silica gel, eluting with ether–light petroleum (b.p. $30\text{--}40^\circ\text{C}$; 1:9), gave the β -silyl enone

(1.54 g, 59%) as a 1:1 mixture of stereoisomers $R_F(\text{CH}_2\text{Cl}_2)$ 0.34 and 0.42; v_{max} (film) 1 737 (CO_2Me), 1 708 (CO), and 1 252 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 7.01 and 6.88 (1 H, 2 \times s, =CH *E* and *Z*), 3.68 (3 H, s, OMe), 2.23 and 2.19 (3 H, 2 \times s, Me), and 0.07 and 0.05 (9 H, 2 \times s, SiMe_3) (Found: M^+ – Me, 185.0630. $\text{C}_9\text{H}_{16}\text{O}_3\text{Si}$ requires $M - \text{Me}$, 185.0633); m/z 185 (100%, $M - \text{Me}$), 169 (7, $M - \text{OMe}$), 157 (4, $M - \text{COMe}$), 125 (26, $\text{C}_6\text{H}_5\text{O}_3$), 89 (34, $\text{C}_2\text{H}_5\text{O}_2\text{Si}$), 83 (23, $\text{C}_4\text{H}_3\text{O}_2$), 75 (22, Me_2SiOH), and 73 (50, SiMe_3).

Methyl 2-Acetyl-3-trimethylsilylbutyrate.—Methyl-lithium (0.94 M solution in ether; 4.6 ml) was added to a stirred slurry of copper(I) iodide (0.42 g, 2.2 mmol) in ether (20 ml). After 10 min, the β -silyl enone (**45**) (0.40 g, 2 mmol) in ether (10 ml) was added dropwise and the mixture kept for 30 min. Aqueous ammonium chloride was added, and the mixture extracted with ether. The ether extract was dried (MgSO_4) and evaporated to give the ketone as a 1:1 mixture of diastereoisomers, $R_F(\text{Et}_2\text{O})$ 0.66; v_{max} (film) 1 740 (CO_2Me), 1 719 (CO), and 1 254 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 3.57 (3 H, s, OMe), 3.24 and 3.12 (1 H, 2 \times d, J 7 and 9 Hz, COCH), 2.03 and 2.01 (3 H, 2 \times s, COMe), 1.5–1.2 (1 H, m, SiCH), 0.86 and 0.78 (3 H, 2 \times d, J 3 and 3.5 Hz, Me), and -0.12 (9 H, s, SiMe_3) (Found: M^+ , 216.1192. $\text{C}_{10}\text{H}_{20}\text{O}_3\text{Si}$ requires M , 216.1182); m/z 216 (1%, M^+), 201 (41, $M - \text{Me}$), 173 (41, $M - \text{Ac}$), 169 (17, $M - \text{C}_2\text{H}_7\text{O}$), 157 (77, $M - \text{CO}_2\text{Me}$), 127 (24, $\text{C}_6\text{H}_7\text{O}_3$), 89 (31, $\text{C}_2\text{H}_5\text{O}_2\text{Si}$), 73 (95, SiMe_3), and 69 (100, $\text{C}_4\text{H}_5\text{O}$).

cis-2-Dimethyl(phenyl)silylcyclopentyl Phenyl Ketone.—Dimethyl(phenyl)silyl-lithium⁴² (0.43 M solution in THF; 77 ml) was stirred with copper(I) cyanide (1.475 g) in THF (5 ml) at 0°C . After 20 min, 1-benzoylcyclopentene⁴³ (2.58 g) was added over 5 min at -23°C and the mixture stirred for 45 min; it was then allowed to come to 0°C . The mixture was poured into saturated aqueous ammonium chloride and extracted with ether (3 \times 50 ml) and the ether layers were dried (MgSO_4) and evaporated. Chromatography of the residue on silica gel eluting with ether–light petroleum (b.p. $30\text{--}40^\circ\text{C}$) (5:95) gave the ketone (4.16 g, 90%), R_F 0.36; v_{max} (film) 1 684 (CO), 1 603 (Ar), and 1 250 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 8.08 (2 H, m, Ar), 7.60 (8 H, m, Ar), 4.15 (1 H, m, CHCO), 2.58–1.35 (7 H, m), and 0.65 and 0.50 (2 \times 3 H, s, SiMe_2) (Found: M^+ , 308.1597. $\text{C}_{20}\text{H}_{24}\text{OSi}$ requires M , 308.1597); m/z 308 (42%, M^+), 293 (43, $M - \text{Me}$), 231 (28, $M - \text{Ph}$), and 135 (100, SiMe_2Ph).

endo-2-Acetyl-exo-3-trimethylsilylbicyclo[2.2.1]hept-5-ene.—4-Trimethylsilylbut-3-en-2-one⁴⁴ (5.25 g, 37 mmol), cyclopentadiene (12.2 g, 185 mmol), and zinc bromide (50 mg) were stirred at 0°C for 1 h and at room temperature for 1 h. The excess of diene was evaporated off, and the residue chromatographed on silica gel, eluting with ether–light petroleum (b.p. $30\text{--}40^\circ\text{C}$) (5:95), to give the ketone (6.52 g, 85%); $R_F(\text{Et}_2\text{O})$ 0.69; v_{max} (film) 1 710 (CO) and 1 250 cm^{-1} (SiMe_3); $\delta(\text{CCl}_4)$ 6.22 (1 H, dd, J 6 and 3 Hz, 3=CH), 5.62 (1 H, dd, J 6 and 3 Hz, C=CH), 3.3–3.1 (1 H, m, COCH), 2.8–2.6 (2 H, m, bridgehead H's), 2.09 (3 H, s, COMe), 1.3–1.1 (2 H, m, CH_2), 1.0–0.8 (1 H, m, SiCH), and 0.01 (9 H, s, SiMe_3) (Found: M^+ , 208.1272. $\text{C}_{12}\text{H}_{20}\text{OSi}$ requires M , 208.1283); m/z 208 (3%, M^+), 193 (5, $M - \text{Me}$), 127 (15, $\text{C}_3\text{H}_2\text{OSiMe}_3$), 118 (18, $M - \text{Me}_3\text{SiOH}$), 117 (20, $M - \text{Me}_3\text{SiOH}_2$), 110 (40, $\text{C}_6\text{H}_{10}\text{Si}$), 91 (15, Me_3SiOH_2), 75 (35, Me_2SiOH), 73 (100, SiMe_3), 69 (27, $\text{C}_4\text{H}_5\text{O}$), and 66 (65, C_5H_6).

endo-2-Acetyl-exo-3-trimethylsilylbicyclo[2.2.1]heptane.—The bicycloheptene (6.32 g, 30.4 mmol) was hydrogenated over palladium (0.15 g, 10% on C) in ether (50 ml) for 2 h, when 1 equiv. of hydrogen had been adsorbed. The mixture was filtered and the solvent evaporated to give the saturated ketone (6.31 g,

99%); $R_F(\text{Et}_2\text{O})$ 0.73; $v_{\text{max.}}(\text{film})$ 1 710 (CO) and 1 249 cm^{-1} (SiMe₃); $\delta(\text{CCl}_4)$ 2.6—2.4 (2 H, m, COCH and bridgehead H), 2.1—1.9 (1 H, m, bridgehead H), 1.89 (3 H, s, COMe), 1.4—0.9 (7 H, m), and -0.23 (9 H, s, SiMe₃) (Found: M^+ , 210.1430. C₁₂H₂₂O₂Si requires M , 210.1440); m/z 210 (10%, M^+), 195 (12, $M - \text{Me}$), 181 (23, $M - \text{C}_2\text{H}_5$), 110 (17, C₇H₁₀O), 75 (48, Me₂SiOH), and 73 (100, SiMe₃).

4-Methyl-4-trimethylsilylpentan-2-one.—4-Trimethylsilylpent-3-en-2-one⁴⁴ (1.56 g, 10 mmol) and lithium dimethylcuprate (11 mmol) in ether (20 ml) were mixed at -78 °C; after the solution had warmed to 0 °C, it was poured into aqueous ammonium chloride, and extracted with ether (3 × 50 ml). The ether layers were dried (MgSO₄), and evaporated, and the residue chromatographed on silica gel eluting with ether—light petroleum (b.p. 30—40 °C) (15:85) to give the ketone^{42,45} (1.59 g, 93%).

Preparation of the γ -Silyl Alcohols

(A) *By Reaction of Methyl-Lithium with Ketones.*—Typically, methyl-lithium (1.4M solution in ether; 10 ml) was added dropwise with stirring to the appropriate ketone (10 mmol) in ether (15 ml) at -78 °C under nitrogen. After 0.5—2 h, the mixture was warmed to 0 °C, poured into saturated aqueous ammonium chloride (20 ml), and extracted with ether (3 × 40 ml). The ether layers were dried (MgSO₄) and evaporated, and the residue chromatographed on silica gel, eluting with ether—light petroleum (b.p. 30—40 °C) (5:95) to give the alcohols. The following alcohols were made by this method.

2-Phenyl-4-trimethylsilylbutan-2-ol (1b) (93%), $v_{\text{max.}}(\text{film})$ 3 400 (OH) and 1 250 cm^{-1} (SiMe₃); $\delta(\text{CDCl}_3)$ 7.40 (5 H, m, Ph), 2.36 (1 H, s, OH), 2.00—1.50 (2 H, m, CH₂), 1.53 (3 H, s, Me), 0.91 (1 H, m, CH_AH_BSi), 0.43 (1 H, m, CH_AH_BSi), and 0.03 (9 H, s, SiMe₃) (Found: M^+ , 222.1443. C₁₃H₂₂O₂Si requires M , 222.1440); m/z 189 (10%, $M - \text{H}_2\text{O} - \text{Me}$) and 73 (100, SiMe₃).

2-Methyl-3-phenyl-4-trimethylsilylbutan-2-ol (1c) (97%), $v_{\text{max.}}(\text{film})$ 3 450 and 1 250 cm^{-1} ; $\delta(\text{CDCl}_3)$ 7.26 (5 H, s, Ph), 2.74 (1 H, dd, J 7 and 9 Hz, CHPh), 1.45—1.09 (3 H, m, OH and CH₂Si), 1.21 (6 H, s, CMe₂), and -0.17 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 221.1364. C₁₄H₂₄O₂Si requires $M - \text{Me}$, 221.1362); m/z 221 (1%, $M - \text{Me}$), 163 (9, $M - \text{SiMe}_3$), and 73 (100, SiMe₃).

3-Methyl-2-phenyl-4-trimethylsilylbutan-2-ol (1g) (97%) as a mixture of diastereoisomers; $v_{\text{max.}}(\text{film})$ 3 450 and 1 250 cm^{-1} ; $\delta_{\text{H}}(\text{CCl}_4)$ 7.42 (5 H, m, Ph), 2.10 (1 H, s, OH), 2.05 (1 H, m, CHMe), 1.58 and 1.56 (3 H, s, Me), 0.98 and 0.92 (3 H, d, J 7 Hz, CHMe), 0.53 (2 H, m, CH₂Si), and 0.07 (9 H, s, SiMe₃) (Found: $M^+ - \text{H}_2\text{O}$, 218.1495. C₁₄H₂₄O₂Si requires $M - \text{H}_2\text{O}$, 218.1491); m/z 221 (1%, $M - \text{Me}$), 218 (0.1, $M - \text{H}_2\text{O}$), 163 (8, $M - \text{SiMe}_3$), and 73 (100, SiMe₃).

2-Phenyl-3-trimethylsilylmethylpentan-2-ol (1h) (98%) as a mixture of diastereoisomers; $v_{\text{max.}}(\text{film})$ 3 450 and 1 252 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.45 (5 H, m, Ph), 1.99 (1 H, s, OH), 1.95 (1 H, m, CHEt), 1.60 (3 H, s, Me), 1.45 (2 H, m, CH₂Me), 1.09—0.32 (5 H, m), and 0.06 (9 H, s, SiMe₃) (Found: $M^+ - \text{H}_2\text{O}$, 232.1648. C₁₅H₂₆O₂Si requires $M - \text{H}_2\text{O}$, 232.1648); m/z 235 (0.2%, $M - \text{Me}$), 232 (1.5, $M - \text{H}_2\text{O}$), 177 (5, $M - \text{SiMe}_3$), and 73 (100, SiMe₃).

4-Methyl-2-phenyl-3-trimethylsilylmethylpentan-2-ol (1i) (97%) as a mixture of diastereoisomers; $v_{\text{max.}}(\text{film})$ 3 450 and 1 250 cm^{-1} ; $\delta(\text{CDCl}_3)$ 7.40 (5 H, m, Ph) 1.98 (2 H, m, methine CH's), 1.70 (1 H, s, OH), 1.49 (3 H, s, Me), 0.80 (3 H, d, J 3.5 Hz, CHMe_AMe_B), 0.71 (3 H, d, J 3.5 Hz, CHMe_AMe_B), 0.62 (2 H, m, CH₂Si), and 0.07 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 249.1677. C₁₆H₂₈O₂Si requires $M - \text{Me}$ 249.1675); m/z , 249 (0.1%, $M - \text{Me}$), 246 (2, $M - \text{H}_2\text{O}$), 231 (10, $M - \text{Me} - \text{H}_2\text{O}$), and 73 (100, SiMe₃).

4,4-Dimethyl-2-phenyl-3-trimethylsilylmethylpentan-2-ol (1j) (95%); $v_{\text{max.}}(\text{film})$ 3 450 and 1 252 cm^{-1} ; $\delta(\text{CDCl}_3)$ 7.45 (5 H, m, Ph), 2.12 (1 H, t, J 5 Hz, CHBu'), 1.84 (1 H, s, OH), 0.91 (9 H, s, Bu'), 0.83 (2 H, m, CH₂Si), and 0.06 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 263.1832. C₁₇H₃₀O₂Si requires $M - \text{Me}$, 263.1832); m/z , 263 (2%, $M - \text{Me}$), 260 (0.5, $M - \text{H}_2\text{O}$), and 73 (100 SiMe₃).

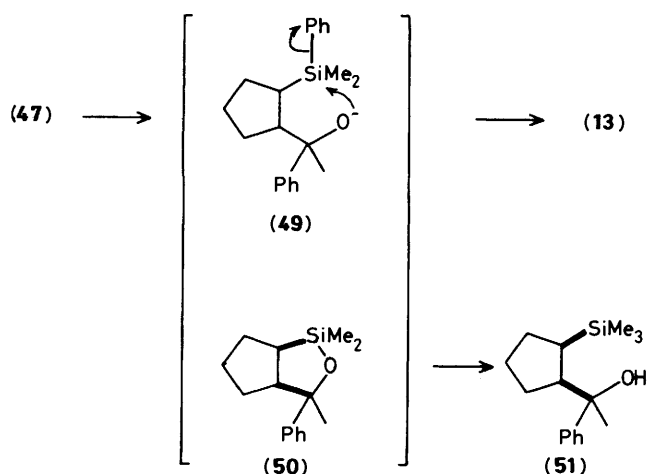
2-endo-(2-Hydroxypropan-2-yl)-3-exo-trimethylsilylbicyclo-(2.2.1)heptane (10) (95%); $v_{\text{max.}}(\text{film})$ 3 500 and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 2.4—1.0 (11 H, m), 1.18 (3 H, s, Me), 1.06 (3 H, s, Me), and -0.06 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 211.1534. C₁₃H₂₆O₂Si requires $M - \text{Me}$, 211.1518); m/z 211 (0.5%, $M - \text{Me}$), 167 (12, $M - \text{CMe}_2\text{OH}$), and 73 (100, SiMe₃).

2-Methyl-4-phenyl-4-trimethylsilylbutan-2-ol (17) from 4-phenyl-4-trimethylsilylbutan-2-one⁴⁴ (89%); $v_{\text{max.}}(\text{film})$ 3 400, 1 600, and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.18 (5 H, m, Ph), 2.15 (3 H, m, CH and CH₂), 1.46 (1 H, s, OH), 1.16 (6 H, s, Me₂), and 0.00 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 221.1365. C₁₄H₂₄O₂Si requires $M - \text{Me}$, 221.1362); m/z 221 (5%, $M - \text{Me}$), 218 (0.5, $M - \text{H}_2\text{O}$), and 73 (100, SiMe₃).

Methyl 3-hydroxy-3-methyl-2-trimethylsilylmethylbutyrate (24) (53%); $v_{\text{max.}}(\text{film})$ 3 550, 1 730 (CO₂Me), and 1 254 cm^{-1} ; $\delta(\text{CCl}_4)$ 3.60 (3 H, s, OMe), 2.4—2.2 (2 H, m, CHCO and OH), 1.10 (3 H, s, Me), 1.08 (3 H, s, Me), 0.9—0.5 (2 H, m, CH₂Si), and -0.07 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me} - \text{H}_2\text{O}$, 185.1009. C₁₀H₂₂O₃Si requires $M - \text{Me} - \text{H}_2\text{O}$, 185.0998); m/z 185 (5%, $M - \text{Me} - \text{H}_2\text{O}$), 171 (9, $M - \text{CH}_3\text{O}_2$), 160 (24, $M - \text{C}_3\text{H}_6\text{O}$), 116 (29, C₅H₈O₃), 89 (64, C₂H₅O₂Si), 75 (32, Me₂SiOH), 73 (100, SiMe₃), 59 (68, CO₂Me), and 55 (89, C₃H₃O).

Methyl 3-hydroxy-3-methyl-2-(1-trimethylsilylethyl)butyrate (26) and **(28)**, the (*SS*, *RR*) isomer **(26)** being eluted first (35%); $R_F(\text{Et}_2\text{O})$ 0.64; $v_{\text{max.}}(\text{film})$ 3 520, 1 720, and 1 252 cm^{-1} ; $\delta(\text{CCl}_4)$ 3.53 (3 H, s, OMe), 2.88 (1 H, br s, OH), 2.30 (1 H, d, J 2 Hz, CHCO), 1.04 (6 H, s, CMe₂), 1.0—0.8 (4 H, m, SiCHMe), and -0.15 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me} - \text{H}_2\text{O}$, 199.1143. C₁₁H₂₄O₃Si requires $M - \text{Me} - \text{H}_2\text{O}$, 199.1155); m/z 199 (3%, $M - \text{Me} - \text{H}_2\text{O}$), 174 (19, $M - \text{C}_2\text{H}_5\text{O}_2$), 173 (10, $M - \text{CO}_2\text{Me}$), 159 (16, $M - \text{SiMe}_3$), 143 (12, $M - \text{C}_2\text{H}_5\text{O}_2\text{Si}$), 127 (9, C₆H₇O₃), 111 (14, C₆H₇O₂), 101 (44, C₅H₉O₂), 89 (27, C₂H₅O₂Si), 83 (12, C₄H₃O₂), 75 (19, Me₂SiOH), 73 (58, SiMe₃), 69 (100, C₄H₅O), and 59 (23, CO₂Me); and the (*RS*, *SR*) isomer **(28)** second (28%), $R_F(\text{Et}_2\text{O})$ 0.61; $v_{\text{max.}}(\text{film})$ 3 480, 1 733, and 1 251 cm^{-1} ; $\delta(\text{CCl}_4)$ 3.49 (3 H, s, OMe), 2.51 (1 H, br s, OH), 2.13 (1 H, d, J 6 Hz, CHCO), 1.07 (3 H, s, Me), 1.03 (3 H, s, Me), 1.1—0.9 (4 H, m, SiCHMe), and -0.18 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me} - \text{H}_2\text{O}$, 199.1154); m/z 199 (7%), 174 (6), 173 (16), 159 (10), 143 (6), 134 (37, C₅H₁₄O₂Si), 111 (16), 101 (20), 89 (26), 83 (20), 75 (23) 73 (50), 69 (100), and 59 (30).

1-Phenyl-1-[2-dimethyl(phenyl)silylcyclopentyl]ethanol (13) (9%); R_F 0.17; $v_{\text{max.}}(\text{film})$ 3 510, 1 600, and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.45 (10 H, m, 2 × Ph), 2.88 (1 H, m, CHCMePhOH), 2.28—1.66 (6 H, m), 1.80 (1 H, s, OH), 1.46 (3 H, s, Me), 1.18 (1 H, m, CHSi), 0.47, (3 H, s, SiMe_AMe_B), and 0.45 (3 H, s, SiMe_AMe_B) (Found: $M^+ - \text{Me}$, 309.1660. C₂₁H₂₈O₂Si requires $M - \text{Me}$, 309.1675); m/z 309 (0.5%, $M - \text{Me}$), 232 (3, $M - \text{Ph}$), and 135 (100, SiMe₂Ph). The major product from this reaction was the corresponding trimethylsilyl derivative, **1-phenyl-1-(2-trimethylsilylcyclopentyl)ethanol (51)** (91%) R_F 0.31; $v_{\text{max.}}(\text{film})$ 3 520, 1 600, and 1 250 cm^{-1} ; (CCl₄), 7.48 (5 H, m, Ph), 2.77 (1 H, m, CHCMePhOH), 2.05—1.61 (6 H, m), 1.66 (1 H, s, OH), 1.51 (3 H, s, Me), 1.14 (1 H, m, CHSi), and 0.04 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 247.1522. C₁₆H₂₆O₂Si requires $M - \text{Me}$, 247.1518); m/z 247 (2%, $M - \text{Me}$), 174 (52, $M - \text{Me} - \text{SiMe}_3$), 75 (100) and 73 (100, SiMe₃). This product is probably the *cis* isomer having been formed by intramolecular displacement of the phenyl group **(49)**→**(50)** followed by methyl-lithium displacing the alkoxide ion **(50)**→**(51)**.



(B) *By Reaction of Ethylmagnesium Iodide with 3-Phenyl-4-trimethylsilylbutan-2-one.*—The ketone (36) (1.1 g, 5 mmol) and ethylmagnesium iodide (10 mmol) were refluxed in THF (15 ml) for 2 h, and worked up as in method (A) to give 3-methyl-2-phenyl-1-trimethylsilylpentan-3-ol (1d) (92%); ν_{\max} (film) 3 450, 1 600, and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.26 (5 H, s, Ph), 2.27 (1 H, dd, J 8.5 and 8 Hz, CHPh), 1.61 (1 H, s, OH), 1.47 (2 H, m, CH₂Me), 1.06 (3 H, s, Me), 1.05 (3 H, t, J 8 Hz, CH₂Me), 1.04 (2 H, m, CH₂Si), and -0.18 (9 H, s, SiMe₃) (Found: $M^+ - \text{H}_2\text{O}$, 232.1646. C₁₅H₂₆O_{Si} requires $M - \text{H}_2\text{O}$, 232.1648); m/z 235 (0.1%, $M - \text{Me}$), 232 (2, $M - \text{H}_2\text{O}$), and 73 (100, SiMe₃).

(C) *By Reaction of Phenylmagnesium Bromide with Ketones.*—Typically phenylmagnesium bromide (7 mmol) and the ketone (5 mmol) were refluxed in THF (10 ml) for 2 h, and the mixture worked up as in method (A). The following alcohols were made by this method.

2,3-Diphenyl-4-trimethylsilylbutan-2-ol (1e) (81%), as a mixture of diastereoisomers, ν_{\max} (film) 3 450, 1 600, and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.36 (10 H, m, Ph), 3.10 (1 H, dd, J 12 and 6 Hz, CHPh of one diastereoisomer, and dd, J 15 and 2 Hz, CHPh, other diastereoisomer), 2.1 (1 H, s, OH), 1.68 and 1.41 (3 H, 2 \times s, Me), 1.33–0.66 (2 H, m, CH₂Si), and -0.16 and -0.20 (9 H, 2 \times s, SiMe₃) (Found: $M - \text{H}_2\text{O}$, 280.1649. C₁₉H₂₀O_{Si} requires $M - \text{H}_2\text{O}$, 280.1648); m/z 280 (0.1%, $M - \text{H}_2\text{O}$), 188 (50, $M - \text{H}_2\text{O} - \text{Ph} - \text{Me}$), and 73 (100, SiMe₃).

4-Methyl-2-phenyl-4-trimethylsilylpentan-2-ol (19) (95%), ν_{\max} (film) 3 450, 1 600, and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.38 (5 H, m, Ph), 2.01 (1 H, d, J 14 Hz, CH_AH_B), 1.95 (1 H, d, J 14 Hz, CH_AH_B), 1.76 (1 H, s, OH), 1.61 (3 H, s, MeCOH), 1.03 (3 H, s, CMe_AMe_B), 0.73 (3 H, s, CMe_AMe_B), and 0.04 (9 H, s, SiMe₃) (Found: M^+ , 250.1759. C₁₅H₂₆O_{Si} requires M , 250.1754); m/z 250 (1%, M^+), 235 (3, $M - \text{Me}$), 232 (1.5, $M - \text{H}_2\text{O}$), and 73 (100, SiMe₃).

(D) *By Reaction of Vinylmagnesium Bromide with the Ketone (36).*—The ketone (1.10 g, 5 mmol) and vinylmagnesium bromide (10 mmol) were refluxed in THF for 2 h, and the mixture worked up as in method (A) to give 3-methyl-4-phenyl-5-trimethylsilylpent-1-en-3-ol (1f) (0.91 g, 74%) as a mixture of diastereoisomers; ν_{\max} (film) 3 450 and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.26 (5 H, s, Ph), 5.98 (1 H, dd, J 17 and 11 Hz, CH=), 5.22 (2 H, m, =CH₂), 2.76 (1 H, dd, J 10 and 6 Hz, CHPh), 1.77 (1 H, s, OH), 1.12 (3 H, s, Me), 1.10 (2 H, m, CH₂Si), and -0.24 (9 H, s, SiMe₃) (Found: $M^+ - \text{H}_2\text{O}$, 230.1506. C₁₅H₂₄O_{Si} requires $M - \text{H}_2\text{O}$, 230.1491); m/z 230 (1%, $M - \text{H}_2\text{O}$), 215 (10, $M - \text{H}_2\text{O} - \text{Me}$), and 73 (100, SiMe₃).

(E) *By Reaction of Lithium Dimethylcuprate on 2-Trimethylsilylmethylcyclohexanone.*—Methyl-lithium (1.4 M solution in ether; 20.4 ml) and copper(I) iodide (2.72 g, 14.3 mmol) were stirred in ether (10 ml) at 0 °C under nitrogen for 10 min. The solution was cooled to -78 °C and methyl-lithium (1.4 M solution in ether; 10.2 ml) added. After 15 min, 2-trimethylsilylmethylcyclohexanone (1.84 g, 10 mmol) in ether (10 ml) was added dropwise, the mixture stirred for 2 h, and worked up as in method (A) to give *cis*-1-methyl-2-trimethylsilylmethylcyclohexan-1-ol *cis*-(1k) (2.00 g, 100%); ν_{\max} (film) 3 450 and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.85–0.95 (12 H, m), 1.01 (3 H, s, Me), and -0.06 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 185.1357. C₁₁H₂₄O_{Si} requires $M - \text{Me}$, 185.1352); m/z 185 (12%, $M - \text{Me}$), 75 (100, Me₂SiOH), and 73 (85, SiMe₃).

(F) *By Reaction of Trimethylsilylmethylmagnesium Chloride on 1-Methylcyclohexene Oxide.*—1-Methylcyclohexene (4.8 g) was stirred with *m*-chloroperbenzoic acid (11.2 g) in dichloromethane (50 ml) at 0 °C for 6 h. Aqueous work-up and distillation gave the oxide (3.91 g, 70%), b.p. 137–138 °C (lit.,⁴⁶ b.p. 137.5–138 °C). This oxide (1.12 g) in ether (5 ml) was added to trimethylsilylmethylmagnesium chloride, prepared from the chloride (2.45 g) and magnesium (0.52 g) in ether (10 ml), and copper(I) chloride (0.1 g), and the mixture stirred for 16 h. Work-up as in method (A) gave *trans*-1-methyl-2-trimethylsilylmethylcyclohexan-1-ol *trans*-(1k) (1.8 g, 90%); $R_F(\text{Et}_2\text{O})$, 0.67; ν_{\max} (film) 3 500 and 1 248 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.7–0.8 (10 H, m), 0.82 (3 H, s, Me), 0.65 (2 H, s, CH₂Si), and -0.18 (9 H, s, SiMe₃) (Found: M^+ , 200.1599. C₁₁H₁₄O_{Si} requires M , 200.1596); m/z 185 (6%, $M - \text{Me}$), 123 (3, $M - \text{SiMe}_3$), 110 (10, C₇H₁₀O), 95 (17, C₆H₇O), 81 (C₆H₉), 75 (100, Me₂SiOH), and 73 (70, SiMe₃).

(G) *By Reaction of Methyl-Lithium on Esters.*—Methyl-lithium (1.4 M solution in ether; 17.8 ml) and the ester (10 mmol) in ether (15 ml) were kept at -78 °C for 30 min, and then warmed to room temperature. Work-up as in method (A) gave the following tertiary alcohols.

2-Methyl-4-trimethylsilylbutan-2-ol (1a) (89%) (from methyl 3-trimethylsilylpropionate); ν_{\max} (film) 3 400 and 1 252 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.67 (3 H, m, CH₂ and OH), 1.67 (6 H, s, Me₂), 0.45 (2 H, m, CH₂Si), and -0.02 (9 H, s, SiMe₃) (Found: $M^+ - \text{H}_2\text{O}$, 142.1165. C₈H₂₀O_{Si} requires $M - \text{H}_2\text{O}$, 142.1178); m/z 142 (0.5%, $M - \text{H}_2\text{O}$ and 73 (100, SiMe₃).

2-(1-Trimethylsilylmethylcyclohexyl)propan-2-ol (15) (83%) (from methyl 1-trimethylsilylmethylcyclohexanecarboxylate); ν_{\max} (film) 3 680 and 1 248 cm^{-1} ; $\delta(\text{CCl}_4)$ 2.01 (1 H, s, OH), 1.8–1.1 (10 H, m), 1.29 (6 H, s, Me₂), 0.89 (2 H, s, CH₂Si), and 0.14 (9 H, s, SiMe₃) (Found: $M^+ - \text{Me}$, 213.1670. C₁₃H₂₈O_{Si} requires $M - \text{Me}$ 213.1675); m/z 213 (2%, $M - \text{Me}$), 169 (13, $M - \text{C}_3\text{H}_7\text{O}$), and 73 (100, SiMe₃).

(H) *By Reaction of Phenylmagnesium Bromide on Ethyl 2-Trimethylsilylmethylbutyrate.*—The ester (2.02 g, 10 mmol) and phenylmagnesium bromide (22 mmol) were refluxed in THF (25 ml) for 2 h and worked up as in method (A) to give 1,1-diphenyl-2-trimethylsilylmethylbutan-1-ol (22) (2.43 g, 78%); ν_{\max} (film) 3 550, 1 600, and 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 7.45 (10 H, m, Ph), 2.76 (1 H, m, CH), 2.31 (1 H, s, OH), 1.76–0.65 (4 H, m), 0.76 (3 H, t, J 8 Hz, Me), and 0.15 (9 H, s, SiMe₃) (Found: $M^+ - \text{H}_2\text{O}$, 294.1803. C₂₀H₂₀O_{Si} requires $M - \text{H}_2\text{O}$, 294.1804); m/z 294 (3%, $M - \text{H}_2\text{O}$), 279 (0.5, $M - \text{H}_2\text{O} - \text{Me}$), and 73 (100, SiMe₃).

Preparation of Silyl Ethers (32) and (33).—Butyl-lithium (1.6 M solution in hexane; 5 ml) was added to the alcohol *trans*-(1k) (1.00 g, 5 mmol) in THF (20 ml) at 0 °C. After 40 min at room temperature, chlorotrimethylsilane (1.25 ml, 10 mmol)

was added, the mixture kept for 2 h, and then evaporated. The residue was chromatographed on silica gel eluting with pentane to give trans-1-methyl-1-trimethylsilyloxy-2-trimethylsilylmethylcyclohexane (**32**) (1.22 g, 90%); ν_{\max} (film) 1 249 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.7–1.1 (9 H, m), 1.01 (3 H, s, Me), 0.94 (1 H, m, SiCH_AH_B), 0.79 (1 H, m, SiCH_AH_B), 0.02 (9 H, s, OSiMe_3), and -0.06 (9 H, s, SiMe_3) (Found: M^+ , 272.1999. $\text{C}_{14}\text{H}_{32}\text{OSi}_2$ requires M , 272.1992); m/z 272 (18%, M^+), 199 (4, $M - \text{SiMe}_3$), 182 (4, $M - \text{Me}_3\text{SiOH}$), 169 (7, $\text{C}_6\text{H}_8\text{OSiMe}_3$), 147 (42, $\text{Me}_2\text{SiOSiMe}_3$), 143 (100, $\text{C}_4\text{H}_6\text{OSiMe}_3$), 140 (32, $\text{C}_5\text{H}_7\text{SiMe}_3$), and 130 (34, $\text{C}_3\text{H}_5\text{OSiMe}_3$).

2-Trimethylsilyloxypropan-2-yl-3-trimethylsilylbicyclo-[2.2.1]heptane (**33**) (95%) was prepared similarly, except that methyl-lithium was used; ν_{\max} (film) 1 250 cm^{-1} ; $\delta(\text{CCl}_4)$ 2.2–2.0 (3 H, m, bridgeheads and COCH), 1.7–0.9 (6 H, m), 1.22 (3 H, s, Me), 1.09 (3 H, s, Me), 0.72 (1 H, dd, J 7 and 2 Hz, SiCH), 0.04 (9 H, s, OSiMe_3), and -0.07 (9 H, s, SiMe_3) (Found: $M^+ - \text{Me}$, 283.1920. $\text{C}_{16}\text{H}_{34}\text{OSi}_2$ requires $M - \text{Me}$, 283.1913); m/z 283 (0.4%, $M - \text{Me}$), 147 (18, $\text{Me}_3\text{SiOSiMe}_2$), 143 (15, $\text{C}_4\text{H}_6\text{OSiMe}_3$), and 131 (100, $\text{C}_3\text{H}_6\text{OSiMe}_3$).

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