The Reactions of Tris(trimethylsilyl)methyl-lithium with Some Carbon Electrophiles †

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Tris(trimethylsilyl)methyl-lithium (1) reacts with non-enolisable aldehydes, ketones, and acid chlorides, and with some epoxides, with the formation of carbon–carbon bonds. This method of preparing functionalized silanes is limited by the readiness with which (1) abstracts a proton, if one is available, rather than attacks at carbon. In the reaction with epoxides, the product alkoxide can transfer a silyl group from carbon to oxygen, and in one case the intermediate so formed reacts to give a cyclopropane (32) in what is a homologue of the Peterson reaction. The 1,4-transfer of a silyl group occurs in other systems when the resulting carbanion is stabilised by such groups as phenylthio and diphenylphosphinoyl.

WE report here some reactions of tris(trimethylsilyl)-methyl-lithium (1) with carbon electrophiles. This reagent is readily available [1] from the reaction of tris-(trimethylsilyl)methane with methyl-lithium in tetrahydrofuran (THF). Although we get some potentially useful compounds, the reactions we sought did not, on the whole, materialise; neverthess, we observed some interesting homologues of the Brook rearrangement,[2] including one which is completed by what amounts to a homo-Peterson reaction.

RESULTS AND DISCUSSION

Our first electrophiles were aldehydes and ketones. As Gröbel and Seebach have also reported,[3] the Peterson reaction [4] readily takes place to give 1,1-disilylalkenes with non-enolisable aldehydes and ketones such as benzophenone (25%), benzaldehyde (72%), cinnamaldehyde (53%), and pivalaldehyde (73%). In our hands, enolisable systems simply underwent deprotonation. Even cyclopropanecarbaldehyde gave largely the reprotonated silane, tris(trimethylsilyl)methane (which was easily detected in the crude reaction mixture by [1]H n.m.r.) and <5% of something which showed the right spectroscopic properties to be [2,2-bis(trimethylsilyl)-vinyl]cyclopropane. We also had difficulty preparing 1,1-bis(trimethylsilyl)ethylene (4) from formaldehyde. This product was clearly present ([1]H n.m.r. signal at δ 6.25) but in very variable amounts from run to run. As an alternative synthesis of this potentially valuable compound,[3] we have found that methoxymethylation [(1) → (2)], or methoxyethoxymethylation [(1) → (3)], followed by treatment with Lewis acid, reliably give 1,1-bis(trimethylsilyl)ethylene (4) in overall yields, based on (1), of 51 and 55%, respectively. We also allylated the silane (1), and converted the product (5) into the allylsilane (6) with N-bromosuccinimide. This compound decomposed to give polymeric products, presumably by way of 1,1-bis(trimethylsilyl)butadiene. The direct reaction of the silane (1) with acrolein similarly led to polymeric products, which further suggests that 1,1-bis(trimethylsilyl)butadiene is likely to prove somewhat unstable.

Our second electrophile was benzoyl chloride. The

† No reprints available.

[1]H n.m.r. spectrum of the reaction mixture in THF clearly showed three separate but equally intense signals from trimethylsilyl groups, which suggested that the silyl enol ether (7) had been produced. An excess of benzoyl chloride followed by an aqueous work-up gave ca. 20% of dibenzoylmethane, which indicates that the silyl enol ether (7) may have reacted with benzoyl chloride without Lewis-acid catalysis, except for that provided by lithium chloride. Acid chlorides generally need Lewis-acid catalysis to react with silyl enol ethers,[5] but we were deterred from pursuing the reaction of (7) when we found that an enolisable acid chloride, acetyl chloride, did not react with (1) to give the analogue of (7), but suffered deprotonation instead. The silyl enol ether (7) was hydrolysed easily to acetophenone, and acetophenone could also be obtained from (1) and benzonitrile. On the other hand, benzoic anhydride and ethyl benzoate did not react with the silane (1); this selectivity might conceivably be useful one day.

In one run with benzoyl chloride under reflux in THF, we got an unexpected and quite different product (8). This must have been produced from two equivalents of benzoyl chloride, one of tris(trimethylsilyl)methyl-lithium (1), and one of the enolate of acetaldehyde, known [6] to be present when strong bases [methyl-lithium, or perhaps (1), in this case] are used in THF. The same product (8) was also prepared, more rationally, from the lithium enolate (9), by treatment successively with benzoyl chloride and (1). The structure was proved by treating (8) with methyl-lithium, which gave the cis-enone (11), the stereochemistry of which was evident by n.m.r. comparison with its trans-isomer (12), prepared from the enol benzoate (10) and bis(trimethyl-silyl)methyl-lithium.[3,7] Both (11) and (12) were easily desilylated to crotonophenone (13).

Our next electrophile was ethylene oxide, which gave the alcohol (14); this could be oxidised successively to the aldehyde (15) and the acid (16). More interestingly, the alcohol (14) reacted with sodium hydride in THF to give the silyl ether (19) and hence, by hydrolysis, the alcohol (20), which has one fewer silyl groups. The silicon transfer (17) → (18) → (19) takes ca. 90 min at room temperature. Potassium t-butoxide in THF worked comparably well, but the lithium and magnesium

alkoxides did not react. Solvents such as ether, dioxan, dimethoxyethane, and benzene were ineffective with the sodium alkoxide.

By analogy with the Brook rearrangement,[2] one would expect 1,4-silyl shifts (17) ⟶ (18) to be endothermic, so that the equilibrium will be pulled over only when a proton source is available. THF, as we have already seen, reacts with strong bases.[6] It seems likely that the
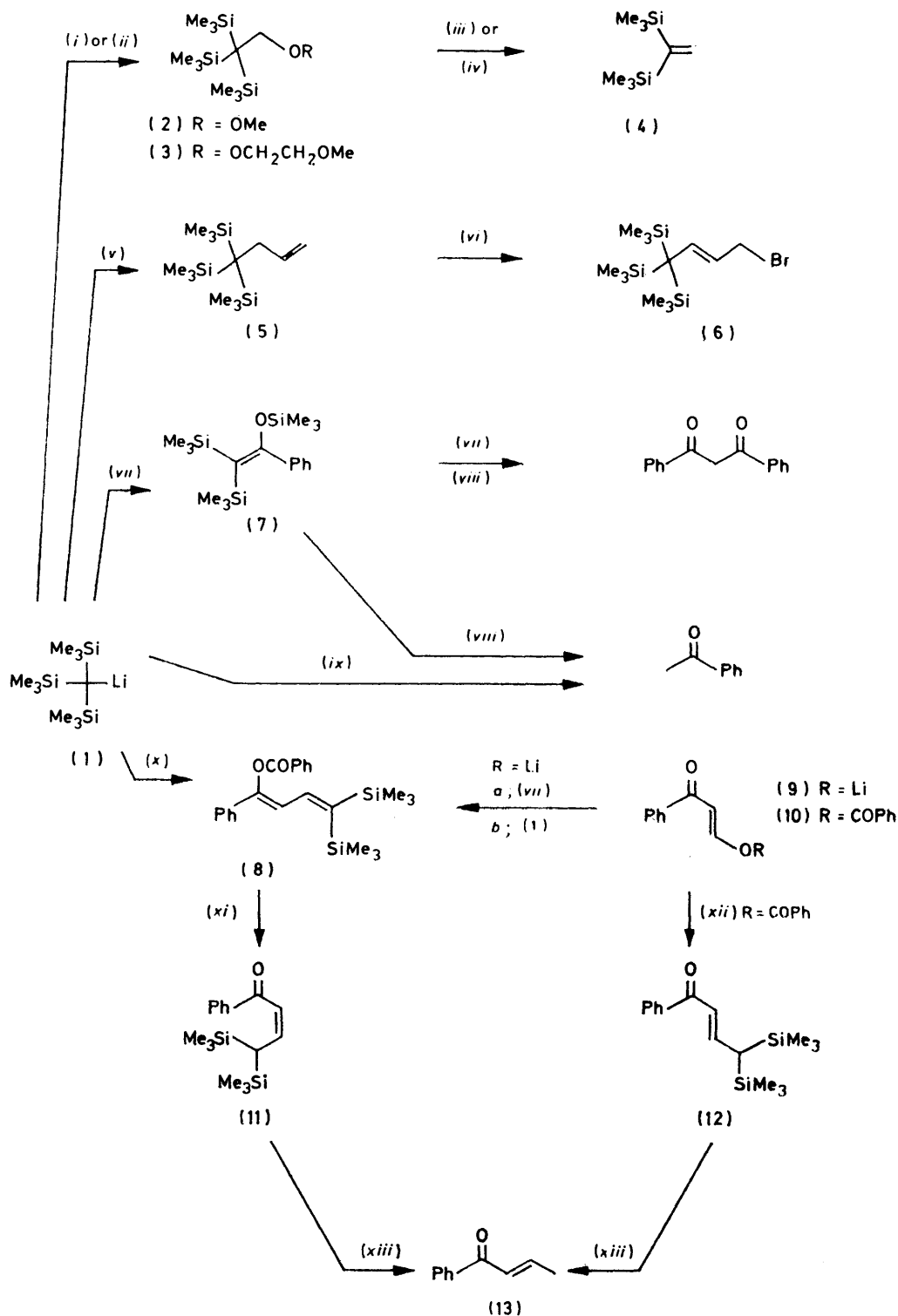
(i) MeOCH$_2$Cl; (ii) MeOCH$_2$CH$_2$OCH$_2$Cl; (iii) BCl$_3$; (iv) ZnBr$_2$; (v) CH$_2$=CHCH$_2$Br; (vi) N-bromosuccinimide; (vii) PhCOCl; (viii) NaHCO$_3$; (ix) PhCN; (x) PhCOCl, THF; see text; (xi) MeLi; (xii) (Me$_3$Si)$_2$CHLi; (xiii) TsOH, benzene
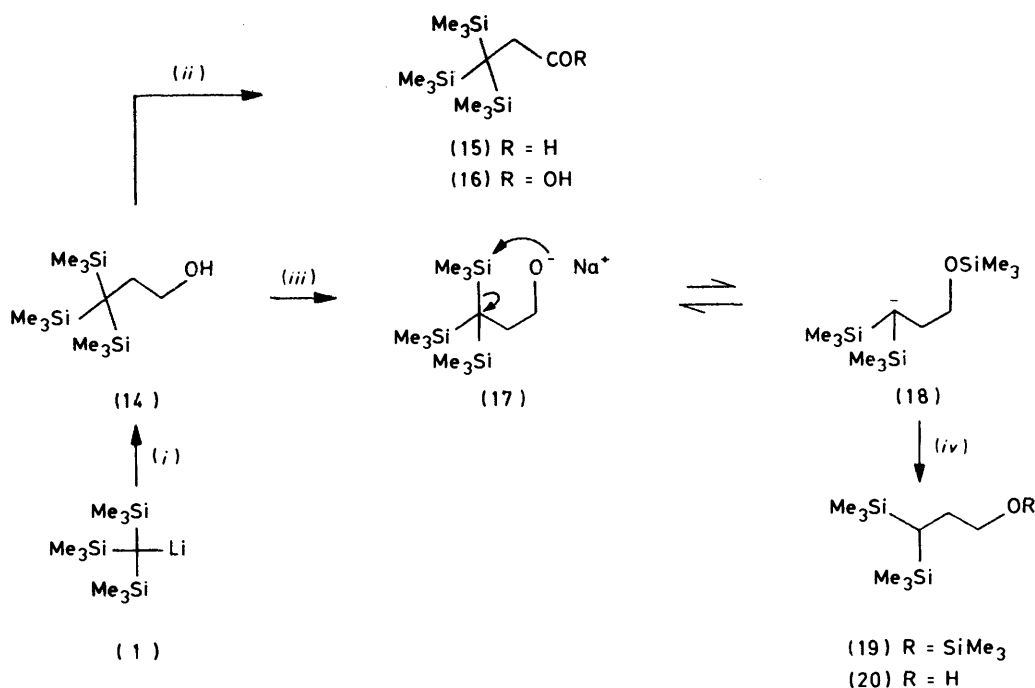
(i) $\overline{CH_2CH_2O}$;   (ii) pyridinium chlorochromate;   (iii) NaH;   (iv) THF

alkyl-sodium intermediate (18) is such a base [although the slightly more hindered and slightly better stabilised lithium base (1) is stable in THF at room temperature], which explains why the rearrangement (17) ⟶ (19) is only noticeable in THF and not in other aprotic solvents. The benzyl ether of glycidol underwent similar reactions.

Stilbene oxide was inert towards (1), and both propylene oxide and cyclohexene oxide protonated (1) (^{1}H n.m.r. observations).

The 1,4-shift of a silyl group has been seen before in other systems, where the resulting carbanion is stabilised by such groups as cyano,[8] phosphonyl,[9] sulphonyl,[10] and
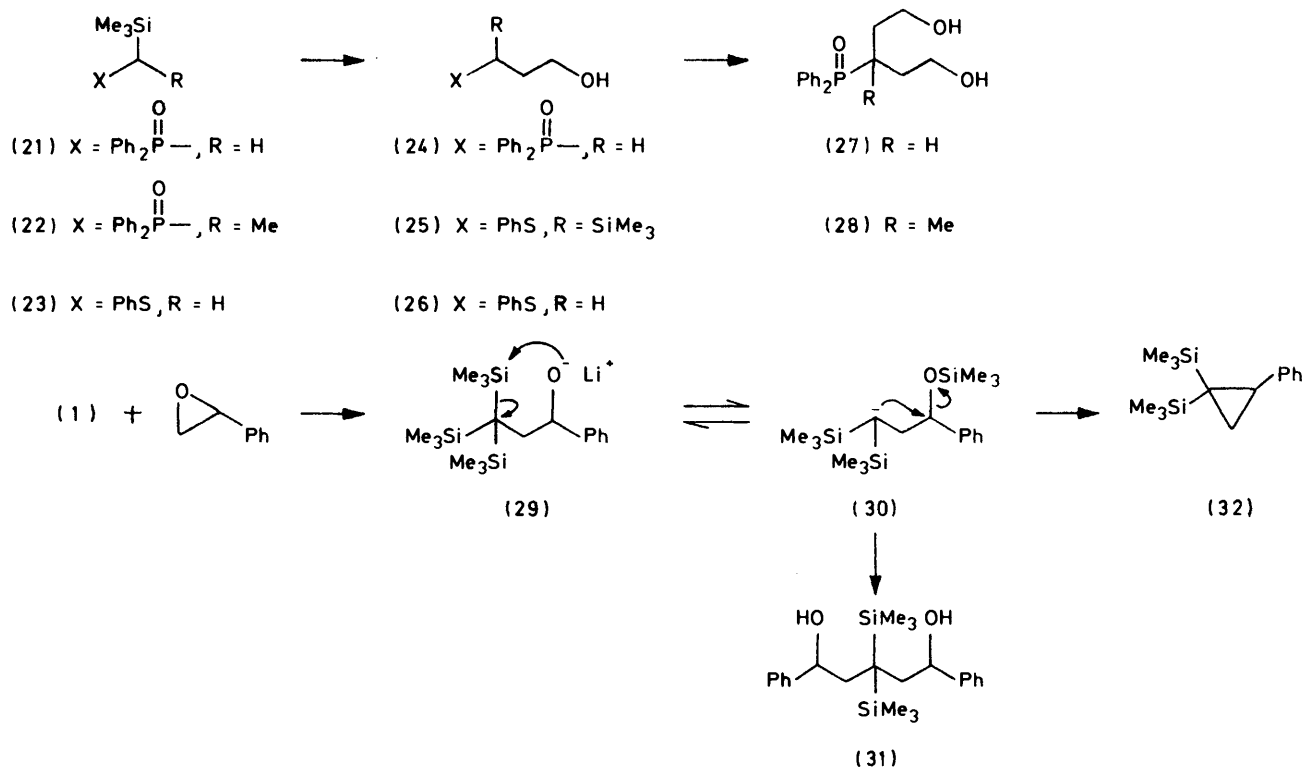
amide.[11] In our case, the two silyl groups evidently provide enough stabilisation, but one silyl group does not, since the alcohol (20) did not rearrange on treatment with sodium hydride in THF. We looked briefly at two other cases of 1,4-silyl shift. The phosphine oxide (21) was easily metallated (and gave the usual Peterson product with benzophenone). When treated with ethylene oxide, the metallated derivative of (21) gave the alcohol (24) and the diol (27); each could be made the major product simply by using one or two equivalents of ethylene oxide. The silyl shift here is effectively so fast, even with the lithium alkoxide, that we were unable to stop it. This was also true with an extra methyl group in the reaction (22) ⟶ (28). Unfortunately, we were also unable to trap the presumed intermediate with any other electrophiles than those already present. (Phenylthiomethyl)trimethylsilane (23) was also easily metallated and trapped with ethylene oxide. The product (25) could be desilylated with sodium hydride in THF, and again we were unable to trap the presumed intermediate with any electrophiles more interesting than a proton.

We have left one epoxide reaction until last. The silane (1) reacted with styrene oxide to give a mixture of two products (31) and (32). We think that both of them come from the 1,4-shifted intermediate (30), the one by attack on another molecule of styrene oxide and the other by intramolecular displacement (30) ⟶ (32) of the silyloxy-group. The overall sequence styrene oxide ⟶ (32) amounts to a homo-Peterson reaction, a possibility which has been discussed,[8,11] and sought, but not hitherto observed. It is rather special; this is the only example we have, and is observed only because the the displacement step (30) ⟶ (32) is taking place at a benzylic position.

The similarity in the features of the 1,2-rearrangement (the Brook rearrangement [2]) (33) ⇌ (34), the 1,4-
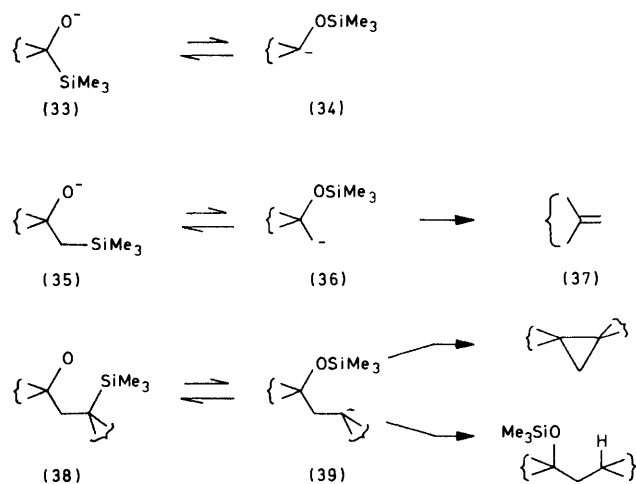
rearrangement (38) ⇌ (39), and the Peterson reaction (35) ⟶ (37), lend support to the suggestion [11] that the latter reaction takes place, in some sense, by 1,3-re-arrangement (35) ⟶ (36) followed by rapid β-elimin-

ation (36) ⟶ (37), a possibility which has also been put forward [12] for the analogous Wittig reaction. The intervention of a pentacovalent silicon anion in any or all of these reactions, either as an intermediate, or as the true structure for the carbanions (34), (36), and (39), remains an attractive alternative.

EXPERIMENTAL

Tris(trimethylsilyl)methyl-lithium (1).—The reagent was prepared as described by Eaborn and his co-workers,[1] and consisted typically of a solution of 5 mmol in 20—25 ml of THF, with 2—4 ml of ether always present from the methyl-lithium used in its preparation.

1,1-Bis(trimethylsilyl)-2,2-diphenylethylene.— Tris(tri-methylsilyl)methyl-lithium (1) [1] (15 mmol) and benzo-phenone (2.5 g, 14 mmol) in ether (10 ml) were refluxed for 18 h, and then poured into water and extracted into ether. The organic layer was washed with water and dried (MgSO₄). The solvent was evaporated to give a liquid which was separated on a column of silica gel (85 g) in dichloromethane to give 1,1-*bis*(trimethylsilyl)-2,2-*diphenylethylene* (760 mg, 25%) as flakes, m.p. 101—102 °C (Found: C, 73.8; H, 8.9. $C_{20}H_{28}Si_2$ requires C, 74.0; H, 8.7%); $\nu_{max.}$ (KBr) 1 530 (C=C), 1 490 (aromatic) and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄) 7.14 (10 H, br s, aromatic) and —0.14 (18 H, s, SiMe₃); m/e 324 (M^+, 38%), 309 (M^+ — 15, 26), 251 (M^+ — 73, 13), 135 ($C_6H_5SiMe_2$, 75), 83 (100), and 73 (80); $\lambda_{max.}$ (EtOH) 235 nm (ε 19 000).

1-Methoxy-2,2,2-tris(trimethylsilyl)ethane (2).—Chloro-methyl methyl ether (3 ml) was added dropwise to a stirred solution of the alkyl-lithium (1) (5 mmol) at —78 °C under nitrogen. The solution was stirred at —78 °C for 30 min, then allowed to warm to room temperature over 2 h. Aqueous work-up and crystallisation from methanol gave the *ether* (2) (1.07 g, 78%) as a white solid, m.p. 149—152 °C (with decomposition and sublimation) (Found: C, 52.1; H, 11.7. $C_{12}H_{32}OSi_3$ requires C, 52.1; H, 11.65%); $\nu_{max.}$ 2 835 (OMe) and 1 258 cm⁻¹ (SiMe₃); δ 3.58 (2 H, s, CH₂), 3.25 (3 H, s, Me), and 0.12 (27 H, s, SiMe₃); m/e 245 (M^+ — OMe, 35%), 172 (M^+ — MeOSiMe₃, 24), 157 (172 — 15, 100), and 73 (SiMe₃, 30).

1-Methoxyethoxy-2,2,2-tris(trimethylsilyl)ethane (3).—Methoxyethoxymethyl chloride [13] (1.15 g) was added drop-wise to a solution of (1) (9 mmol) at —78 °C under nitrogen, kept for 1 h at —78 °C and then allowed to warm to room temperature over 20 h. Chromatography on silica (90 g) eluting with light petroleum and distillation gave the *ether* (3) (2.36 g, 82%) (Found: C, 52.6; H, 11.1. $C_{14}H_{36}O_2Si_3$ requires C, 52.4; H, 11.3%); $\nu_{max.}$ 2 810 (OMe) and 1 251 cm⁻¹ (SiMe₃); δ 3.50 (2 H, s, CH₂), 3.39 (4 H, s, CH₂CH₂), 3.26 (3 H, s, Me) and 0.12 (27 H, s, SiMe₃); m/e 231 (M^+ — MeOCH₂CH₂OCH₂, 24%), 217 (15), 172 (9), 157 (46), 89 (MeC₃H₆O₂⁺, 90), and 73 (SiMe₃, 100).

1,1-Bis(trimethylsilyl)ethylene (4).—Method A. Boron tri-chloride (0.2 ml) was added dropwise to a solution of the ether (2) (120 mg) in dry dichloromethane (5 ml) and kept at —78 °C under nitrogen for 1 h. After an aqueous wash, carbon tetrachloride was added and the dichloromethane carefully removed by distillation to give a solution of (4) in carbon tetrachloride [δ 0.06 (18 H, s, SiMe₃) and 6.26 (2 H, s, CH₂)] as the only silicon-containing product. Calibration against dichloroethylene, as an internal standard, gave a yield of 65%.

Method B. The ether (3) (1.64 g) and zinc bromide (4 g) (dried over phosphorus pentaoxide *in vacuo*) were stirred in

dry dichloromethane (30 ml) for 3 days under nitrogen. After filtration, most of the solvent was removed on a rotary evaporator at 0 °C and the remainder was distilled through a 70 × 6 mm Vigreux column to give the ethylene (4) (550 mg, 67%), b.p. 148—149 °C (lit.,[14] 151 °C at 756 mmHg); $\nu_{max.}$ 1 569 (C=C) and 1 251 cm^{-1} (SiMe$_3$); δ (CCl$_4$) 6.26 (2 H, s, CH$_2$) and 0.06 (18 H, s, SiMe$_3$).

4,4,4-*Tris(trimethylsilyl)but-1-ene* (5).—Allyl bromide (2 ml) was added dropwise at 0 °C to the solution of (1) (9 mmol). Work-up in the usual manner gave a semi-crystalline gum which was recrystallised from methanol to give prisms, m.p. 106—110 °C, of the *alkene* (5) (1.62 g, 66%) (Found: C, 56.8; H, 11.45. C$_{13}$H$_{32}$Si$_3$ requires C, 57.3; H, 11.75%); $\nu_{max.}$ 1 634 (C=C) and 1 252 cm^{-1} (SiMe$_3$); δ 6.01 (1 H, ddt, *J* 10, 17, and 6 Hz, C–CH=), 5.16—4.90 (2 H, m, =CH$_A$H$_B$), 2.51 (2 H, br d, *J* 6 Hz, CH$_2$), and 0.17 (27 H, s, SiMe$_3$); *m/e* 216 (*M*$^+$ − C$_4$H$_8$, 6%), 171 (10), 157 (16), and 73 (100).

1-*Bromo-4,4,4-tris(trimethylsilyl)but-2-ene* (6).—The silane (5) (533 mg) and *N*-bromosuccinimide (342 mg) in carbon tetrachloride (25 ml) were refluxed for 1 h. The solution was filtered, refluxed for another 0.5 h and the solvent removed to give a pale orange liquid, a single compound by t.l.c. (R_F 0.6, CH$_2$Cl$_2$), tentatively identified as the *allyl bromide* (6) (510 mg, 74%); $\nu_{max.}$ 1 653 (C=C) and 1 258 cm^{-1} (SiMe$_3$); δ 5.65 (1 H, dt, *J* 6 and 17 Hz, CH$_2$–CH=), 5.38 (1 H, dm, *J* 17 Hz, =CH), 3.83 (2 H, br d, *J* 6 Hz, CH$_2$), and 0.05 (27 H, s, SiMe$_3$). Attempted distillation caused the formation of a tar.

The Reaction of (1) *with Benzoyl Chloride*.—(*a*) Benzoyl chloride (0.58 ml, 5 mmol) was added in one portion to a solution of tris(trimethylsilyl)methyl-lithium (1) (5 mmol) with rapid stirring at 0 °C. The solution lightened in colour immediately. A sample was withdrawn within 2 min and syringed into an n.m.r. tube, flushed with nitrogen, and sealed with a rubber serum cap. Four ^{1}H n.m.r. singlets were observed in the spectrum at δ 0.30, 0.16, −0.05, and −0.20. The mixture was poured into sodium hydrogencarbonate solution, extracted with ether, and dried (MgSO$_4$). The solvent was removed *in vacuo* to leave a light red oil from which acetophenone was collected as the semicarbazone (592 mg, 68%), m.p. 195—197 °C (lit.,[15] 198 °C).

(*b*) Benzoyl chloride (1.21 ml, 10 mmol) was added dropwise at −78 °C to a stirred solution of (1) (5 mmol) under nitrogen. The solution was stirred for 1 h at this temperature, allowed to warm to room temperature and then poured into sodium hydrogencarbonate solution. An aqueous work-up gave a red oil which on trituration with hexane gave red crystals. Recrystallisation from hexane gave straw-coloured platelets of dibenzoylmethane (196 mg, 18%), m.p. 75—76 °C (lit.,[15] 78 °C); $\nu_{max.}$ 1 605 (C=O) and 1 550 cm^{-1}. The ^{1}H n.m.r. spectrum was identical with that of an authentic sample. Chromatography of the mother liquors [dichloromethane–light petroleum (1 : 1)] gave a second crop (42 mg, 4%).

(*c*) Benzoyl chloride (1.20 ml, 10 mmol) was added just below reflux temperature to a solution of tris(trimethylsilyl)methyl-lithium (1) (5 mmol) during 1 min and then refluxed for 2 h. Thin layer chromatography (t.l.c. [CH$_2$Cl$_2$–hexane (1 : 1)] indicated no dibenzoylmethane but showed a new u.v. active spot (R_F 0.70). Chromatography on silica (120 g) in dichloromethane gave 1-*benzoyloxy-4,4-bis(trimethylsilyl)-1-phenylbutadiene* (8) as platelets (132 mg), m.p. 108—110 °C (from light petroleum) (Found: C, 69.8;

H, 7.75. C$_{22}$H$_{30}$O$_2$Si$_2$ requires C, 70.0; H, 7.65%); $\nu_{max.}$ 1 748 (C=O), 1 252 (SiMe$_3$) and 1 241 cm^{-1} (C–O); δ 8.45—8.20 (2 H, m, *o*-H aromatic), 7.85—7.20 (9 H, m, aromatic and dienic), 6.85 (1 H, d, *J* 11 Hz, dienic H), 0.40 (9 H, s, SiMe$_3$), and 0.14 (9 H, s, SiMe$_3$); *m/e* 394 (*M*$^+$, 28%), 289 (*M*$^+$ − PhCO, 8), 201 (15), 105 (100), and 73 (65); $\lambda_{max.}$ (EtOH) 303 and 232 nm (ε 28 500 and 23 500).

1-*Benzoyloxy-4,4-bis(trimethylsilyl)-1-phenylbutadiene* (8). —Methyl formate (11.2 g) was added dropwise to a stirred mixture of acetophenone (15 g) and lithium wire (800 mg) in ether (100 ml). The solution was stirred overnight, and the off-white solid was collected, washed with cold hexane, and dried *in vacuo*. Benzoyl chloride (0.58 ml) was added to a solution of this enolate (770 mg) in dry ether (25 ml) and after 5 min, a solution of tris(trimethylsilyl)methyl-lithium (1) (5 mmol) was added and the solution kept at room temperature for 2 h. An aqueous work-up and chromatography on silica (55 g) [hexane–dichloromethane (1 : 1)] gave the ketobenzoate (8) [313 mg, 16% based on tris(trimethylsilyl)methane used].

(Z)-3,3-*Bis(trimethylsilyl)prop-1-enyl Phenyl Ketone* (11). —Methyl-lithium (0.34 ml of a 2.2M solution in ether) was added dropwise at 0 °C to a solution of the benzoate (8) (134 mg, 0.34 mmol) in ether under nitrogen and kept for 2 h. Preparative t.l.c. [light petroleum–ether (5 : 1)] gave the *ketone* (11) (69 mg 80%) as an oil, R_F 0.5; $\nu_{max.}$ 1 659 (C=O), 1 600, 1 582 (aromatic), and 1 252 cm^{-1} (SiMe$_3$); δ (CDCl$_3$) 7.94—7.80 (2 H, m, *o*-H aromatic), 7.58—7.16 (3 H, m, aromatic), 6.67 (1 H, d, *J* 10 Hz, =CHCO), 6.35 (1 H, dd, *J* 10 and 13 Hz, =CH–C), 3.61 (1 H, d, *J* 13 Hz, CH), and 0.07 (18 H, s, SiMe$_3$) (Found: *M*$^+$, 290.1510. C$_{16}$H$_{26}$OSi$_2$ requires *M*, 290.1521); *m/e* 290 (*M*$^+$, 30%), 216 (100), 201 (15), 187, 147, and 73.

(E)-3,3-*Bis(trimethylsilyl)propenyl Phenyl Ketone* (12).— n-Butyl-lithium (1.2 ml of a 1.5M solution in hexane) was added to bis(trimethylsilyl)methane (270 mg) in *NNN'N'*-tetramethylethylenediamine (200 mg) at room temperature under nitrogen. After 7 days the solution was cooled to −78 °C and a solution of benzoyloxymethyleneaceto-phenone [16] (10) (400 mg) in dry THF (10 ml) was added dropwise and allowed to come to room temperature over 2 h. An aqueous work-up and preparative t.l.c. [light petroleum–ether (5 : 1)] gave the *ketone* (12) (98 mg, 23%) as an oil; $\nu_{max.}$ 1 665 (C=O), 1 601, 1 589 (aromatic), and 1 252 cm^{-1} (SiMe$_3$); δ (CCl$_4$) 8.10—7.86 (2 H, m, *o*-H aromatic), 7.70—7.36 (3 H, m, aromatic), 7.18 (1 H, dd, *J* 13 and 15 Hz, =CH–C), 6.61 (1 H, d, *J* 15 Hz, =CHCO), 1.61 (1 H, d, *J* 13 Hz, CH), and 0.17 (17 H, s, SiMe$_3$) (Found: *M*$^+$, 290.1524. C$_{16}$H$_{26}$OSi$_2$ requires *M*, 290.1521); *m/e* 290 (*M*$^+$, 20%), 216 (58), 187 (52), 147 (68), 105 (100), and 73 (75).

The Action of Acid on the Ketosilanes (11) *and* (12).—The ketosilane (11) or (12) (10 mg) in benzene (2 ml) was added to a solution of toluene-*p*-sulphonic acid (0.25 g) in benzene (5 ml) and kept for 12 h. The solution was poured into sodium hydrogencarbonate solution, extracted into ether, and dried (MgSO$_4$). Evaporation of the solvent gave, in both cases, crotonophenone, $\nu_{max.}$ 1 677 and 1 630 cm^{-1}, identical with an authentic sample.

The Reaction of (1) *with Benzonitrile*.—Benzonitrile (0.49 ml) was added at 0 °C to a stirred solution of tris-(trimethylsilyl)methyl-lithium (1) (5 mmol), and the mixture kept at 0 °C for 90 min. An aqueous work-up gave aceto-phenone, collected as the semicarbazone (694 mg, 81%), m.p. 195—197 °C (lit.,[15] 198 °C).

3,3,3-*Tris(trimethylsilyl)propan*-1-*ol* (14).—Ethylene oxide (4 g) was added dropwise at 0 °C to a solution of tris-(trimethylsilyl)methyl-lithium (1) (54 mmol) and the mixture kept for 30 min. An aqueous work-up and crystallisation from methanol gave the *alcohol* (14) as small plates, m.p. 128—129 °C (13.4 g, 90%) (Found: C, 52.1; H, 11.6. $C_{12}H_{32}OSi_3$ requires C, 52.10; H, 11.65%); $\nu_{max.}$ 3 610 (OH) and 1 251 cm^{-1} (SiMe$_3$); δ 3.9—3.68 (2 H, m, CH$_2$O), 2.0—1.81 (2 H, m, CH$_2$), 1.55 (1 H, s, OH, removed by D$_2$O), and 0.11 (27 H, s, SiMe$_3$); m/e 261 (M^+ − 15, 3%), 245 (M^+ − CH$_2$OH, 11), 171 (172 − H, 30), 157 (172 − 15, 25), 147 (25), and 73 (100); the 3,5-*dinitrobenzoate* had m.p. 121—122 °C, straw-coloured needles from methanol (Found: C, 48.2; H, 7.15; N, 5.5. $C_{19}H_{34}N_2O_6Si_3$ requires C, 48.5; H, 7.3; N, 5.9%); the acetate had m.p. 81—83 °C (from EtOH) (Found: C, 52.6; H, 10.7. $C_{14}H_{24}O_2Si_3$ requires C, 52.8; H, 10.75%); $\nu_{max.}$ 1 745 (C=O) and 1 254 cm^{-1} (SiMe$_3$); δ 4.30—4.13 (2 H, m, CH$_2$O), 2.03 (3 H, s, Me), 2.03—1.83 (2 H, m, CH$_2$), and 0.17 (27 H, s, SiMe$_3$); m/e 318 (M, 16%), 217 (13), 171 (17), and 73 (100).

3,3,3-*Tris(trimethylsilyl)propanal* (15).—The alcohol (14) (150 mg) in dichloromethane (2 ml) was added to pyridinium chlorochromate (186 mg) in dichloromethane (1 ml) and the mixture stirred for 90 min. An aqueous work-up gave the *aldehyde* (15) (143 mg, 95%); $\nu_{max.}$ 1 720 and 1 255 cm^{-1}; δ 9.9 (1 H, t, J 1.5 Hz, HC=O), 2.6 (2 H, d, J 1.5 Hz, CH$_2$), and 0.18 (9 H, s, SiMe$_3$); the *dinitrophenylhydrazone* was prepared (Found: C, 47.55; H, 7.4; N, 12.1. $C_{18}H_{34}N_4O_4Si_3$ requires C, 47.6; H, 7.5; N, 12.3%).

3,3,3-*Tris(trimethylsilyl)propionic Acid* (16).—The *acid* resulted from atmospheric oxidation of the aldehyde (15) as prisms, m.p. 120 °C (Found: C, 49.3; H, 10.4. $C_{12}H_{30}O_2Si_3$ requires C, 49.6; H, 10.4%); $\nu_{max.}$ 3 400 br (OH), 1 255 cm^{-1}, δ 2.4 (2 H, s, CH$_2$), and 0.12 (9 H, s, SiMe$_3$).

3,3-*Bis(trimethylsilyl)propan*-1-*ol* (20).—The alcohol (14) (640 mg) in dry THF (10 ml) was added to sodium hydride (52 mg of a 60% dispersion in paraffin oil, washed three times with light petroleum). The mixture was stirred for 2 h, poured into water, extracted with ether, and the extract dried (MgSO$_4$). The solvent was evaporated to leave the *trimethylsilyl ether* (19) (320 mg, 100%). An analytical sample was prepared by short-path distillation (Found: C, 52.15; H, 11.75. $C_{12}H_{32}OSi_3$ requires C, 52.1; H, 11.65%); $\nu_{max.}$ (film) 1 251 and 1 085 cm^{-1}; δ 3.47 (2 H, t, J 8.5 Hz, CH$_2$O), 1.49 (2 H, dt, J 5 and 8 Hz, CH$_2$), 0.12 (9 H, s, OSiMe), 0.03 (18 H, s, OSiMe$_3$), and −0.42 (1 H, t, J 5 Hz, CHSi); m/e 261 (M^+ − 15, 30%), 186 (M^+ − OSiMe$_3$ − H, 35), 147 (100), 99 (15), and 73 (20). In another reaction, the reaction mixture was poured into water and stirred for 30 min before work-up to give the *alcohol* (20) (473 mg, 99%). An analytical sample was prepared by bulb-to-bulb distillation, oven temperature 85 °C at 25 mmHg (Found: C, 52.8; H, 11.7. $C_9H_{24}OSi_2$ requires C, 52.8; H, 11.8%); $\nu_{max.}$ (film) 3 320 br (OH), 2 950, 1 265, and 1 252 cm^{-1}; δ 3.57 (2 H, t, J 8 Hz, CH$_2$O), 1.73 (2 H, dt, J 5.5 and 8 Hz, CH$_2$), 1.62 (1 H, s, OH, removed by D$_2$O), 0.03 (18 H, s, SiMe$_3$), and −0.32 (1 H, t, J 5.5 Hz, CHSi); m/e 189 (M^+ − 15, 14%), 147 (100), 133 (25), 113 (34), 99 (45), and 73 (48); the 3,5-*dinitrobenzoate* had m.p. 72.5—73.5 °C (needles from methanol) (Found: C, 48.4; H, 6.9; N, 6.95. $C_{16}H_{26}N_2O_6Si_2$ requires C, 48.2; H, 6.6; N, 7.0%).

The Action of (1) *on* 1-*Benzyloxy*-2,3-*epoxypropane*.—The benzyl ether of glycidol (1.71 g, 12 mmol) was added dropwise at −50 °C to a stirred solution of (1) (12.5 mmol) and the mixture allowed to warm to 0 °C over 90 min, and kept

at 0° for 30 min. Aqueous work-up gave a pale yellow liquid (3.8 g) which consisted of two major components [t.l.c., light petroleum–EtOAc–CH$_2$Cl$_2$ (10 : 1 : 1)]. Column chromatography on silica (150 g) with the same solvent mixture gave 1-*benzyloxy*-2-*trimethylsilyloxy*-4-4-*bis(trimethylsilyl)butane* (742 mg, 18%), R_F (CH$_2$Cl$_2$) 0.65; $\nu_{max.}$ 1 252 (SiMe$_3$), 1 123 (C–O), and 1 091 cm^{-1} (C–O–Si); δ 7.3 (5 H, s, aromatic), 4.5 (2 H, s, PhCH$_2$), 3.6 (1 H, m, CHO), 3.3 (2 H, d, J 6 Hz, CH$_2$O), 1.7—1.0 (3 H, m, CH$_2$ and CHSi), 0.1 (9 H, s, OSiMe$_3$), and 0.05 (18 H, s, SiMe$_3$) (Found: M^+, 396.2418. $C_{20}H_{40}O_2Si_3$ requires M, 396.2438); m/e 396 (M^+, 3%), 381 (M^+ − 15, 3), 275 (40), 179 (41), 147 (Me$_3$SiOSiMe$_2$), 113 (90), 91 (PhCH$_2$, 72), and 73 (SiMe$_3$, 90); and 1-*benzyloxy*-4,4,4-*tris(trimethylsilyl)butan*-2-*ol* (2.66 g, 64%), R_F(CH$_2$Cl$_2$) 0.4, b.p. 102—104 °C/0.1 mmHg; $\nu_{max.}$ 3 580 (OH), 1 261, and 1 255 cm^{-1}; δ 7.1 (5 H, s, aromatic), 4.4 (2 H, s, PhCH_2), 2.2—0.9 (4 H, m, aliphatic and OH), and 0.05 (27 H, s, SiMe$_3$) (Found: M^+ − 15, 381.2088. $C_{19}H_{37}O_2Si_3$ requires M − 15, 381.2100); m/e 395 (M^+ − 1, 0.5%), 381 (M^+ − 15, 13), 165 (28), 157 (51), 113 (26), 91 (100), and 73 (100).

*1,2-*Epoxy*-4,4,4-*tris(trimethylsilyl)butane*.—* Epichlorohydrin (0.78 ml, 10 mmol) was added dropwise at −78 °C to a stirred solution of (1) over 5 min, kept at −78 °C for 2 h and then warmed to room temperature over 2 h. Aqueous work-up gave the *epoxide*, m.p. 160—164 °C (from methanol) (1.91 g, 66%) (Found: C, 54.1; H, 11.1. $C_{13}H_{32}OSi_3$ requires C, 54.1; H, 11.15%); $\nu_{max.}$ 3 035 and 1 254 cm^{-1}; δ (CCl$_4$) 3.01 (1 H, m, CH), 2.79 (1 H, dd, J 4 and 5 Hz, CH_AH_B), 2.45 (1 H, dd, J 2.5 and 5 Hz, CH$_AH_B$), 1.97 (2 H, m, CH$_2$), and 0.22 (27 H, s, SiMe$_3$); m/e 289 (M^+ + 1, 12%), 185 (42), 157 (172 − 15, 80), 147 (100), 117 (50), and 73 (SiMe$_3$, 82).

Diphenylphosphinoyl(trimethylsilyl)methane (21).—n-Butyl-lithium (22.5 ml of a 1.6M solution in hexane) was added dropwise to a stirred solution of methyldiphenylphosphine oxide (7.5 g) in dry THF (100 ml) under nitrogen at 0 °C. After 1 h, chlorotrimethylsilane (4.5 ml) was added over 2 min, and the solution allowed to warm to room temperature over 30 min. Aqueous work-up gave the phosphine oxide (21) (8.1 g, 81%) as plates, m.p. 117—118 °C (from EtOAc) (lit.,[17] m.p. 118—119 °C) (Found: C, 66.7; H, 7.3; P, 10.65. Calc. for $C_{16}H_{21}OPSi$: C, 66.6; H, 7.3; P, 10.7%); $\nu_{max.}$ (CHCl$_3$) 1 190 (P=O) and 1 253 cm^{-1} (SiMe$_3$); δ (CDCl$_3$) 8.0—7.25 (10 H, m, aromatic), 1.62 (2 H, d, J 16 Hz, CH$_2$), and −0.10 (9 H, s, SiMe$_3$); m/e 288 (M^+, 14%), 287 (M^+ − 1, 30), 273 (M^+ − 15, 100), and 197 (70).

*1,1-*Diphenyl*-2-*diphenylphosphinoylethylene*.—* n-Butyllithium (0.21 ml of a 2.0M solution in hexane) was added to a solution of the phosphine oxide (21) (120 mg) in dry ether (10 ml) at 0 °C under nitrogen. Benzophenone (75 mg) in dry ether (5 ml) was added, and the solution stirred for 30 min at 0 °C. Aqueous work-up gave the *vinylphosphine oxide* (122 mg, 58%) as needles, m.p. 191—193 °C (from EtOAc) (Found: C, 81.4; H, 5.7; P, 7.85. $C_{26}H_{21}OP$ requires C, 81.4; H, 5.5; P, 8.1%); δ (CDCl$_3$) 7.8—6.95 (20 H, m, Ph$_2$PO and Ph) and 6.65 (1 H, d, J 18 Hz, =CH); m/e 380 (M^+, 100%), 303 (M^+ − 77, 20), and 201 (Ph$_2$PO, 40); $\lambda_{max.}$ (EtOH) 273 nm (ε 32 300).

The Reaction of Ethylene Oxide with the Lithium Derivative of (21).—n-Butyl-lithium (1.8 ml of a 1.7M solution in hexane) was added to a solution of the phosphine oxide (21) (780 mg) in ether (25 ml) at 0 °C. After 45 min, ethylene oxide (0.63 ml of a solution, 5.69 g in 30 ml THF) was

added, and the solution kept for 12 h. Preparative t.l.c. on silica in EtOAc gave an alcohol formulated as (24) (350 mg, 51%); $v_{max.}$ 3 310 (OH), 1 445 (PPh, and 1 175 cm^{-1}; δ (CDCl$_3$) 8.0—7.3 (10 H, m, Ph$_2$P), 3.72 (2 H, t, J 5 Hz, CH$_2$O), and 2.7—1.7 (5 H, m, CH$_2$CH$_2$P and OH). A similar reaction, but using an excess (2 ml) of ethylene oxide over 24 h, gave 3-*diphenylphosphinoylpentane*-1,5-*diol* (27) as plates, m.p. 134—136 °C (from acetone–light petroleum) (Found: C, 67.1; H, 6.95; P, 9.7. C$_{17}$H$_{21}$O$_3$P requires C, 67.1; H, 6.9; P, 10.2%); $v_{max.}$ 3 580 (OH), 1 443 (Ph–P), and 1 184 (P=O); δ (CDCl$_3$) 7.94—7.40 (10 H, m, Ph$_2$P), 3.90 (2 H, s, OH, removed by D$_2$O), 3.66 (4 H, t, J 6.5 Hz, CH$_2$O), 3.18—2.78 (1 H, m, CHP), and 20.2—1.90 (4 H, m, CH$_2$CP); m/e 272 ($M^+ - 32$, 1%) and 201 (100).

(1-*Trimethylsilylethyl*)*diphenylphosphine Oxide* (22).—n-Butyl-lithium (23 ml of a 1.9M solution in hexane) was added dropwise to a stirred solution of ethyldiphenylphosphine oxide (5.1 g) in dry THF (25 ml) under nitrogen at 0 °C. After 45 min, trimethylchlorosilane (4 ml) was added drop-wise over 5 min at -78 °C, and the solution allowed to warm to room temperature over 2 h to give the *phosphine oxide* (22) (5.3 g, 79%) as plates, m.p. 147.5—148.5 °C (from EtOAc) (Found: C, 67.0; H, 7.6; P, 10.3. C$_{17}$H$_{23}$OPSi requires C, 66.8; H, 7.65; P, 10.2%); $v_{max.}$ (CHCl$_3$) 1 441 (Ph–P), 1 251 (SiMe$_3$), and 1 194 cm^{-1} (P=O); δ (CDCl$_3$) 8.00—7.40 (10 H, m Ph$_2$PO), 1.94 (1 H, dq, J 7.5 and 11 Hz, CHP), 1.26 (3 H, dd, J 18 and 11 Hz, Me), and 0.06 (9 H, s, SiMe$_3$); m/e 302 (M^+, 21%), 301 ($M^+ - 1$, 68), 287 ($M^+ - 15$, 100), and 274 (Ph$_2$POSiMe$_3$, 80).

3-*Diphenylphosphinoyl-3-methylpentane*-1,5-*diol* (28).—n-Butyl-lithium (4.4 ml of a 1.6M solution in hexane) was added to the phosphine oxide (22) (1.92 g) at 0 °C. After 45 min, ethylene oxide (5 ml) was added and the solution kept for 12 h. Aqueous work-up gave the *diol* (28) as prisms, m.p. 146—148 °C (from ethyl acetate–light petroleum) (1.27 g, 66%) (Found: C, 67.6; H, 7.3; P, 7.4. C$_{18}$H$_{23}$O$_3$PSi requires C, 67.9; H, 7.3; P, 9.7%); $v_{max.}$ (CHCl$_3$) 3 300 (OH), 1 440 (PPh), and 1 165 cm^{-1} (P=O); δ (CDCl$_3$) 8.35—7.85 (4 H, m, o-H aromatic), 7.65—7.40 (6 H, m, aromatic), 4.55 (2 H, br s, OH, removed by D$_2$O), 3.77 (4 H, t, J 7 Hz, CH$_2$O), 2.1 (4 H, dt, J 7 and 5 Hz, CH$_2$CP), and 1.4 (3 H, d, J 16 Hz, Me); m/e 286 ($M^+ - 32$, 2%) and 201 (100).

3-*Phenylthio-3-trimethylsilylpropane*-1-*ol* (25).—n-Butyl-lithium (2.5 ml of a 2.0M solution in hexane) was added dropwise to a stirred solution of trimethylsilylthioanisole [3] (23) (2.28 g, 1.17 mmol) and 1,4-diazabicyclo[2.2.2]octane (1.32 g) in dry THF (30 ml), at 0 °C under nitrogen. After 45 min, ethylene oxide (5 ml) was added to the pale yellow solution and the mixture kept for 10 min at 0 °C. Distillation gave the *propanol* (25) (2.16 g, 77%), b.p. 110—115 °C/0.1 mmHg (Found: C, 59.4; H, 8.4. C$_{12}$H$_{20}$OSSi requires C, 59.9; H, 8.4%); $v_{max.}$ (film) 3 610 (OH), 3 400 (OH), and 1 249 cm^{-1} (SiMe$_3$); δ (CCl$_4$) 7.50—7.16 (5 H, m, aromatic), 3.75 (2 H, t, J 6 Hz, CH$_2$O), 3.57 (1 H, dd, J 5 and 9 Hz, CHS), 2.20—1.75 (2 H, m, CH$_2$), 1.17 (1 H, s, OH, removed by D$_2$O), and 0.24 (9 H, s, SiMe$_3$); m/e 240 (M^+, 30%), 212 ($M^+ - 28$, 30), and 181 ($M^+ - 15 - C_2H_4$-O, 100).

3-(*Phenylthio*)*propan*-1-*ol* (26).—The alcohol (25) (202 mg) in THF (5 ml) was added to a suspension of sodium hydride in THF (10 ml) and stirred for 2 h. An orange oil (115 mg, 82%) was identified by n.m.r. as the desilylated propanol (26); $v_{max.}$ (CCl$_4$) 3 500 cm^{-1}; δ (CCl$_4$) 7.40—7.15 (5 H, s, aromatic), 4.10 (2 H, t, J 6 Hz, CH$_2$S), 3.75 (2 H, t,

J 7 Hz, CH$_2$O), 2.15—1.65 (2 H, m, CH$_2$), and 1.24 (1 H, s, OH, removed by D$_2$O).

The Reaction of (1) *with Styrene Oxide*.—Styrene oxide (1.20 g, 10 mmol) was added dropwise at 0 °C over 10 min to a rapidly stirred solution of (1) (10 mmol) under nitrogen and the solution kept for 4 h. Aqueous work-up and crystallisation from methanol gave 3,3-*bis*(*trimethylsilyl*)-1,5-*diphenylpentane*-1,5-*diol* (31) (302 mg, 13%), as needles, m.p. 237—239 °C (apparently one diastereoisomer) (Found: C, 68.7; H, 9.1. C$_{23}$H$_{36}$O$_2$Si$_2$ requires C, 69.0; H, 9.1%); $v_{max.}$ (HBr) 3 300 br (OH), 1 500, 1 266, and 1 259 cm^{-1} (SiMe$_3$); δ (CDCl$_3$) 7.32 (10 H, s, Ph), 5.05 (2 H, dd, J 1.5 and 11 Hz, CHO), 3.55 (2 H, s, OH, removed by D$_2$O), 2.77 (2 H, dd, J 11 and 15 Hz, CH_AH$_B$), 1.77 (2 H, dd, J 1.5 and 15 Hz, CH$_A$$H_B$), and 0.18 (13 H, s, SiMe$_3$); m/e 368 ($M^+ - 32$, 0.5%), 203 (24), 179 (25), 148 (30), 129 (37), and 73 (100). Distillation of the mother-liquors from the crystallisation gave 1,1-*bis*(*trimethylsilyl*)-2-*phenylcyclopropane* (32) (1.8 g, 69%), b.p. 66—69 °C/0.1 mmHg; $v_{max.}$ (film) 3 030, 2 955, and 1 252 cm^{-1} (SiMe$_3$); δ (CCl$_4$) 7.27 (5 H, br s, Ph), 2.39 (1 H, dd, J 5 and 7 Hz, PhCH), 1.25 (1 H, dd, J 4 and 5 Hz, CH_AH$_B$), 1.07 (1 H, dd, J 4 and 7 Hz, CH$_A$$H_B$), 0.16 (9 H, s, SiMe$_3$), and -0.23 (9 H, s, SiMe$_3$) (Found: M^+, 262.1568. C$_{15}$H$_{26}$Si$_2$ requires M, 262.1572); m/e 262 (M^+, 22%), 247 ($M^+ - 15$, 19), 234 ($M^+ - C_2H_4$, 17), 174 (247 $-$ SiMe$_3$; m^* 121, 59), 159 (174 $-$ Me, m^* 146, 66) and 73 (SiMe$_3$, 100); $\lambda_{max.}$ (EtOH) 221 nm (ε 6 600).

The Reaction of Bis(*trimethylsilyl*)*methyl-lithium with Styrene Oxide*.—The same reaction did not occur with bis-(trimethylsilyl)methyl-lithium in place of (1). Styrene oxide (1.43 ml, 12.5 mmol) was added to a stirred solution of bis(trimethylsilyl)methyl-lithium (prepared as described above) in TMEDA (2 ml) over 10 min and kept for 15 min. Distillation gave 3,3-*bis*(*trimethylsilyl*)-1-*phenylpropanol* (1.86 g, 53%), b.p. 108—111 °C/0.1 mmHg, as prisms, m.p. 78—80 °C (from methanol) (Found: C, 64.3; H, 10.15. C$_{15}$H$_{28}$OSi$_2$ requires C, 64.2; H, 10.05%); $v_{max.}$ (film) 3 400 br (OH), 1 491 (aromatic) and 1 250 cm^{-1} (SiMe$_3$); δ 7.33 (5 H, s, aromatic), 5.59 (1 H, dd, J 5.5 and 7 Hz, PhCH), 2.44 (1 H, s, OH, removed by D$_2$O), 1.98—1.75 (3 H, m, CH$_2$ and CH), and 0.14 and 0.07 (18 H, 2s, SiMe$_3$); m/e 263 ($M^+ - 17$, 5%), 262 ($M^+ - 18$, 6), 236 (15), 179 (19), 145 (20), and 73 (100).

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