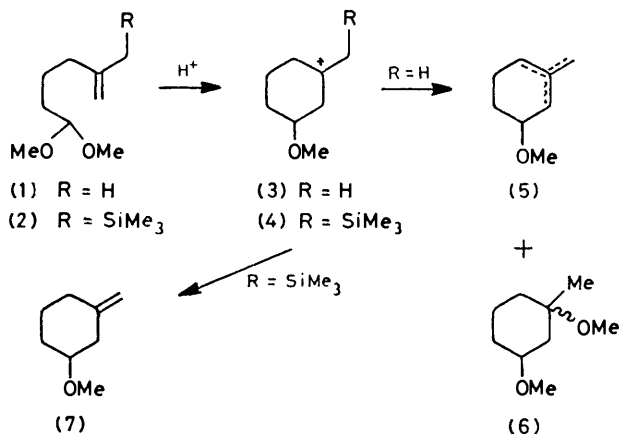


Controlling the Outcome of a Carbocation-Initiated Cyclisation †

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The allylsilane, 6,6-dimethoxy-2-(trimethylsilylmethyl)hex-1-ene (2) gives 3-methylenecyclohexyl methyl ether (7) on treatment with tin(IV) chloride, whereas cyclisation of the corresponding compound without the silyl group (1) was known to give five products (5)–(6). The synthesis of the allylsilane (2) is described.

JOHNSON and his co-workers found, in a model study,¹ that the cyclisation of the acetal (1) in acid gave a mixture of products (5)–(6). This was not unexpected, since there was no control over the fate of the carbocation intermediate (3). We reasoned, from a generalisation first made explicit by Eaborn and Bott,² that the corresponding cation (4), obtained from the acetal (2), would lose the silyl group faster than a proton, and possibly faster than it was attacked at carbon by methanol. This pattern of reactivity is that expected of an allylsilane^{3,4} (and is also the pattern which has recently been found⁵ in intermolecular, acid-catalysed reactions between allylsilanes and acetals). Thus it seemed likely that the allylsilane function would control the outcome of the carbocation-initiated cyclisation, and



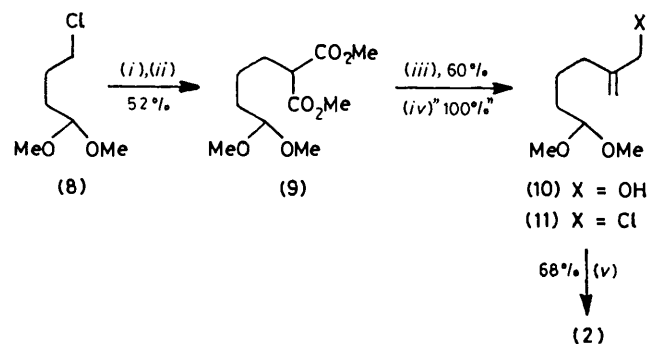
a single product (7) would be obtained. In a preliminary communication,⁶ we reported that this model reaction does indeed work; the acetal (2) cyclises to the olefin (7) (72%) on treatment with tin(IV) chloride in carbon tetrachloride at room temperature for 3 min. We report here experimental details for the preparation and cyclisation of the allylsilane (2), and our brief examination of some other possible routes to 2-substituted allylsilanes. In the meantime, Johnson and his co-workers⁷ have very satisfactorily applied this idea to the more important field of polyolefin cyclisation.

RESULTS AND DISCUSSION

The synthesis of the allylsilane (2) is shown in Scheme 1; it is based on the malonate-to-allyl alcohol conversion studied by Marshall and his co-workers,⁸ and on the case

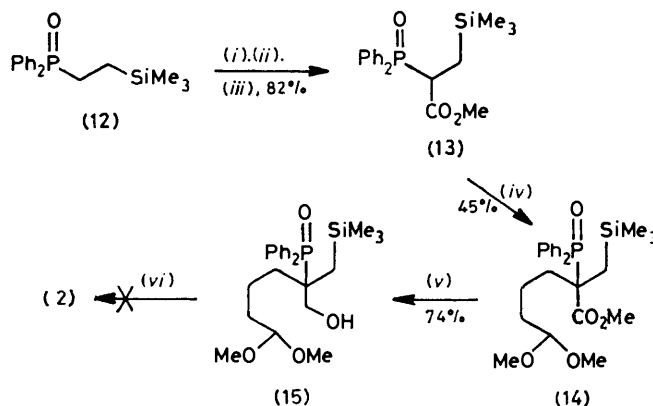
† No reprints available.

of the Wurtz-type of reaction for converting a halide into a silane.⁹ An alternative route (Scheme 2) was tried, because, had it worked, it might have been more versatile; however, the alkylation step (13)→(14) was poor,



SCHEME 1 (i) NaI-Me₂CO; (ii) CH₂(CO₂Me)₂-NaOMe; (iii) NaH-LiAlH₄; (iv) Ph₃PCl₂; (v) Na-Me₃SiCl

and the final step, the Horner-Wittig elimination (15)→(2), did not work. Related work in this laboratory¹⁰ has confirmed that the usually general Horner-Wittig elimination can fail in the synthesis of allylsilanes; for example, the intermediate (17) underwent fragmentation (17)→(16) rather than elimination to give the allylsilane (18). (The corresponding conventional Wittig reaction,

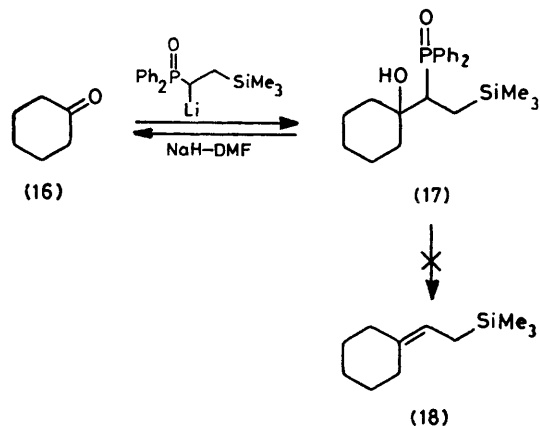


SCHEME 2 (i) BuⁿLi; (ii) CO₂; (iii) CH₂N₂; (iv) I[CH₂]₃CH(OMe)₂; (v) LiBH₄; (vi) NaH-DMF

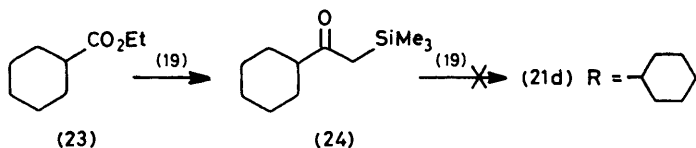
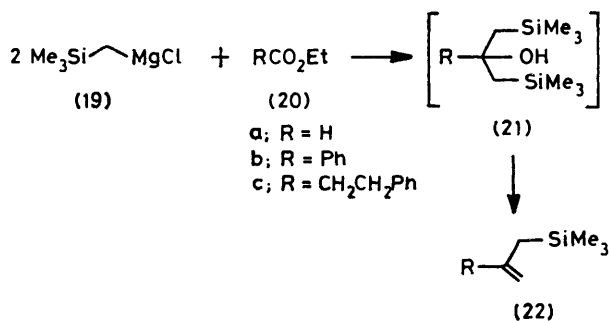
however, can be used in the synthesis of the latter allylsilane.¹¹)

Another route to 2-substituted allylsilanes (Scheme 3) was tried with somewhat more success. Trimethylsilylmethyl magnesium chloride (19) has been reported to react with ethyl formate to give the alcohol (21a) and

subsequently the allyl silane (22a).¹² We have repeated and improved the yields of these reactions. The same Grignard reagent (19) has also been reported to react with methyl cyclohexanecarboxylate (23) to give the

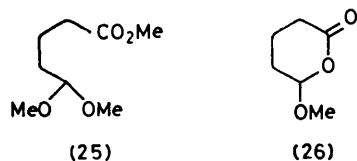


ketone (24).¹³ We found¹⁴ that this ketone is resistant to further attack of the same Grignard reagent, although it does react with phenyl-¹³ and methyl-lithium.¹⁴ However, the slightly less hindered esters (20b and c) react



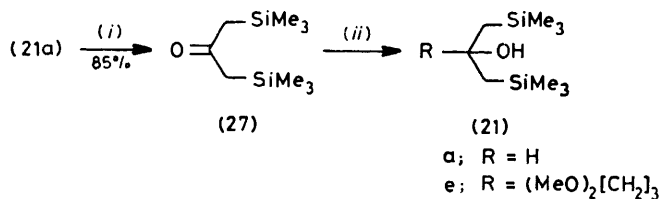
SCHEME 3

with an excess of the Grignard reagent (19) to give initially the tertiary alcohols (21b) and (21c), and subsequently the allylsilanes (22) in moderate yield. This promising route, which we have not investigated further,



was not applied to the synthesis of (2), because the ester required (25), prepared by the known route,¹⁵ was contaminated by the cyclic acetal (26). A variation of this approach (Scheme 4) was unpromising, because a

model Grignard reagent, isopentylmagnesium iodide, *reduced* the ketone (27) to the alcohol (21a); there was therefore little hope that the appropriate Grignard reagent would convert it to the alcohol (21e) and hence to the allylsilane (2).

SCHEME 4 (i) AgCO₃-Celite; (ii) Me₂CH[CH₂]₂MgI

EXPERIMENTAL

Cyclisation of 6,6-Dimethoxy-2-trimethylsilylmethylhex-1-ene (2) with Tin(IV) Chloride.—Anhydrous tin(IV) chloride (90 μ l, 195 mg, freshly distilled) was added under nitrogen at room temperature to a stirred solution of the olefin (2) (504 mg) in carbon tetrachloride (30 ml, freshly distilled from calcium hydride). After 3 min, the mixture was poured into saturated sodium carbonate solution (50 ml) and extracted with carbon tetrachloride (3 \times 10 ml). The combined organic layers were dried (Na₂SO₄) and distilled under reduced pressure using a 37-cm \times 2-cm Vigreux column to remove the carbon tetrachloride (b.p. 29 $^{\circ}$ C at 100 Torr). The residue (1 ml) contained 3-methylenecyclohexyl methyl ether (7) (0.20 \pm 0.01 g; 72% \pm 3%, estimated by n.m.r. with biphenyl as internal standard); ν_{max} (CCl₄) 1 645 cm⁻¹ (C=C); τ (CCl₄) 5.37 (2 H, s, C=CH₂), 6.55—7.05 (4 H, m, overlain by singlet at 6.72, CHOMe), 7.50 (1 H, dd, J 4, 11 Hz, CH_AH_B), and 7.7—9.0 (7 H, m, CH₂ and CH_AH_B) (Found: M^+ , 126.104 5. C₈H₁₄O requires M , 126.104 4); m/e 126 (9%, M^+), 111 (4, M^+ - Me), 95 (45, M - MeOH), and 78 (100). Further treatment (0.5 h) under these conditions isomerised (7) to the mixture of olefins (5) and (6) as shown by the disappearance of the signal at τ 5.37 and the appearance of a multiplet at τ 4.65—4.95.

For comparison, the olefin (1) was treated with tin(IV) chloride under the same conditions (Johnson² did not actually use tin(IV) chloride on this compound; however, he usually found that exocyclic olefins were minor products in similar cyclisations using tin(IV) chloride). The products purified by t.l.c. (silica gel), R_F (CH₂Cl₂) 0.4, had ν_{max} 1 640 w cm⁻¹ (C=C) and weak resonances at τ 4.6—4.8 [m, C=CH, m (5) and (6)] and 5.37 [br s, C=CH₂, in (7)]; the strong resonances (representing ca. 85% of the mixture) were at τ 6.4—6.8 (4 H, overlain by a singlet at 6.72) and 7.6—9.0 (11 H); m/e 164 (43%), 162 (70), 127 (80), 126 (94) and 95 (100). This product is probably 3-methoxy-1-methylcyclohexyl chloride.

Reaction of 6,6-Dimethoxy-2-trimethylsilylmethylhex-1-ene (2) with Hydrogen Chloride in Methanol.—The olefin (2) (460 mg) was stirred with a solution of hydrogen chloride gas in dry methanol (50 ml, 0.012M) for 15 min. The mixture was poured into saturated sodium carbonate solution (50 ml) and extracted with light petroleum (b.p. 60—80 $^{\circ}$ C, 3 \times 20 ml). The petrol layer was washed with water (6 \times 50 ml), dried (Na₂SO₄), and distilled under reduced pressure using a 37-cm \times 2-cm Vigreux column to remove the light petroleum (b.p. 25 $^{\circ}$ C at 100 Torr). The

residue (1 ml) was diluted with carbon tetrachloride (20 ml) and similarly distilled under reduced pressure. The residue (0.5 ml) contained 6,6-dimethoxy-2-methylhex-1-ene (1) (0.24 ± 0.01 g; $76\% \pm 3\%$, estimated by n.m.r. with biphenyl as internal standard); ν_{\max} (CCl_4) 1635 cm^{-1} ($\text{C}=\text{C}$); $\tau(\text{CCl}_4)$ 5.36 (2 H, br s, $\text{C}=\text{CH}_2$), 5.66—5.81 [1 H, $\text{CH}(\text{OMe})_2$], 6.82 (6 H, s, OMe), and 7.9—8.9 (9 H, m, overlain by broad singlet at 8.31, CH_2 and Me); m/e 126 (8%, $M^+ - \text{MeOH}$), 111 (17), 94 (85), and 78 (100) (Found: $M^+ - \text{MeOH}$ 126.105 1. $\text{C}_8\text{H}_{14}\text{O}$ requires M , 126.104 4).

4-Chloro-1,1-dimethoxybutane (8).—We used a method based upon that of Pleshakov *et al.*¹⁵ A stirred suspension of 5% palladium-barium sulphate catalyst (4 g) in toluene (500 ml, distilled from phosphorus pentoxide and stored over sodium) and 4-chlorobutyryl chloride (40 g) was heated under reflux while a 1:1 mixture of hydrogen and nitrogen was bubbled through the reaction mixture. When no more hydrogen chloride was evolved (*ca.* 4—6 h) the mixture was cooled, filtered (Celite), treated with a solution of sulphuric acid (1 ml) in methanol (100 ml), and maintained at room temperature for 0.5 h. The mixture was washed successively with saturated aqueous sodium hydrogencarbonate (200 ml), water (4×100 ml), saturated sodium chloride solution (200 ml), and then dried (Na_2SO_4). Most of the toluene was removed by distillation (37-cm \times 2-cm Vigreux column) under reduced pressure (b.p. 51°C at 100 Torr) and the residue distilled (10-cm \times 1-cm helices column) to give 4-chloro-1,1-dimethoxybutane (8) (22.7 g, 53%), b.p. $76\text{--}78^\circ\text{C}$ at 20 Torr (lit.,¹⁶ $84\text{--}85^\circ\text{C}$ at 25 Torr); $\tau(\text{CCl}_4)$ 5.60—5.85 [1 H $\text{CH}(\text{OMe})$], 6.35—6.85 (2 H, m, CH_2Cl), 6.81 (6 H, s, OMe), and 8.2—8.4 (4 H, m, CH_2); m/e 153/151 (0.3/1%, $M^+ - \text{H}$), and 122/120 (33/100, $M^+ - \text{MeOH}$). Yields were not always reproducible; a rapid gas flow removed hydrogen chloride as it was produced and minimised polymerisation of the intermediate aldehyde.

Dimethyl 4,4-Dimethoxybutylmalonate (9).—4-Chloro-1,1-dimethoxybutane (7.60 g) was added under nitrogen at room temperature to a solution of sodium iodide (7.5 g, dried at 70°C and 0.2 Torr for 2 h) in acetone (50 ml, distilled from anhydrous potassium carbonate). The mixture was left at room temperature in the dark for 24 h, filtered, evaporated *in vacuo*, diluted with light petroleum (b.p. $60\text{--}80^\circ\text{C}$), filtered, and evaporated *in vacuo*. The crude iodide, a red oil, was added without further purification to a solution of sodium (1.72 g) in dry methanol (70 ml) under nitrogen to which had been added dimethyl malonate (9.90 g, freshly distilled); the mixture was heated under reflux for 67 h, cooled, diluted with ether (200 ml), washed with saturated sodium chloride solution (100 ml), dried (Na_2SO_4), and evaporated *in vacuo*. Distillation gave the dimethyl ester (9) (6.48 g, 52%), b.p. $105\text{--}108^\circ\text{C}$ at 0.99 Torr (Found: C, 53.4; H, 7.85. $\text{C}_{11}\text{H}_{20}\text{O}_6$ requires C, 53.2; H, 8.10%); ν_{\max} (CCl_4) 1730 cm^{-1} ($\text{C}=\text{O}$); $\tau(\text{CCl}_4)$ 5.60—5.85 [1 H, $\text{CH}(\text{OMe})_2$], 6.33 (6 H, s, CO_2Me), 6.70—6.95 (7 H, m, overlain by singlet at 6.81, CH and OMe), and 8.0—8.9 (6 H, m, CH_2); m/e 247 (0.5%, $M^+ - \text{H}$), 217 (4, $M^+ - \text{MeOH}$), 153 (20), and 75 (100).

6,6-Dimethoxy-2-hydroxymethylhex-1-ene (10).—Reduction of the ester (9) (4.96 g) under the conditions of Marshall *et al.*⁸ gave the allyl alcohol (10) (2.09 g, 60%), b.p. $80\text{--}84^\circ\text{C}$ at 0.07 Torr (Found: C, 62.0; H, 10.4. $\text{C}_9\text{H}_{18}\text{O}_3$ requires C, 62.0; H, 10.4%); ν_{\max} (CCl_4) 3420 (OH) and 1640 cm^{-1} ($\text{C}=\text{C}$); $\tau(\text{CCl}_4)$ 5.02 (1 H, br s, $\text{C}=\text{CH}_2$), 5.20 (1 H, br s, $\text{C}=\text{CH}_2$), 5.6—5.8 [1 H, triplet-like, $\text{CH}(\text{OMe})_2$], 6.04 (2 H, br s, CH_2OH), 6.79 (6 H, s, OMe), 7.1—

7.3 (1 H, m, OH), 7.8—8.1 (2 H, m, allylic CH_2), and 8.3—8.7 (4 H, m, CH_2); m/e 174 (2%, M^+), 173 (9, $M^+ - \text{H}$) 143 (7, $M^+ - \text{MeO}$), 142 (7, $M^+ - \text{MeOH}$), 125 (24), 111 (84), and 75 (100).

6,6-Dimethoxy-2-trimethylsilylmethylhex-1-ene (2).—A solution of triphenylphosphine dichloride¹⁷ [from triphenylphosphine (3.71 g)] in dry acetonitrile (50 ml) and dry triethylamine (10 ml) under nitrogen at room temperature was mixed with a solution of the alcohol (10) (1.23 g) in acetonitrile (10 ml). After 0.5 h the mixture was poured into sodium carbonate solution (50 ml, saturated) and extracted with light petroleum (b.p. $60\text{--}80^\circ\text{C}$, 4×50 ml). The combined organic layers were washed successively with water (2×50 ml), saturated sodium chloride solution (100 ml), dried (Na_2SO_4), and evaporated *in vacuo*. The crude allyl chloride (11) [$\tau(\text{CCl}_4)$ 4.90 (1 H, br s, $\text{C}=\text{CH}_2$), 5.06 (1 H, br s, $\text{C}=\text{CH}_2$), 5.6—5.8 [1 H, $\text{CH}(\text{OMe})_2$], 6.02 (2 H, s, CH_2Cl), 6.83 (6 H, s, OMe), 7.7—8.0 (2 H, m, allylic CH_2), and 8.3—8.7 (4 H, m, CH_2)] was used without further purification.

Sodium sand (640 mg) was suspended in dry ether (30 ml) containing ethyl acetate (0.1 ml), chlorotrimethylsilane (2.1 ml, freshly distilled) and dry triethylamine (3.1 ml). The crude allyl chloride was added as a solution in dry ether (4 ml), and the mixture stirred at room temperature for 72 h, filtered, evaporated *in vacuo*, and distilled to give 6,6-dimethoxy-2-trimethylsilylmethylhex-1-ene (2) (1.09 g, 68%), b.p. $72\text{--}73^\circ\text{C}$ at 0.5 Torr (Found: C, 63.1; H, 11.5. $\text{C}_{12}\text{H}_{26}\text{O}_2\text{Si}$ requires C, 62.8; H, 11.3%); ν_{\max} (CCl_4) 1630 ($\text{C}=\text{C}$) and 1250 cm^{-1} (SiMe_3); $\tau(\text{CCl}_4)$ 5.4—5.6 (2 H, m, $\text{C}=\text{CH}_2$), 5.6—5.8 [1 H, $\text{CH}(\text{OMe})_2$], 6.77 (6 H, s, OMe), 7.9—8.6 (8 H, m, CH_2), and 10.01 (9 H, s, SiMe_3); m/e 230 (14%, M^+), 229 (22, $M^+ - \text{H}$), 198 (25, $M^+ - \text{MeOH}$), and 105 (100).

Methyl 2-(Diphenyloxophosphoranyl)-3-trimethylsilylpropionate (13).—*n*-Butyl-lithium (13.4 ml of a 1.6M solution in hexane) was added to a stirred solution of diphenyl-2-trimethylsilylethylphosphine oxide (12)¹⁸ (6.49 g) in dry tetrahydrofuran (THF) (50 ml) under nitrogen at room temperature. The mixture was maintained at room temperature for 1 h, and added dropwise to a solution of dry carbon dioxide gas in dry THF (50 ml) at -78°C . The mixture was allowed to reach room temperature, poured into aqueous sodium hydroxide solution (100 ml, 10%), and the organic layer extracted with aqueous sodium hydroxide solution (2×10 ml, 10%); the combined aqueous extracts were acidified (concentrated hydrochloric acid) and extracted with chloroform (3×50 ml). The above process was repeated; the final organic extracts were dried (Na_2SO_4) and evaporated *in vacuo* to give 2-(diphenyloxophosphoranyl)-3-trimethylsilylpropionic acid (6.37 g, 85%), m.p. $190\text{--}191^\circ\text{C}$ (from $\text{EtOH-H}_2\text{O}$) (Found: C, 62.4; H, 6.70; P, 9.00. $\text{C}_{15}\text{H}_{23}\text{O}_3\text{PSi}$ requires C, 62.4; H, 6.70; P, 8.90%); ν_{\max} (CHCl_3) $4400\text{--}2400$ (OH), 1715 ($\text{C}=\text{O}$), 1440 (PPh), 1250 (SiMe_3), and 1180 ($\text{C}=\text{O}$); $\tau(\text{CDCl}_3)$ -1.3 (1 H, s, OH), 1.9—2.7 (10 H, m, Ph_2PO), 6.2—6.7 (1 H, CH), 8.4—9.5 (2 H, m, CH_2), and 9.98 (9 H, s, SiMe_3); m/e 346 (2%, M^+), 331 (61, $M^+ - \text{Me}$), 302 (21, $M^+ - \text{CO}_2$), 291 (15), 274, (37, $\text{Ph}_2\text{POSiMe}_3$), 229 (99), 202 (100, Ph_2POH), and 201 (55, Ph_2PO). Diazomethane, prepared from *N*-nitroso-*N*-methylurea (50 g) in ether (300 ml) was added to the acid (5.17 g) in chloroform (100 ml): Acetic acid was added to destroy any excess of diazomethane; the organic layer was washed with saturated sodium carbonate solution (50 ml), dried (Na_2SO_4), and

evaporated *in vacuo* to give the ester (13) (4.95 g, 96%), m.p. 105–106 °C (from hexane) (Found: C, 63.6; H, 7.0; P, 8.6. $C_{16}H_{25}O_3PSi$ requires C, 63.3; H, 7.00; P, 8.60%); ν_{max} (CHCl₃) 1 730 (C=O), 1 440 (PPh), 1 252 (SiMe₃), and 1 150 cm⁻¹ (P=O); τ (CDCl₃) 1.9–2.7 (10 H, m, Ph₂PO), 6.2–6.7 (4 H, m, overlain by singlet at 6.56, CH and OMe), 8.4–9.5 (2 H, m, CH₂), and 9.98 (9 H, s, SiMe₃); *m/e* 360 (7%, M⁺), 345 (100, M⁺ – Me), 291 (55), 274 (70, Ph₂POSiMe₃), 202 (63, Ph₂POH), and 201 (45, Ph₂PO).

Methyl 6,6-Dimethoxy-2-(diphenyloxophosphoranyl)-2-trimethylsilylmethylhexanoate (14).—Chloro-1,1-dimethoxybutane (381 mg) was added under nitrogen at room temperature to a solution of sodium iodide (0.4 g, dried at 70 °C and 0.2 Torr for 2 h) and acetone (10 ml, distilled from anhydrous potassium carbonate). The mixture was kept at room temperature in the dark for 24 h, filtered, evaporated *in vacuo*, diluted with light petroleum (b.p. 60–80 °C), filtered, and evaporated *in vacuo*. The crude iodide was added as a solution in hexamethylphosphoramide (HMPA) (2 ml) (distilled from calcium hydride) to a stirred suspension of sodium hydride [100 mg of a 50% dispersion in oil; washed with light petroleum (b.p. 60–80 °C)] in HMPA (30 ml) containing the ester (13) (720 mg). The mixture was maintained at room temperature for 64 h, poured into water (500 ml), and extracted with dichloromethane (3 × 150 ml). The combined organic layers were washed successively with water (6 × 200 ml), dried (Na₂SO₄), and evaporated *in vacuo*. Preparative t.l.c. (silica gel) gave the ester (14) as an oil (430 mg, 45%), *R_F* (Et₂O) 0.3; ν_{max} (CCl₄) 1 715 (C=O), 1 440 (PPh), 1 250 (SiMe₃), and 1 180 cm⁻¹ (P=O); τ (CCl₄) 1.8–2.7 (10 H, m, Ph₂PO), 5.65–5.85 [1 H, m, CH(OMe)₂], 6.62 (3 H, s, CO₂Me), 6.80 (3 H, s, OMe) and 6.83 (3 H, s, OMe), 7.8–9.3 (8 H, m, CH₂), and 9.87 (9 H, s, SiMe₃); *m/e* 476 (0.4%, M⁺), 461 (27, M⁺ – Me), 445 (14, M⁺ – MeO), 429 (10), 345 (33) 291 (55), 275 (37, M⁺ – Ph₂PO), 274 (100), 202 (62, Ph₂POH), and 201 (72, Ph₂PO) (Found: M⁺ – Me, 461.192 7. C₂₄H₃₄O₅PSi requires M – Me, 461.189 4. M⁺ – Ph₂PO, 275.167 2. C₁₃H₂₇O₄Si requires M – Ph₂PO 275.167 8).

6,6-Dimethoxy-2-(diphenyloxophosphoranyl)-2-trimethylsilylmethylhexan-1-ol (15).—A mixture of the ester (14) (448 mg), lithium borohydride (1 g), and dry THF (15 ml) was refluxed under nitrogen for 72 h. The cooled mixture was poured into water (100 ml) and extracted with chloroform (3 × 50 ml). The combined organic layers were washed successively with water (100 ml), saturated sodium chloride solution (100 ml), dried (Na₂SO₄), and evaporated *in vacuo* to give the alcohol (15) (311 mg, 74%), m.p. 167–168 °C (from hexane) (Found: C, 64.0; H, 8.10; P, 6.95. C₂₄H₃₇O₄PSi requires C, 64.2; H, 8.30; P, 6.95%); ν_{max} (CCl₄) 3 320 (OH), 1 445 (PPh), 1 255 (SiMe₃), and 1 180 cm⁻¹ (P=O); τ (CDCl₃) 1.8–2.7 (10 H, m, Ph₂PO), 4.8–5.4 (1 H, m, OH), 5.75–5.95 [1 H, m, CH(OMe)₂], 6.05–6.20 (1 H, m, CH_AH_BOH), 6.30–6.55 (1 H, m, CH_AH_BOH), 6.80 (6 H, s, OMe), 7.9–9.3 (8 H, m, CH₂) and 9.94 (9 H, s, SiMe₃); *m/e* 448 (0.2%, M⁺), 433 (30, M⁺ – Me), 417 (27, M⁺ – MeO), 401 (95), 385 (41), 315 (67), 274 (62), 202 (100, Ph₂POH) and 201 (90, Ph₂PO).

Attempted Preparation of 6,6-Dimethoxy-2-trimethylsilylmethylhex-1-ene (2) from 6,6-Dimethoxy-2-(diphenyloxophosphoranyl)-2-trimethylsilylmethylhexan-1-ol (15).—The alcohol (15) (112 mg) in dimethylformamide (20 ml, distilled from calcium hydride) was added to sodium hydride (15 mg of a 50% dispersion in oil; washed with dry ether) under nitrogen and stirred at room temperature for 18 h. Water

(100 ml) was added slowly and the mixture was extracted with light petroleum (b.p. 60–80 °C, 3 × 50 ml). The combined organic layers were washed successively with water (6 × 100 ml), dried (Na₂SO₄), and evaporated *in vacuo*. The residue (1 mg) gave a blank n.m.r. spectrum.

1,3-Bistrimethylsilylpropan-2-ol (21a).—Chloromethyltrimethylsilane (4.60 g) was added to a stirred suspension of magnesium turnings (0.9 g) in dry ether (20 ml) under nitrogen and reaction initiated with a crystal of iodine, ethylene dibromide (0.2 ml), and heat. The mixture was refluxed for 2 h, when all the magnesium had dissolved. A solution of ethyl formate (1.11 g, 1.22 ml) in dry ether (40 ml) was added dropwise under nitrogen to the stirred solution of the Grignard reagent at –22 °C during 0.5 h. The mixture was maintained at –22 °C for 1 h, allowed to reach room temperature, and stirred at room temperature for a further 0.5 h. Saturated ammonium chloride solution (50 ml) was added to the mixture with stirring at –10 °C, and the mixture extracted with ether (3 × 30 ml). The combined organic layers were dried (Na₂SO₄) and distilled (37-cm × 2-cm Vigreux column) to remove the ether. The residue contained the alcohol (21a) and allyltrimethylsilane in the ratio (n.m.r.) of 2 : 1. Distillation gave 1,3-bistrimethylsilylpropan-2-ol (21a) (1.53 g, 50%), b.p. 69–71 °C at 4.5 Torr (lit.,¹² 74–75 °C at 7 Torr); ν_{max} (CCl₄) 3.340 cm⁻¹ (OH); τ (CCl₄) 6.08 (1 H, quintet, J 6 Hz, CHOH), 7.0–7.6 (1 H, m, OH), 9.21 (4 H, d, J 6 Hz, CH₂), and 9.92 (18 H, s, SiMe₃); *m/e* 189 (2%, M⁺ – Me), 147 (100), 98 (50), and 73 (59, SiMe₃) (M⁺ absent). The alcohol showed ca. 30% decomposition, to allyltrimethylsilane, water, and hexamethyldisiloxane, after 2 weeks at room temperature.

2-Phenyl-3-trimethylsilylpropene (22b).—A solution of methyl benzoate (0.68 g) in dry ether (5 ml) was added to the Grignard reagent (19) from chloromethyltrimethylsilane (1.83 g) in ether (10 ml) and refluxed for 41 h. Ammonium chloride solution (50 ml, saturated) was added dropwise and the mixture was extracted with ether (3 × 30 ml). The combined organic layers were dried (Na₂SO₄) and evaporated *in vacuo*. The oil contained trimethylsilylacetophenone; τ (CCl₄) 1.7–2.9 (aromatic protons), 7.14 (2 H, s, CH₂) and 9.75 (9 H, s, SiMe₃); and (22b). Preparative t.l.c. (silica gel, benzene) gave 2-phenyl-3-trimethylsilylpropene (22b) (470 mg, 49%) as an oil, *R_F* 0.8; ν_{max} (film) 1 620 (C=C), 1 600 and 1 500 cm⁻¹ (aromatic); τ (CCl₄) 2.6–2.9 (5 H, m, Ph), 4.93 (1 H, d, J 2 Hz, C=CH_AH_B), 5.18 (1 H, m, C=CH_AH_B), 8.00 (2 H, s, CH₂), and 10.00 (9 H, s, SiMe₃) (Found: M⁺, 190.117 1. C₁₂H₁₈Si requires M, 190.117 7); *m/e* 190 (75%), 175 (58, M⁺ – Me), 117 (58, M⁺ – Me₃Si) and 73 (100, Me₃Si). The same preparative t.l.c. gave acetophenone (211 mg, 35%), *R_F* 0.4, identical (n.m.r. and i.r.) with an authentic sample.

4-Phenyl-2-(trimethylsilylmethyl)but-1-ene (22c).—A solution of ethyl hydrocinnamate (1.78 g) in dry ether (5 ml) was added to the Grignard reagent (19) from chloromethyltrimethylsilane (4.6 g) in ether (20 ml) and the reaction mixture stirred for 4.5 days under nitrogen at room temperature. Saturated ammonium chloride solution (50 ml) was added dropwise, and the mixture was extracted with ether (3 × 30 ml). The combined organic layers were dried (Na₂SO₄) and evaporated *in vacuo*. The oil in dry dichloromethane (60 ml) was stirred with silical gel (50 g, Fisons chromatography grade) for 2 days, filtered, and evaporated *in vacuo*. Column chromatography on silica gel (100 g) and elution with dichloromethane gave 4-phenyl-2-(trimethylsilylmethyl)butene (22c) (0.98 g, 45%) as an oil (Found: C,

77.2; H, 10.30. $C_{14}H_{22}Si$ requires C, 77.0; H, 10.15%); R_F (CH_2Cl_2) 0.9; $\nu_{max.}$ (CCl_4) 1 630 (C=C), and 1 600 and 1 500 cm^{-1} (aromatic); $\tau(CCl_4)$ 2.7—3.0 (5 H, m, Ph), 5.37 (1 H, br s, $C=CH_AH_B$), 5.48 (1 H, br s, $C=CH_AH_B$), 7.16—7.38 (2 H, m, CH_2Ph), 7.65—7.88 (2 H, m, $CH_2C=C$), 8.44 (2 H, s, CH_2Si), and 9.93 (9 H, s, $SiMe_3$); m/e 218 (12%, M^+), 203 (6, $M^+ - Me$), 145 (15, $M^+ - Me_3Si$), 119 (75), 117 (93) and 73 (100, Me_3Si). Further elution gave a mixture (0.5 g), which appeared to contain the Claisen condensation product of the starting ester.

The Alcohol (17).—The synthesis of the alcohol has already been described.¹⁸ Treatment with bases in a variety of conditions gave diphenyl-2-trimethylsilylethylphosphine oxide as the only identifiable product. (Experiments carried out by Drs. R. L. Snowden and C. D. Floyd.)

1,3-Bistrimethylsilylpropan-2-one (27).—1,3-Bistrimethylsilylpropan-2-ol (21a) (408 mg) was heated under reflux in a nitrogen atmosphere in the dark for 1 h with a suspension of silver carbonate on Celite [11.6 g, prepared from silver nitrate (6.8 g), and purified Celite (6.0 g), and dried at 0.2 Torr and 40 °C over phosphorus pentoxide in the dark], in dry benzene (60 ml). The cooled mixture was filtered, and evaporated *in vacuo* to give the crude *ketone* (27) (340 mg) as an oil; $\nu_{max.}$ (CCl_4) 1 675 (C=O) and 1 250 cm^{-1} ($SiMe_3$); $\tau(CCl_4)$ 8.05 (4 H, s, CH_2) and 9.95 (18 H, s, $SiMe_3$); m/e 202 (94%, M^+), 186 (42), 147 (100), 130 (58), and 73 (31, Me_3Si). The ketone decomposed completely after four days at room temperature and hence was used immediately without further purification.

Reaction of 1,3-Bistrimethylsilylpropan-2-one (27) with *Isopentylmagnesium iodide*.—A solution of the ketone (27) prepared above in dry ether (5 ml) was added at room temperature under nitrogen with stirring to a solution of isopentylmagnesium iodide [prepared from isopentyl iodide (594 mg) and magnesium turnings (72 mg) in dry ether (10 ml)]. The mixture was kept at room temperature for 68 h, poured into saturated ammonium chloride solution (30 ml), and extracted with ether (3 × 30 ml). The combined organic layers were washed with sodium chloride solution (50 ml, saturated), dried ($NaSO_4$), and evaporated *in vacuo*. Preparative t.l.c. gave 1,3-bistrimethylsilylpropan-2-ol (21a) (87 mg), (i.r. and n.m.r.) as the only identifiable product.

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