

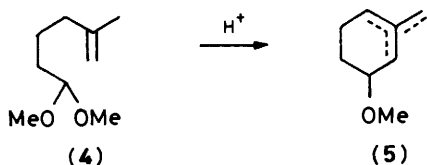
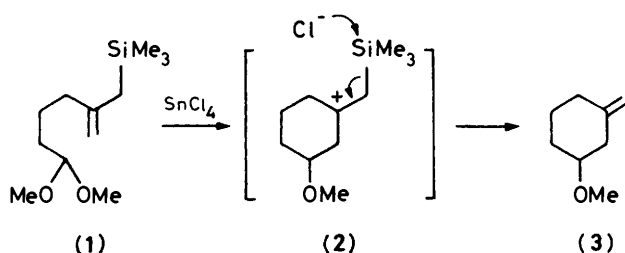
Controlling the Outcome of a Carbocation-initiated Cyclisation †

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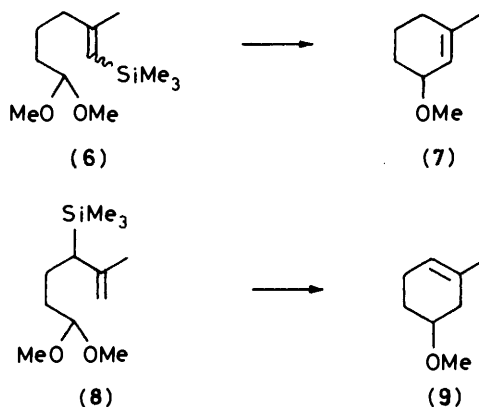
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The *Z*- and *E*-vinylsilanes, 6,6-dimethoxy-2-methyl-1-trimethylsilylhex-1-ene (**6**), gave only 3-methoxy-1-methylcyclohexene (**7**) on treatment with zinc bromide, and the allylsilane, 6,6-dimethoxy-2-methyl-3-trimethylsilylhex-1-ene (**8**), gave only 5-methoxy-1-methylcyclohexene (**9**) on treatment with tin(IV) chloride. Taken together with an earlier result, these results show that the silyl group completely controls the outcome of this carbocationic cyclisation. The syntheses of the two starting vinyl- and allyl-silanes, (**6**) and (**8**), illustrate the usefulness of the silyl-cuprate reagent in the construction of specific vinyl- and allyl-silanes.

In one of our first publications in organosilicon chemistry,¹ we reported that the acetal (**1**) cyclised to give only the alkene (**3**), in which the site of the double bond had been controlled by the ready loss of the silyl group (**2**)→(**3**). This result was in contrast



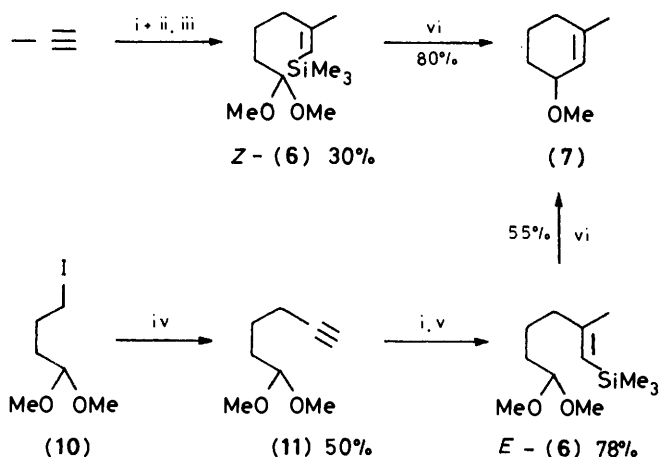
to the reaction of the acetal (**4**), which had been investigated earlier by Johnson and his co-workers,² who found that it gave all three possible alkenes (**5**) when treated with acid. When we did this early work, we chose to make the allylsilane (**1**) because it was easy,³ and because at that time there was no reliable method for making either the vinylsilane (**6**) or the allylsilane (**8**). We were therefore led to seek out new methods for introducing silyl groups into organic molecules,⁴ and found that silyl-cuprate reagents are extraordinarily useful. They react



with $\alpha\beta$ -unsaturated carbonyl compounds,⁵ with acetylenes,⁶ and with tertiary allylic acetates,⁷ and the products of these reactions lend themselves to further manipulation.^{5,6,8,9} Most strikingly, they provide methods for the synthesis of 2,2-disubstituted vinylsilanes,⁶ and of allylsilanes in which the silyl group is at the more substituted end of the allyl fragment⁹—precisely what we need if we are to make the vinylsilane (**6**) and the allylsilane (**8**). In this paper we report the synthesis of the vinylsilane (**6**) and the allylsilane (**8**), and their cyclisations to the alkenes (**7**) and (**9**) respectively. We have, therefore, completed the study we began 10 years ago: the outcome is fully controlled by the position of the silyl group, and the reaction can properly be called regioselective.† Simultaneously we have shown just how powerful the silyl-cuprate reagent is for the controlled introduction of silyl groups.

Results

The *Z*- and *E*-isomers of the vinylsilane (**6**) were separately prepared from our bis(trimethylsilyl)cuprate¹¹ as shown in Scheme 1. The synthesis was easy, but the cyclisation proved to be difficult: the problem was that the product (**7**) was unstable

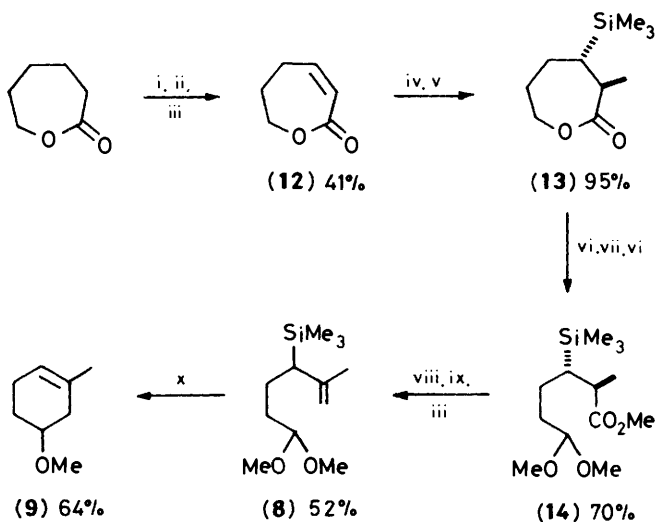


Scheme 1. Reagents: i, $(\text{Me}_3\text{Si})_2\text{CuLi}$, HMPA, THF; ii, NaI; iii, (10); iv, $\text{HC}\equiv\text{CLi}$, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, DMSO; v, MeI; vi, ZnBr_2 , CCl_4

† No reprints available.

‡ By analogy with Zimmerman's definition of stereoselective and stereospecific,¹⁰ the reaction of (**1**) alone might be described as only regioselective, but with the demonstration that the reactions of (**1**), (**6**), and (**8**) all give different products, the reaction can now safely be called regioselective.

towards most of the Lewis acids (SnCl_4 , AlCl_3 , $\text{BF}_3 \cdot \text{OEt}_2$, Me_3SiOTf , Et_2AlCl , EtAlCl_2 , TiCl_4) powerful enough to promote the cyclisation. The product in these cases was probably 1-methylcyclohexa-1,3-diene, as judged by the ^1H n.m.r. spectrum, but we did not pursue this side-track after we found a Lewis acid, zinc bromide, which allowed the concentration of the allylic ether (7) to build up to a measurable extent before its decomposition. Following the reaction by ^1H n.m.r. spectroscopy, we were able to stop the reaction at the optimum moment and to isolate the ether (7) in 80% yield (n.m.r.) from *Z*-(6), and in 55% yield (n.m.r.) from *E*-(6). The ether (7) was not contaminated with either of the ethers (3) or (9), which, unlike the ether (7), were stable to the reaction conditions, and which would have been easily detected by the characteristic signals in the ^1H n.m.r. spectrum of the methine and the olefinic hydrogens. The two stereoisomeric vinylsilanes (6) reacted at slightly different rates. Although the reaction is heterogeneous, and the rate therefore somewhat dependent upon the state of the zinc bromide, we carried out several runs on each isomer under comparable conditions, using the same batch of zinc bromide handled in the same way, and found regularly that *Z*-(6) was consumed about twice as fast as *E*-(6). This explains the higher yield from *Z*-(6), since the product was not exposed to the catalyst for as long as it was in the case of *E*-(6). Typically the reaction from *Z*-(6) took 12 h at 10 °C, while that from *E*-(6) took 24 h. That the *Z*-isomer should react faster is compatible with Chan's observation¹² that vinylsilanes react with carbon electrophiles with retention of configuration. The *E*-isomer in this case is constrained to react with inversion of configuration. The intramolecular reaction of a vinylsilane with an acetal is already known.¹³ In the known examples, the product was deliberately allowed to undergo elimination, and the initial position of the double bond was not investigated. The intramolecular reaction of vinylsilanes with a dithioacetal group is also known,¹⁴ but the first-formed allylic thioether was unstable with respect to 1,3 shift of the sulphide group. Intermolecular reaction of vinylsilanes with acetals is also known,¹⁵ but again the first-formed products reacted further. It appears that the reaction (6)→(7) is the first simple reaction of a vinylsilane with an acetal.



Scheme 2. Reagents: i, LDA; ii, PhSeBr ; iii, H_2O_2 ; iv, $(\text{Me}_3\text{Si})_2\text{CuLi}$, HMPA, THF; v, MeI ; vi, H_2SO_4 , MeOH ; vii, PCC; viii, LiAlH_4 ; ix, $\text{O}_2\text{NC}_6\text{H}_4\text{SeCN}$, Bu_3P , Py ; x, SnCl_4 , CH_2Cl_2 , 1 °C, 5 min

The allylsilane (8) was also prepared from our bis(trimethylsilyl)cuprate,¹¹ using a route (Scheme 2) adapted from our method⁹ for synthesising allylsilanes with silicon at the more-

substituted end of the allyl system. The synthesis was long, but essentially uneventful, and the cyclisation worked with the first Lewis acid we tried. The yield of the allylsilane (8) was 14% based on caprolactone, and the cyclisation gave the ether (9) in 64% yield (isolated), in spite of its high volatility. There were no other detectable products.

Experimental

4,4-Dimethoxybutyl Iodide (10).—4,4-Dimethoxybutyl chloride³ (5.0 g, 32.8 mmol) and sodium iodide (5.0 g, 33.4 mmol; dried *in vacuo* at 50 °C overnight) in dry acetone (50 ml) were stirred under nitrogen in the dark at 56 °C for 10 h. The resulting yellow solution was filtered and the solvent was evaporated under reduced pressure to give a yellow oil. Carbon tetrachloride (50 ml) was added to the resulting residue to precipitate the inorganic salts. The mixture was filtered again and the filtrate was evaporated under reduced pressure to give a brown oil. The oil was shown by n.m.r. spectroscopy to contain the iodoacetal (10), 4-hydroxy-4-methylpentan-2-one and a small amount of 4-iodobutanol. This oil was stirred with methanol (10 ml) and concentrated sulphuric acid (0.5 ml) under nitrogen in the dark at room temperature for 0.5 h. The solution was poured into saturated aqueous sodium hydrogen carbonate (50 ml) and extracted with dichloromethane (3×50 ml). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (2×25 ml), dried (Na_2CO_3), filtered, evaporated under reduced pressure and distilled to give the *iodo-acetal* (10) (6.40 g, 80%) as a light brown oil, b.p. 45–46 °C/0.2 mmHg, v_{max} (neat) 1 130 cm^{-1} (acetal); $\delta(\text{CDCl}_3)$ 4.30 (1 H, t, J 5 Hz, CH), 3.28 (6 H, s, 2 OMe), 3.18 (2 H, t, J 5 Hz, CH_2I), and 2.0–1.5 (4 H, m, CH_2CH_2) (Found: $M^+ - \text{H}$, 242.9861. $\text{C}_6\text{H}_{13}\text{O}_2\text{I}$ requires $M - \text{H}$, 242.9882), m/z 243 (10%, $M - \text{H}$), 213 (25, $M - \text{OMe}$), 117 [7, $M - \text{CH}(\text{OMe})_2$], and 75 [100, $\text{CH}(\text{OMe})_2$]. This compound was relatively unstable at room temperature and turned dark brown within 2 days at 0 °C.

(Z)-6,6-Dimethoxy-2-methyl-1-trimethylsilylhex-1-ene (6).—Sodium iodide (8.6 g, 57.4 mmol) and hexamethylphosphoric triamide (HMPA) (80 ml) were cooled under nitrogen to 0 °C. Methyl-lithium (lithium bromide free, 65.0 ml, 1.6M solution in ether, 104 mmol) was added dropwise with stirring over a period of 10 min at 0–3 °C. The resulting red trimethylsilyl-lithium solution was stirred at 0 °C for 10 min, and then cooled to –23 °C. Ether (20 ml) was added and the resulting deep red solution was stirred at –23 °C for 15 min. Anhydrous copper(I) cyanide (4.3 g, 47.8 mmol; dried *in vacuo* at 80 °C overnight) was added in small portions and the mixture stirred at –23 °C for 30 min (the mixture became pale green and later changed to deep brown). Propyne (1 150 ml at 20 °C, 47.9 mmol) was injected into the above solution. After being stirred for another 30 min at –23 °C, the solution was quenched with freshly distilled 4,4-dimethoxybutyl iodide (6.9 g, 28.3 mmol). Stirring was continued for another 4 h at –23 °C and the solution allowed to warm to 0 °C over 0.5 h. The mixture was then poured into saturated ammonium chloride solution (100 ml) and extracted with ether (3×75 ml). The combined organic layers were washed with saturated aqueous ammonium chloride (4×50 ml), dried (MgSO_4), filtered, and evaporated under reduced pressure to give a pale yellow oil, which was chromatographed on silica gel (150 g) eluting with ether–light petroleum (b.p. 30–40 °C) (1:9) and then distilled to give the *vinylsilane Z*-(6) (1.95 g, 30%), b.p. 75–80 °C/0.05 mmHg, v_{max} (neat) 2 840 (acetal) and 1 620 cm^{-1} ($\text{C}=\text{C}$); $\delta(\text{CDCl}_3, 250 \text{ MHz})$ 5.18 (1 H, m, $\text{CH}=\text{C}$), 4.35 [1 H, t, J 5 Hz, $\text{HC}(\text{OMe})_2$], 3.29 (6 H, s, 2 OMe), 2.10 (2 H, t, J 7 Hz, $\text{CH}_2\text{C}=\text{C}$), 1.79 (3 H, d, J 1 Hz, $\text{MeC}=\text{C}$), 1.57–1.32 (4 H, m, CH_2CH_2), and 0.06 (9 H s,

SiMe₃); $\delta(\text{CDCl}_3)$ 155.4 (C-2), 125.1 (C-1), 104.4 (C-6), 52.6 (methoxy-C), 37.2 (C-3), 32.5 (C-5), 26.2 (methyl-C), 23.7 (C-4), and 0.3 (trimethylsilyl-C) (Found: $M^+ - \text{MeOH}$, 198.1448. C₁₂H₂₆SiO₂ requires $M - \text{MeOH}$, 198.1440, m/z 230 (1.2%, M^+), 198 (4, $M - \text{MeOH}$), 183 (3, $M - \text{MeOH} - \text{Me}$), 125 (60, $M - \text{MeOH} - \text{SiMe}_3$), 95 (100, $M - \text{MeO} - \text{SiMe}_3\text{O-Me}$), 94 (80, $M - \text{MeOH} - \text{SiMe}_3\text{OMe}$), 89 (64), 83 (60), 75 [60, HC(OMe)₂], and 73 (SiMe₃).

6,6-Dimethoxyhex-1-yne (**11**).—The iodide (**10**) (2.73 g, 11.2 mmol) in dry dimethyl sulphoxide (DMSO) (1 ml) was added dropwise to a stirred suspension of lithium acetylide-ethylenediamine complex (1.3 g, 14.1 mmol) in DMSO (7 ml) under nitrogen at 8 °C. The mixture was stirred at this temperature for 2 h. Excess of lithium acetylide was destroyed by saturated aqueous ammonium chloride (10 ml). The mixture was extracted with dichloromethane (3 × 25 ml), and the combined organic solvents washed with water (50 ml), dried (NaHCO₃), filtered, evaporated under reduced pressure and distilled to give the acetylene (**11**) (0.789 g, 50%), b.p. 67–69 °C/20 mmHg, v_{max} (neat) 3 298 (CC-H), 2 825 (acetal), and 2 122 cm⁻¹ (C≡C); $\delta(\text{CDCl}_3)$, 4.45 [1 H, t, J 5 Hz, HC(OMe)₂], 3.36 (6 H, s, 2 OMe), 2.16 (2 H, dt, J 7 and 2 Hz, CH₂C≡C), 1.98 (1 H, t, J 2 Hz, C≡CH), and 1.95–1.50 (4 H, m, CH₂CH₂) (Found: $M^+ - \text{OMe}$, 111.0810. C₈H₁₄O₂ requires $M - \text{OMe}$, 111.0810, m/z 142 (0.5%, M^+), 141 (1, $M - \text{H}$), 111 ($M - \text{OMe}$), and 75 [100, HC(OMe)₂].

(E)-6,6-Dimethoxy-2-methyl-1-trimethylsilylhex-1-ene (**6**).—Hexamethyldisilane (3.67 g, 25.1 mmol) and HMPA (30 ml) was cooled under nitrogen to 0 °C, and methyl-lithium (LiBr-free, 15.0 ml, 1.6M solution in ether, 24.0 mmol) was added dropwise at 0–3 °C. The resulting red solution was stirred at 0 °C for 10 min, chilled to –23 °C, and dry tetrahydrofuran (5 ml) added; the resulting solution was then stirred at –23 °C for 30 min. Anhydrous copper(I) cyanide (1.13 g, 12.5 mmol) was added in small portions, and the deep brown solution stirred at –23 °C for 30 min. A solution of the acetylene (**11**) (1.19 g, 8.4 mmol) in dry THF (2 ml) was added to the solution with stirring for another 15 min. Dry methyl iodide (6.0 g, 42.3 mmol) was added and the solution stirred at –23 °C for 2 h, allowed to warm to 0 °C over a period of 1 h, and poured into saturated ammonium chloride (3 × 50 ml), dried (NaHCO₃), filtered and evaporated under reduced pressure to give a colourless oil, which was chromatographed on silica gel (50 g) eluting with ether–light petroleum (b.p. 30–40 °C) (1:9) to give the vinylsilane *E*-(**16**) (1.50 g, 78%) (R_F 0.40). A pure sample was prepared by distillation, b.p. 65–70 °C/0.05 mmHg, v_{max} (neat) 2 835 (acetal), 1 620 (C=C), and 1 250 cm⁻¹ (SiMe₃); $\delta(\text{CDCl}_3)$, 250 MHz) 5.18 (1 H, m, HC=C), 4.36 [1 H, t, J 5 Hz, HC(OMe)₃], 3.30 (6 H, s, 2 OMe), 2.06 (2 H, t, J 7 Hz, CH₂C=C), 1.75 (3 H, d, J 1 Hz, MeC=C), 1.70–1.40 (4 H, m, CH₂CH₂), and 0.07 (9 H, s, SiMe₃); $\delta(\text{CDCl}_3)$ 154.8 (C-2), 123.4 (C-1), 104.6 (C-6), 52.7 (methoxy-C), 42.3 (C-3), 32.1 (C-5), 22.7, 21.4 (C-4, methyl-C), and 0.1 (trimethylsilyl-C) (Found: M^+ , 230.1698. C₁₂H₂₆SiO₂ requires M , 230.1702, m/z 230 (3%, M^+), 215 (0.5, $M - \text{CH}_3$), 198 (4, $M - \text{MeOH}$), 140 (30), 125 (75, $M - \text{MeOH} - \text{SiMe}_3$), 95 (65, $M - \text{MeO} - \text{SiMe}_3\text{OMe}$), 94 (78, $M - \text{MeOH} - \text{SiMe}_3\text{OMe}$), 89 (66), 75 [73, HC(OMe)₂], 73 (SiMe₃), 57 (100), and 56 (73).

Reaction of *Z*-(**6**) with Zinc Bromide.—Anhydrous zinc bromide (93 mg, 0.41 mmol; dried *in vacuo* at 80 °C overnight) and *Z*-(**6**) (127 mg, 0.55 mmol) in dry carbon tetrachloride (2.0 ml; distilled from P₂O₅) were stirred under nitrogen at 10 °C for 12 h. The resulting mixture was poured into saturated aqueous sodium hydrogen carbonate (5 ml) and extracted with carbon tetrachloride (2 × 25 ml). The combined organic extracts were

dried (NaHCO₃) and filtered. The organic solvent was fractionally distilled under reduced pressure. The residue was then distilled to give the unsaturated cyclic ether (**7**) (49 mg, 70%), b.p. (oven temperature) 60–70 °C/20 mmHg. Both the ¹H n.m.r. spectrum and the mass spectrum of the product and an authentic sample¹⁶ were identical: $\delta(\text{CDCl}_3)$ 138.9 (C-1), 121.9 (C-2), 74.7 (C-3), 55.6 (methoxy-C), 30.3 (C-6), 27.6 (C-4), 23.7 (methyl-C), and 19.3 (C-5). No other regioisomeric cyclic ether was detected. However, longer reaction time (3 days) led to a decomposition product from the cyclic ether (**7**). This was characterised by the appearance of an olefinic signal around δ 6.2.

Reaction of *E*-(**6**) with Zinc Bromide.—The reaction was carried out on the vinylsilane *E*-(**6**) (210 mg), as described for the *Z*-isomer except that 24 h of stirring was needed with zinc bromide (154 mg). The weight of the product (**7**) (63 ± 3 mg, 55 ± 3%) was determined by ¹H n.m.r. spectroscopy using *m*-dinitrobenzene as internal standard. No isomeric ether was detected in the crude product. Prolonged reaction time (3 days) led to the decomposition of the cyclic ether (**7**) as shown by the decrease of the methoxy signal and the appearance of another olefin signal at δ 6.3.

2-Phenylselenohexan-6-olide.—The procedure was a modification of that described by Reich.¹⁷ *n*-Butyl-lithium (1.75M solution in hexane; 78.0 ml, 0.137 mol) was added dropwise to HMPA (28.2 g, 0.157 mol) and di-isopropylamine (15.9 g, 0.157 mol) in dry THF (400 ml) under nitrogen at –70 °C for 15 min. Hexan-6-olide (15.6 g, 0.137 mol) in dry THF (20 ml) was added dropwise, and the solution stirred at –70 °C for 15 min. Phenylseleninyl bromide (32.3 g, 0.137 mol) in dry THF (100 ml) was added rapidly between –70 and –60 °C, and the solution stirred at –70 °C for 15 min. Water (20 ml) was added and the THF was evaporated under reduced pressure. The yellow residue was extracted with ether–light petroleum (b.p. 30–40 °C) (2:1) (4 × 100 ml). The combined organic solvents were washed with water (4 × 25 ml), dried (MgSO₄), filtered, and evaporated under reduced pressure. The residue in ether (50 ml) was kept at –20 °C overnight to give the phenylselenohexanolide (14.1 g) as cubes, m.p. 71.5–73 °C (lit.,¹⁷ 73–75 °C). The mother liquors were chromatographed on silica gel (200 g) eluting with dichloromethane to give more phenylselenohexanolide (4.2 g; combined yield 18.3 g, 50%) (R_F 0.54), v_{max} (CHCl₃) 1 710 cm⁻¹ (C=O); $\delta(\text{CDCl}_3)$ 7.70–7.55, 7.47–7.27 (5 H, m, Ph), 4.77–4.46 (1 H, m, PhSeCH), 4.44–4.17 (2 H, m, OCH₂), and 2.37–1.52 (6 H, m, 3 CH₂); m/z 272 (18%, $M^+ ^{82}\text{Se}$), 270 (100, $M^+ ^{80}\text{Se}$), 269 (18, $M^+ ^{79}\text{Se}$), 268 (50, $M^+ ^{78}\text{Se}$), 267 (17, $M^+ ^{77}\text{Se}$), 266 (18, $M^+ ^{76}\text{Se}$), 158 (65, Ph⁸⁰SeH), 157 (24, Ph⁸⁰Se), 156 (33, Ph⁷⁸SeH), 120 (45), 118 (50), 78 (70, PhH), and 77 (45, Ph).

Hex-2-en-6-olide (**12**).—Hydrogen peroxide (30%; 8.0 ml, 78 mmol) was added dropwise with stirring to the phenylselenohexanolide (16.45 g, 61 mmol) in tetrahydrofuran (400 ml) at 25 °C, the temperature being kept between 30 and 33 °C for 2.5 h. The resulting yellow solution was evaporated under reduced pressure and benzeneseleninic acid (3.2 g) was precipitated as colourless crystals by the addition of diethyl ether–light petroleum (b.p. 30–40 °C) (1:1) (100 ml). The solid was filtered off and washed with ether (2 × 50 ml). The filtrate was concentrated under reduced pressure to give a red oil, which was chromatographed on silica gel (200 g) eluting with ether–light petroleum (b.p. 30–40 °C) (1:1). The lactone (**12**) was isolated as a pale yellow oil (R_F 0.19), which was further purified by distillation to give a colourless liquid (5.60 g, 82%), b.p. 68–69 °C/0.1 mmHg, v_{max} (neat) 1 697 (C=O) and 1 631 cm⁻¹ (C=C); $\delta(\text{CDCl}_3)$ 6.48 (1 H, dt, J 12 and 4 Hz, HC=CHCO), 5.97 (1 H, dt, J 12 and 1.5 Hz, HC=CHCO), 4.40–4.23 (2 H, m, OCH₂),

2.70—2.38 (2 H, m, $\text{CH}_2\text{C}=\text{C}$), and 2.28—1.97 (2 H, m, $\text{CH}_2\text{CH}_2\text{O}$) (Found: M^+ , 112.0527. $\text{C}_6\text{H}_8\text{O}_2$ requires M , 112.0524), m/z 112 (70%, M^+), 111 (76, $M - \text{H}$), 84 (79, $M - \text{CO}$), 82 (49, $M - \text{CH}_2\text{O}$), 71 (100), 54 (75), and 53 (44).

2-Methyl-3-trimethylsilylhexan-6-olide (13).—A solution of methyl-lithium (LiBr-free, 1.6M in ether; 28.0 ml, 44.8 ml) was added dropwise with stirring to hexamethyldisilane (6.22 g, 42.5 mmol) and HMPA (33 ml) under nitrogen at 0—3 °C. The resulting red solution was stirred at –5 to 0 °C for 15 min and then cooled to –23 °C. Dry THF (50 ml) was added and the mixture was again cooled to –23 °C. Copper(I) cyanide (1.86 g, 20.7 mmol; dried *in vacuo* at 60 °C overnight) was added in small portions. The reaction was very exothermic and the resulting solution was stirred vigorously at –23 °C for 20 min. The unsaturated lactone (**12**) (1.5 g, 13.4 mmol) in dry THF (2 ml) was added at –23 °C over 0.5 h, followed by methyl iodide (13.6, 96.4 mmol) and stirring at –23 °C for 0.5 h. The mixture was allowed to warm to 0 °C over 1 h, and then poured into saturated aqueous ammonium chloride (50 ml) and extracted with ether (4 × 50 ml). The combined ethereal layers were washed with saturated aqueous ammonium chloride (4 × 50 ml), dried (MgSO_4), filtered, and evaporated under reduced pressure to give a colourless oil. The residue was chromatographed on silica gel (80 g) eluting with dichloromethane and distilled to give the lactone (**13**) (2.55 g, 95%) (R_F 0.43), b.p. 104—104.5 °C/0.2 mmHg, v_{max} (neat) 1 728 (C=O) and 1 260 cm^{-1} (SiMe_3); δ (CCl_4 , CH_2Cl_2 as internal standard) 4.28—4.07 (2 H, m, OCH_2), 2.76 (1 H, dq, J 10 and 7 Hz, MeCH), 2.15—1.45 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.18 (3 H, d, J 7 Hz, Me), 0.93—0.59 (1 H, m, HCSiMe_3), and –0.02 (9 H, s, SiMe_3) (Found: $M^+ - \text{Me}$, 185.0995. $\text{C}_{10}\text{H}_{20}\text{SiO}_2$ requires $M - \text{Me}$ 185.0998), m/z (0.2%, M^+), 185 (28, $M - \text{Me}$), 157 (14), 99 (19, $M - \text{SiMe}_3 - \text{CO}$), 82 (15), 75 (42), and 73 (100, SiMe_3).

Methyl 6-Hydroxy-2-methyl-3-trimethylsilylhexanoate.—The lactone (**13**) (2.82 g, 14.1 mmol) and sulphuric acid (2 drops) in dry methanol (25 ml) were stirred at 20—23 °C for 6 h. The solution was made alkaline with potassium carbonate powder. Water (1 ml) was added and the organic solvent was evaporated under reduced pressure. The residue was extracted with chloroform (3 × 25 ml) and the combined organic layers were washed with water (15 ml), dried (NaHCO_3), and evaporated under reduced pressure to give the hydroxy-ester (2.92 g, 89%) as an oil, v_{max} (neat) 3 600—3 120 (OH), 1 734 (CO), and 1 258 cm^{-1} (SiMe_3); δ (CCl_4 , CHCl_3 as internal standard) 3.46 (3 H, s, OMe), 3.38 (2 H, t, J 6 Hz, CH_2O), 2.81 (1 H, br, OH, exchangeable with D_2O), 2.50 (1 H, dq, J 7 and 5 Hz, CHCOOMe), 1.53—0.74 (5 H, m, $\text{CH}_2\text{CH}_2\text{CHSi}$), 0.99 (3 H, d, J 7 Hz, Me), and –0.15 (9 H, s, SiMe_3) (Found: M^+ , 232.1488. $\text{C}_{11}\text{H}_{24}\text{SiO}_3$ requires M , 232.1495), m/z 232 (6%, M^+), 217 (24, $M - \text{Me}$), 201 (10, $M - \text{OMe}$), 187 (12, $M - \text{HOCH}_2\text{CH}_2$), 173 (67, $M - \text{CO}_2\text{Me}$ or $M - \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 159 (11, $M - \text{SiMe}_3$), 89 (48), 83 (26), 75 (30), 73 (100, SiMe_3), 69 (85), 59 (22, CO_2Me), and 55 (67).

Methyl 2-Methyl-6-oxo-3-trimethylsilylhexanoate.—The hydroxy-ester (4.18 g, 18.0 mmol) and pyridinium chlorochromate (7.00 g, 32.5 mmol) were stirred in dry dichloromethane (25 ml) at 15 °C for 1 h. The resulting solution was diluted with ether (15 ml) and filtered through Celite. The filter cake was washed with ether (2 × 50 ml). The combined filtrates were evaporated under reduced pressure to give a brown oil, which was chromatographed on silica gel (80 g) eluting with chloroform and distilled to give the aldehyde-ester (3.31 g, 80%), b.p. 75—80 °C/0.05 mmHg, R_F 0.53, v_{max} (neat) 2 716 (HCO), 1 734 ($\text{MeOC}=\text{O}$), 1 726 (CO), and 1 260 cm^{-1} (SiMe_3); δ (CCl_4 , CHCl_3 as internal standard) 9.53 (1 H, t, J 1.5 Hz, HCO), 3.47 (3

H, s, CO_2Me), 2.44 (1 H, dq, J 7 and 5 Hz, CHCO_2Me), 2.27 (2 H, dt, J 7 and 1.5 Hz, CH_2CHO), 1.69—1.33 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHO}$), 0.97 (3 H, d, J 7 Hz, CH_3), 1.02—0.80 (1 H, m, CHSiMe_3), and –0.15 (9 H, s, SiMe_3) (Found: M^+ , 230.1336. $\text{C}_{11}\text{H}_{22}\text{SiO}_3$ requires M , 230.1338); m/z 231 (0.5%, $M + \text{H}$), 230 (0.3, M^+), 229 (1, $M - \text{H}$), 215 (23, $M - \text{Me}$), 202 (2, $M - \text{CO}$), 201 (2, $M - \text{CHO}$), 187 (14, $M - \text{CH}_2\text{CHO}$), 173 (23, $M - \text{CH}_2\text{CH}_2\text{CHO}$), 171 (10, $M - \text{CO}_2\text{Me}$), 159 (14), 116 (14), 101 (37), 89 (70), 75 (19), 73 (100, SiMe_3), 59 (35, CO_2Me) and 55 (50).

Methyl 6,6-Dimethoxy-2-methyl-3-trimethylsilylhexanoate (14).—The aldehyde-ester (1.745 g, 7.57 mmol) and sulphuric acid (3 drops) in dry methanol (20 ml) were kept at 20—23 °C for 6 h. The resulting solution was poured into saturated aqueous sodium hydrogen carbonate (2 ml), excess of methanol was evaporated under reduced pressure, and the residue was diluted with chloroform (50 ml) and washed with saturated aqueous sodium hydrogen carbonate (5 ml). The organic layer was dried (Na_2CO_3), filtered, and evaporated under reduced pressure to give the acetal-ester (**14**) (2.077 g, 99%) as a colourless oil, v_{max} (neat) 2 840 (acetal), 1 734 (CO) and 1 259 cm^{-1} (SiMe_3); δ (CCl_4 , CHCl_3 as internal standard) 4.17 [1 H, t, J 6 Hz, $\text{HC}(\text{OMe})_2$], 3.51 (3 H, s, CO_2Me), 3.12 [6 H, s, $\text{C}(\text{OMe})_2$], 2.53 (1 H, dq, J 7 and 5 Hz, CHCO_2Me), 1.61—1.05 (4 H, m, CH_2CH_2), 1.03 (3 H, d, J 7 Hz, CH_3CH), 1.03—0.86 (1 H, m, HCSiMe_3), and –0.12 (9 H, s, SiMe_3) (Found: $M^+ - \text{CH}_3$, 261.1541. $\text{C}_{13}\text{H}_{28}\text{SiO}_4$ requires $M - \text{Me}$, 261.1522), m/z 276 (0.7%, M^+), 261 (26, $M - \text{Me}$), 245 (25, $M - \text{MeO}$), 229 (88), 201 [14, $M - (\text{MeO})_2\text{CH}$], 173 [46, $M - \text{C}_2\text{H}_4\text{-CH}(\text{OMe})_2$], 89 (91), 75 [77, $(\text{MeO})_2\text{CH}$], and 73 (100, SiMe_3).

6,6-Dimethoxy-2-methyl-3-trimethylsilylhexanol.—The acetal-ester (**14**) (2.077 g, 7.5 mmol) in dry THF (5 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.60 g, 15.8 mmol) in THF (50 ml) at 10 °C, and stirred at this temperature for 3 h. Ethyl acetate (5 ml) was added and the solvent evaporated under reduced pressure. The residue was mixed with water (50 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (50 ml), dried (Na_2CO_3), filtered, and evaporated under reduced pressure to give the hydroxy-acetal (1.72 g, 92%) as a colourless oil, v_{max} (neat) 3 600—3 160 (OH), 2 830 (acetal), and 1 267 cm^{-1} (SiMe_3); δ (CCl_4 , CHCl_3 as internal standard) 4.16 [1 H, t, J 5 Hz, $\text{HC}(\text{OMe})_2$], 3.30 (2 H, d, J 7 Hz, CH_2OH), 3.11 [6 H, s, $\text{C}(\text{OMe})_2$], 2.76—2.44 (1 H, br, OH, exchangeable with D_2O), 1.94—1.00 (5 H, m, CH_2CH_2 and CHMe), 0.83 (3 H, d, J 7 Hz, CHMe), 0.71—0.53 (1 H, m, SiCH), and –0.13 (9 H, s, SiMe_3) (Found: $M^+ - \text{MeOH}$, 216.1539. $\text{C}_{12}\text{H}_{28}\text{SiO}_3$ requires $M - \text{MeOH}$, 216.1545), m/z 247 (0.1%, $M^+ - \text{H}$), 216 (1, $M - \text{MeOH}$), 201 (5, $M - \text{MeOH} - \text{Me}$), 188 (10), 157 (25), 143 (18), 126 (10), 103 (29), 95 (57), 75 [71, $\text{HC}(\text{OMe})_2$], 73 (43, SiMe_3), and 58 (100, $\text{C}_3\text{H}_6\text{O}$).

6,6-Dimethoxy-2-methyl-3-trimethylsilylhexyl o-Nitrophenyl Selenide.—Tri-*n*-butylphosphine (2.51 g, 12.4 mmol) was added dropwise to a stirred mixture of the alcohol (2.60 g, 10.5 mmol), *o*-nitrophenylselenocyanate (2.82 g, 12.4 mmol) and pyridine (3.0 ml) in dry THF (25 ml) under nitrogen at 20 °C for 1 h. The resulting deep-red solution was evaporated under reduced pressure to give a viscous oil, which was chromatographed on silica gel (100 g) eluting with ethyl acetate–hexane (1:5) to give the selenide (3.62 g, 80%) as a yellow oil (R_F 0.38), v_{max} (neat) 2 840 (acetal), 1 515, 1 336 (ArNO_2), and 1 254 cm^{-1} (SiMe_3); δ (CDCl_3 , CH_2Cl_2 as internal standard) 8.28 (1 H, d, J 9 Hz, *H ortho* to NO_2), 7.60—7.19 (3 H, m, other aromatic H), 4.32 [1 H, t, J 5 Hz, $\text{CH}(\text{OMe})_2$], 3.28 [6 H, s, $\text{C}(\text{OMe})_2$], 3.04—2.78 (2 H,

m, CH_2Se), 2.23—1.89 (1 H, m, CHCH_2Se), 1.79—1.30 [4 H, m, $\text{CH}_2\text{CH}_2\text{C}(\text{OMe})_2$], 1.10 (3 H, d, J 7 Hz, CHMe), 0.98—0.71 (1 H, m, HCSiMe_3), and 0.02 (9 H, s, SiMe_3); m/z 433 (2%, M^+ ^{80}Se), 431 (1, M^+ ^{78}Se), 401 (1, $M^{80}\text{Se} - \text{MeOH}$), 399 (0.5, $M^{78}\text{Se} - \text{MeOH}$), 386 (2, $M^{80}\text{Se} - \text{MeOH} - \text{Me}$), 384 (1, $M^{78}\text{Se} - \text{MeOH} - \text{Me}$), 260 (6), 258 (3), 202 (3, $\text{O}_2\text{NC}_6\text{H}_4^{80}\text{Se}$), 186 (22, $\text{ONC}_6\text{H}_4^{80}\text{Se}$), 184 (11, $\text{ONC}_6\text{H}_4^{78}\text{Se}$), 127 (12), 125 (6), 95 (75), 89 (18), 83 (19), 75 [38, $\text{HC}(\text{OMe})_2$], and 73 (100, SiMe_3).

6,6-Dimethoxy-2-methyl-3-trimethylsilylhex-1-ene (8).—The selenide (0.51 g, 1.18 mmol), hydrogen peroxide (30%; 2.0 ml, 19.5 mmol) and pyridine (0.28 g) were stirred in THF (10 ml) at 20—23 °C for 6 h. The resulting solution was poured into saturated aqueous sodium hydrogen carbonate (10 ml) and extracted with ether (3 × 25 ml). The combined ethereal solvents were washed with saturated aqueous sodium hydrogen carbonate (2 × 25 ml), dried (NaHCO_3), filtered and evaporated under reduced pressure to give a yellow oil, which was chromatographed on silica gel (20 g) eluting with ethyl acetate—light petroleum (b.p. 30—40 °C) (1:10) followed by distillation to give the allylsilane (**8**) as an oil (0.19 g, 70%), b.p. 60—70 °C/0.05 mmHg, R_F 0.62, v_{max} (neat) 2 840 (acetal), 1 636 ($\text{C}=\text{CH}_2$), and 1 253 cm^{-1} (SiMe_3); $\delta(\text{CDCl}_3, \text{CHCl}_3$ as internal standard) 4.66 (1 H, m, $\text{C}=\text{CH}_A\text{H}_B$), 4.48 (1 H, m, $\text{C}=\text{CH}_A\text{H}_B$), 4.28 [1 H, t, J 5 Hz, $\text{HC}(\text{OMe})_2$], 3.22 [6 H, s, $\text{C}(\text{OMe})_2$], 1.69 (3 H, s, $\text{MeC}=\text{C}$), 1.73—1.25 (5 H, m, $\text{CH}_2\text{CH}_2\text{CHSi}$), and -0.10 (9 H, s, SiMe_3); $\delta(\text{CDCl}_3)$ 146.4 (C-2), 108.7 (C-1), 104.6 (C-6), 52.8 and 52.3 (methoxy-C), 38.0 (C-3), 32.1 (C-5), 23.5 (methyl-C), 23.3 (C-4), and -2.6 (trimethylsilyl-C) (Found: M^+ , 230.1717. $\text{C}_{12}\text{H}_{26}\text{SiO}_2$ requires M , 230.1702), m/z 230 (10%, M^+), 215 (1, $M - \text{Me}$), 198 (17, $M - \text{OMe}$), 157 (4, $M - \text{SiMe}_3$), 126 (6, $M - \text{SiMe}_3 - \text{MeO}$), 125 (5, $M - \text{SiMe}_3 - \text{MeOH}$), 95 (44, $M - \text{Me}_3\text{SiOMe} - \text{MeO}$), 94 (100, $M - \text{Me}_3\text{SiOMe} - \text{MeOH}$), 89 (40), 79 (23), 75 [20, $\text{HC}(\text{OMe})_2$], and 73 (43, SiMe_3).

Reaction of the Allylsilane (8) with Tin(IV) Chloride.—Anhydrous tin(IV) chloride (350 mg, 1.35 mmol) was added with stirring to the allylsilane (**8**) (310 mg, 1.35 mmol) in dry dichloromethane (10 ml) under nitrogen at 1 °C for 5 min. The pale red solution was poured into saturated aqueous sodium hydrogen carbonate (5 ml) and extracted with carbon tetrachloride (2 × 50 ml). The combined organic solvents were dried (Na_2CO_3) and fractionally distilled under reduced

pressure (water bath temperature was kept below 23 °C). The residue was then distilled to give 4-methoxy-2-methylcyclohex-1-ene (**9**) (109 mg, 64%) as an oil, b.p. 60—70 °C/20 mmHg, v_{max} (neat) 1 107 cm^{-1} (OMe); $\delta(\text{CDCl}_3)$ 5.39—5.20 (1 H, m, $\text{CH}=\text{CO}$), 3.55—3.25 (1 H, m, HCOMe), 3.29 (3 H, s, OMe), 2.20—1.30 (6 H, m, 3 CH_2), and 1.56 (3 H, br, s, $=\text{CMe}$); $\delta(\text{CDCl}_3)$ 131.4 (C-2), 120.7 (C-1), 77.0 (C-4), 55.7 (methoxy-C), 36.0 (C-3), 26.9 (C-6), 23.5 (methyl-C) and 23.3 (C-5) (Found: M^+ , 126.1037. $\text{C}_8\text{H}_{14}\text{O}$ requires M , 126.1045), m/z 126 (20%, M^+), 111 (6, $M - \text{Me}$), 95 (15, $M - \text{OMe}$), 94 (100, $M - \text{MeOH}$), 68 (54, C_5H_8), and 58 (60, $\text{CH}_2=\text{CHOMe}$). No regioisomeric cyclic ether was observed in the ^1H n.m.r. or ^{13}C n.m.r. spectrum.

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