

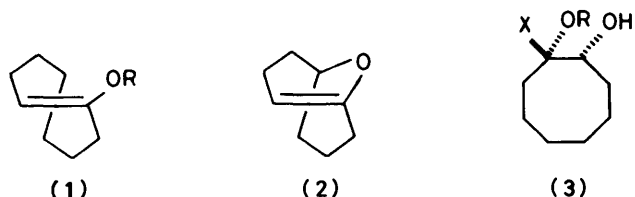
## *trans*-Cycloalkenes.† Part 13.1 1-Methylthiomethoxy-*trans*-cyclo-octene and 1-Methoxy-*trans*-cyclo-octene by Peterson Elimination

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Methods are described, based on model experiments with cyclohexyl analogues, for the preparation of *c*-2-methylthiomethoxy-*t*-2-trimethylsilylcyclo-octan-*r*-1-ol (**21**) and *c*-2-methoxy-*t*-2-trimethylsilylcyclo-octan-*r*-1-ol (**22**). These underwent a stereospecific elimination on treatment with  $\text{KH-Me}_2\text{SO}$  to give respectively 1-methylthiomethoxy-*trans*-cyclo-octene (**23**) and 1-methoxy-*trans*-cyclo-octene (**25**) as transient compounds which fairly rapidly isomerised to their *cis*-isomers.

There are no reports of any simple *trans*-cyclo-octenes bearing a mesomerically electron-donating substituent on the double bond. We decided therefore to attempt the preparation of a 1-alkoxy-*trans*-cyclo-octene (**1**) partly for comparison with other 1-substituted *trans*-cyclo-octenes such as 1-methyl-*trans*-cyclo-octene<sup>2</sup> and partly for comparison with the known bridgehead bicyclic enol ether (**2**).<sup>3</sup> Based on previous experience it was evident that the most promising route to compounds of type (**1**) would involve the *syn*-elimination of  $\text{XOH}$  from a precursor (**3**) with the stereochemistry shown. Since we had previously found<sup>4</sup> that the Peterson elimination<sup>5</sup> was a viable way of preparing *trans*-cyclo-octene, it was decided to investigate the approach using (**3**;  $\text{X} = \text{Me}_3\text{Si}$ ).



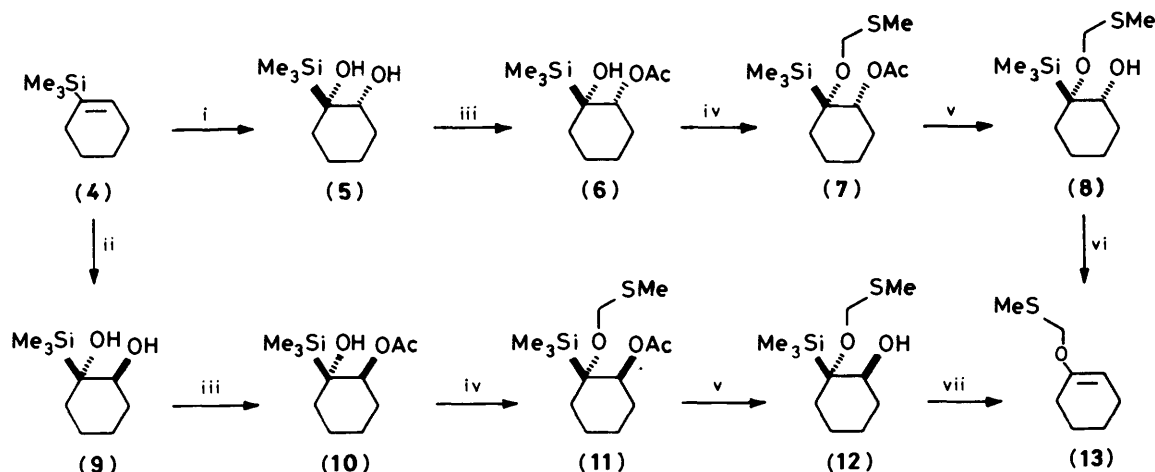
The obvious precursor of (**3**;  $\text{X} = \text{Me}_3\text{Si}$ ) was 1-trimethylsilylcyclo-octene.<sup>4,6</sup> Thus a *syn*-hydroxylation followed by alkylation of the more hindered tertiary hydroxy group was required. In order to develop appropriate protection-deprotection procedures model experiments in the six-membered series were carried out, and these are summarised in Scheme 1.

Acetate was chosen to protect the 2-hydroxy group in the diols (**5**) and (**9**) and methylthiomethyl<sup>7</sup> proved to be the most convenient blocking group for attachment to the 1-hydroxy group. The feasibility of desulphurisation of one of the methylthiomethyl ethers using Raney nickel was demonstrated by the high yield conversion of the sulphide (**11**) into the methyl ether (**14**). Hydrolyses, (**7**)→(**8**) and (**11**)→(**12**) were followed by  $\beta$ -hydroxy silane elimination under conditions appropriate for a *syn*-[(**12**)→(**13**)] or *anti*-[(**8**)→(**13**)] process.<sup>5</sup> Either way, the novel enol ether (**13**) was obtained in high yield as an oil which slowly decomposed with time to give cyclohexanone as the main product. Treatment of the  $\beta$ -hydroxy silanes (**8**) and (**12**) with potassium *t*-butoxide in dimethyl sulphoxide (DMSO) led to highly stereospecific desilylation with retention of configuration<sup>8</sup> to give the monomethyl thiomethyl ethers (**15**) and (**16**)<sup>‡</sup> respectively.

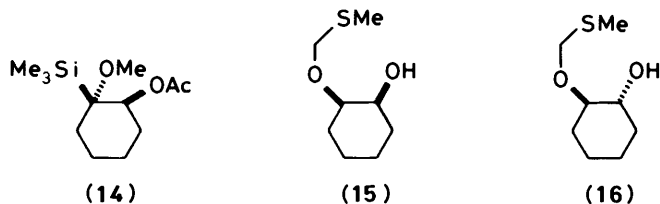
Returning now to the eight-membered ring, 1-trimethylsilylcyclo-octene was converted (Scheme 2) into the methylthiomethyl ether (**20**) using a route analogous to that used for

† We shall continue to use the terms *cis*- and *trans*- in this series of papers to designate the way in which the ring system is joined to the double bond. This avoids any possible confusion arising out of a change from *E*- to *Z*- when groups of high priority in the sequence rule are attached to the double bond.

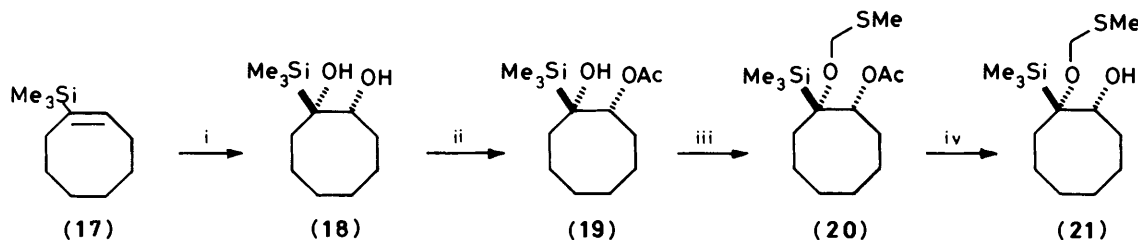
‡ An authentic sample of compound (**16**) was prepared for comparison by methylthiomethylation of *trans*-2-acetoxycyclohexanol followed by hydrolysis of the acetoxy group (see the Experimental section)



Scheme 1. Reagents: i,  $\text{OsO}_4$ -*N*-methylmorpholine *N*-oxide- $\text{H}_2\text{O}$ - $\text{Me}_2\text{CO}$ ; ii, (a)  $\text{MeCO}_3\text{H}$ ; (b)  $\text{H}_2\text{SO}_4$ -water- $\text{Me}_2\text{CO}$ ; iii,  $\text{Ac}_2\text{O}$ -Py- $20^\circ\text{C}$ ; iv, DMSO- $\text{AcOH}$ - $\text{Ac}_2\text{O}$ - $18^\circ\text{C}$ ; v,  $\text{KOH}$ - $\text{MeOH}$ - $50^\circ\text{C}$ ; vi,  $\text{MeSO}_2\text{Cl}$ -Py- $0^\circ\text{C}$ ; vii,  $\text{KH}$ -THF- $0^\circ\text{C}$

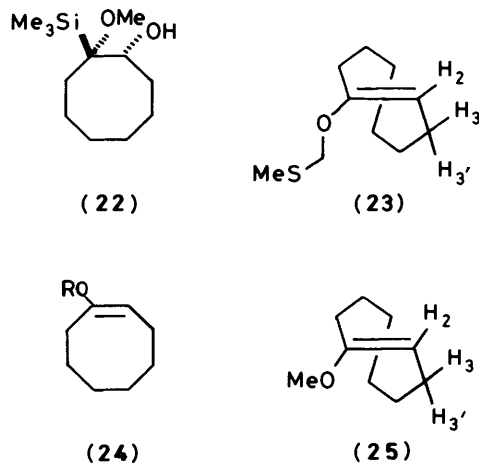


the conversion of (4)→(8). The only significant difference found was that the monoacetate (19) was less stable than the cyclohexyl analogues (6) and (10) and readily decomposed to cyclo-octanone under mildly acidic or basic conditions.



Scheme 2. Reagents: i,  $\text{OsO}_4$ -*N*-methylmorpholine *N*-oxide-water- $\text{Me}_2\text{CO}$ ; ii,  $\text{Ac}_2\text{O}$ -Py-DMAP; iii, DMSO- $\text{AcOH}$ - $\text{Ac}_2\text{O}$ ; iv, KOH-MeOH

The methyl ether (22) was also prepared. Thus, desulphurisation of compound (20) using Raney nickel in benzene at 25–30 °C (milder conditions were required than those used for preparation of (14) owing to the greater fragility of the eight-membered ring compound) followed by hydrolysis gave the ether (22) in 74% yield.



Treatment of the methylthiomethyl ether (21) with potassium hydride in THF, the conditions found best for the conversion (12)→(13), led to consumption of all the starting material. The n.m.r. spectrum of the product showed a doublet of doublets in the olefinic region at  $\delta$  4.93 with apparent coupling constants  $J_{2,3}$  and  $J_{2,3'}$  4 and 12.5 Hz respectively, similar to those for the olefinic proton in *trans*-cyclo-octene (4.5 and 10 Hz)<sup>9</sup> and 1-methyl-*trans*-cyclo-octene<sup>2</sup> (5.5 and 10 Hz). The compound produced is thus considered to be 1-methylthiomethoxy-*trans*-cyclo-octene (23). It is unstable, readily isomerising (half-life *ca.* 40 min at 18 °C) to the *cis*-enol ether (24; R =  $\text{MeSCH}_2$ ) which showed a triplet ( $J$  7.5 Hz) at  $\delta$  4.53 in the n.m.r. spectrum characteristic of the olefinic proton of a *cis*-cyclo-octene. Compound (24; R =  $\text{MeSCH}_2$ ) was also unstable, decomposing

slowly to cyclo-octanone, *cf.* the behaviour of the six-membered ring analogue (13) already mentioned.

In the hope that the methyl enol ethers might be more stable, the methyl ether (22) was treated with potassium hydride in THF. Again an unstable enol ether was obtained, considered to be 1-methoxy-*trans*-cyclo-octene (25) on the basis of the doublet of doublets in the n.m.r. spectrum attributable to the olefinic proton ( $\delta$  4.63, apparent,  $J_{2,3}$  4.3 and  $J_{2,3'}$  12.3 Hz) and isomerisation to the known *cis*-enol ether (24; R = Me). A freshly prepared sample contained *ca.* 91% *trans*-(25) and 9% *cis*-enol ether (24; R = Me). The *trans*→*cis* isomerisation could be conveniently followed by n.m.r. spectroscopy since the methoxy signals were readily distinguishable. Reasonable

straight line plots of  $\ln$  [peak height] against time were obtained indicating that the isomerisation is first order with respect to substrate. Approximate rate constants of 0.013  $\text{min}^{-1}$  and 0.006  $\text{min}^{-1}$  (at 36 °C) were derived for solutions in  $\text{CCl}_4$  and  $\text{CDCl}_3$  respectively corresponding to half-lives of *ca.* 50 and 120 min.

The relative instability of the alkoxy-*trans*-cyclo-octenes (23) and (25) is in marked contrast to 1-methyl-*trans*-cyclo-octene which can be purified by preparative g.l.c. and stored for 6 months without deterioration.<sup>2</sup> The ease of isomerisation of compound (25) may be due to the bond order of the double bond being further reduced by mesomeric electron release from the oxygen atom,<sup>10</sup> however, the possibility of a protonation-deprotonation mechanism for isomerisation cannot be excluded.

## Experimental

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer, n.m.r. spectra on a Perkin-Elmer R32 (90 MHz) or R24 (60 MHz) instrument using  $\text{CHCl}_3$  ( $\delta$  7.27) or  $\text{CH}_2\text{Cl}_2$  ( $\delta$  5.25) as internal standards for compounds containing a  $\text{Me}_3\text{Si}$  group.

1-Trimethylsilyl-*cis*-cyclohexane-1,2-diol (5).—1-Trimethylsilylcyclohexene<sup>11</sup> (4) (15 g, 0.098 mol), *N*-methylmorpholine *N*-oxide (18.8 g, 0.16 mol) and *t*-butyl alcohol (10 ml) were added to water (17.5 ml) and acetone (170 ml). Osmium tetroxide (190 mg, 0.7 mmol) was then added and the resulting dark brown mixture stirred at 50 °C. After 36 h when g.l.c. (OV17; 150 °C) showed that all the vinylsilane had been consumed, the acetone was evaporated under reduced pressure and water (300 ml) was added. The aqueous solution was extracted with ether (4 × 75 ml) and the combined ether extracts were washed with 2M-HCl (200 ml), saturated aqueous sodium carbonate, and brine, and then dried ( $\text{MgSO}_4$ ). Evaporation of the ether gave a brown solid (12.9 g) which was crystallised from light petroleum (b.p. 60–80 °C) to give white crystals of the *cis*-diol (5) (11.8 g, 70%, m.p. 85–88 °C (Found: C, 57.7; H, 10.8.  $\text{C}_9\text{H}_{20}\text{O}_2\text{Si}$  requires C, 57.4; H, 10.7%);  $\delta$ ( $\text{CDCl}_3$ ) 3.65 (1 H, m,  $W_{\text{H}}$  16 Hz, 2-H), 1.1–1.9 (10 H, complex, 8 H after  $\text{D}_2\text{O}$  exch.), and 0.1 (9 H, s,  $\text{SiMe}_3$ );  $\nu_{\text{max}}$ ( $\text{CCl}_4$ ) 3 580, 3 720 (br, OH), 1 380, 1 245, (C-Si), 1 050, and 957  $\text{cm}^{-1}$ ).

1-Trimethylsilyl-*cis*-cyclo-octene (17).—To sodium sand (16 g, 0.70 mol) in dry ether (200 ml) was added, with stirring under nitrogen, trimethylsilyl chloride (32 g, 0.29 mol), ethyl acetate (1 ml), and 1-bromo-*cis*-cyclo-octene<sup>12</sup> (1 ml). After ca. 10 min the solution became blue and the ether began to reflux. 1-Bromo-*cis*-cyclo-octene (54 g, 0.29 mol) was then added dropwise during 1 h and the mixture was stirred under nitrogen for a further 12 h. The solid was filtered off and washed with dry ether (75 ml), the washings and filtrate were combined, and the ether evaporated to give a yellow oil. This was distilled to give 1-trimethylsilyl-*cis*-cyclo-octene (17) as a colourless liquid (40 g, 77%), b.p. 56–64 °C at 1 mmHg (lit.,<sup>6</sup> b.p. 73–74 °C at 7 mmHg);  $\delta(\text{CDCl}_3)$  5.9 (1 H, t, 2-H), 1.2–2.3 (12 H, complex), and 0.1 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\text{max}}$ . (liquid film) 3 030 (=C–H), 1 620 (C=C), 1 250, and 840 cm<sup>-1</sup> (C–Si).

1-Trimethylsilyl-*cis*-cyclo-octane-1,2-diol (18).—1-Trimethylsilyl-*cis*-cyclo-octene (17) (17.5 g, 0.096 mol), *N*-methylmorpholine *N*-oxide (17.5 g, 0.15 mol), and *t*-butyl alcohol (10 ml) were added to water (25 ml) and acetone (300 ml). Osmium tetroxide (180 mg, 0.66 mmol) was then added and the resulting dark brown mixture stirred at 50 °C. After 240 h t.l.c. using light petroleum (b.p. 40–60 °C)–ether (1:1) as the eluant indicated that all the vinylsilane has been consumed. The acetone was evaporated under reduced pressure and water (280 ml) was added. The aqueous solution was extracted with ether (5 × 60 ml) and the combined ether extracts were washed with 2M-HCl (180 ml), saturated aqueous sodium carbonate, and brine, and then dried (MgSO<sub>4</sub>). Evaporation of the ether gave a brown solid (14.6 g) which was recrystallised from light petroleum (b.p. 60–80 °C) to give 1-trimethylsilyl-*cis*-cyclo-octane-1,2-diol (18) as a white solid (13.2 g, 74%), m.p. 88–90 °C (Found: C, 61.05; H, 11.2. C<sub>11</sub>H<sub>24</sub>O<sub>2</sub>Si requires C, 61.0; H, 11.55%);  $\delta(\text{CDCl}_3)$  4.05 (1 H, br, *J* 9 Hz, 2-H), 1.1–2.3 (14 H, complex, 12 H after D<sub>2</sub>O exch.), and 0.2 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\text{max}}$ . (CHCl<sub>3</sub>) 3 630, 3 560br (OH), 1 450, 1 250, 1 048, 951, and 844 cm<sup>-1</sup> (C–Si).

*t*-2-Acetoxy-1-trimethylsilylcyclohexan-*r*-1-ol (10).—To a solution of 1-trimethylsilyl-*trans*-cyclohexane-1,2-diol<sup>4</sup> (9) (4.5 g, 23.9 mol) in dry pyridine (25 ml) was added acetic anhydride (5.0 ml, 5.37 g, 52.7 mmol). The mixture was stirred at 40 °C for 40 h and then poured into a mixture of ether (100 ml) and 2M-HCl (100 ml). The aqueous layer was extracted with more ether (2 × 40 ml) and the combined ether extracts were then washed with saturated aqueous sodium carbonate and brine and then dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by short-path distillation at 0.01 mmHg and 110–120 °C gave the *trans*-hydroxy acetate (10) (5.3 g, 96%) as a colourless oil (Found: C, 57.7; H, 9.65. C<sub>11</sub>H<sub>22</sub>O<sub>3</sub>Si requires C, 57.35; H, 9.6%);  $\delta(\text{CDCl}_3)$  4.85 (1 H, m, *W*<sub>H</sub> 13 Hz, 2-H), 2.05 (3 H, s, MeCO), 1.0–2.1 (9 H, complex, 8H after D<sub>2</sub>O exch.), and 0.1 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\text{max}}$ . (liquid film) 3 495 (br, OH), 1 723, 1 743 (C=O), 1 240, and 840 cm<sup>-1</sup> (C–Si).

*c*-2-Acetoxy-1-trimethylsilylcyclohexan-*r*-1-ol (6).—In a similar way 1-trimethylsilyl-*cis*-cyclohexane-1,2-diol (5) (3.5 g, 18.6 mmol) gave the *cis*-hydroxy acetate (6) (4.18 g, 97%) as a colourless oil (Found: C, 57.0; H, 9.85. C<sub>11</sub>H<sub>22</sub>O<sub>3</sub>Si requires C, 57.35; H, 9.6%);  $\delta(\text{CDCl}_3)$  4.9 (1 H, m, 2-H, *W*<sub>H</sub> 17.5 Hz), 2.1 (3 H, s, MeCO), 1.0–2.1 (9 H, complex, 8 H after D<sub>2</sub>O exch.), and 0.1 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\text{max}}$ . (liquid film) 3 520 (br, OH), 1 720, 1 740 (C=O), 1 245, and 840 cm<sup>-1</sup> (C–Si).

*c*-2-Acetoxy-1-trimethylsilylcyclo-octan-*r*-1-ol (19).—To a solution of 1-trimethylsilyl-*cis*-cyclo-octane-1,2-diol (18) (3.5 g, 16.2 mmol) in dichloromethane (55 ml) was added dry pyridine (2.7 ml, 2.6 g, 33.4 mmol) and acetic acid anhydride (3.0 ml, 3.3 g,

32 mmol). The mixture was cooled to –20 °C (carbon tetrachloride–solid CO<sub>2</sub>) and then 4-dimethylaminopyridine (180 mg, 1.5 mmol) was added, with stirring, and the temperature was maintained at –20 °C for a further 75 min. Methanol (1 ml) was added and after a further 5 min the mixture was poured into a mixture of ether (100 ml) and water (100 ml). The aqueous layer was extracted with more ether (2 × 50 ml), the combined ether extracts were washed with 2M-HCl (75 ml), saturated aqueous sodium carbonate, and brine and then dried (MgSO<sub>4</sub>). The ether was evaporated under reduced pressure using a cold water bath to give the *cis*-hydroxy acetate (19) (4.05 g, 97%) (Found: C, 60.1; H, 9.9. C<sub>13</sub>H<sub>26</sub>O<sub>3</sub>Si requires C, 60.4; H, 10.1%);  $\delta(\text{CDCl}_3)$  5.05 (1 H, br, *J* 7.5 Hz, 2-H), 2.05 (3 H, s, MeCO), 1.0–2.0 (13 H, complex, 12 H after D<sub>2</sub>O exch.), 0.1 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\text{max}}$ . (liquid film) 3 500 (br, OH), 1 737 (C=O), 1 250, and 840 cm<sup>-1</sup> (C–Si); *m/z* 199 (54%), 127 (100), 109 (33), and 105 (55).

The *cis*-hydroxy acetate (19) was unstable and decomposed with time to give mainly cyclo-octanone. Decomposition was observed on attempted distillation or preparative t.l.c. which gave a mixture of products. Purification was brought about by the removal of volatile impurities using an oil pump (0.01 mmHg) and following such treatment the compound was used immediately.

*c*-2-Acetoxy-1-methylthiomethoxy-*r*-1-trimethylsilylcyclohexane (11).—*t*-2-Acetoxy-1-trimethylsilylcyclohexan-*r*-1-ol (10) (5.3 g, 23.0 mmol) was added to a mixture of dry DMSO (67 ml), glacial acetic acid (18 ml) and acetic anhydride (45 ml). The mixture was kept at 15 °C for 68 h and was then poured slowly into a mixture of chloroform (200 ml) and saturated aqueous sodium carbonate (250 ml). The aqueous layer was extracted with further chloroform (2 × 150 ml) and the combined organic layers were washed with saturated aqueous sodium carbonate (200 ml), water (200 ml), and brine and then dried (CaCl<sub>2</sub>). Evaporation of the solvent followed by short path distillation at 0.005 mmHg and 80–100 °C to give the *methylthiomethyl ether* (11) as a colourless oil (5.8 g, 87%) (Found: C, 54.15; H, 8.9; S, 11.2. C<sub>13</sub>H<sub>26</sub>O<sub>3</sub>SSi requires C, 53.75; H, 9.0; S, 11.05%);  $\delta(\text{CDCl}_3)$  5.2 (1 H, m, *W*<sub>H</sub> 13.5 Hz, 2-H), 4.55 (2 H, s, OCH<sub>2</sub>S), 2.2 (3 H, s, SMe), 2.05 (3 H, s, MeCO), 1.2–2.3 (8 H, complex), and 0.2 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\text{max}}$ . (liquid film) 1 740 (C=O), 1 370, 1 240, and 840 cm<sup>-1</sup> (C–Si).

*t*-2-Acetoxy-1-methylthiomethoxy-*r*-1-trimethylsilylcyclohexane (7).—In a similar way *c*-2-acetoxy-1-trimethylsilylcyclohexan-*r*-1-ol (6) (4.18 g, 18.2 mmol) gave the *methylthiomethyl ether* (7) as a colourless oil (3.95 g, 75%) (Found: C, 54.05; H, 9.05; S, 11.2. C<sub>13</sub>H<sub>26</sub>O<sub>3</sub>SSi requires C, 53.75; H, 9.0; S, 11.05%);  $\delta(\text{CDCl}_3)$  4.8 (1 H, m, *W*<sub>H</sub> 14 Hz, 2-H), 4.7 (2 H, s, OCH<sub>2</sub>S), 2.3 (3 H, s, SMe), 2.1 (3 H, s, MeCO), 1.1–2.2 (8 H, complex), and 0.15 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\text{max}}$ . (liquid film) 1 730 (C=O), 1 370, 1 240, and 840 cm<sup>-1</sup> (C–Si).

*t*-2-Methylthiomethoxy-2-trimethylsilylcyclohexan-*r*-1-ol (12).—*c*-2-Acetoxy-1-methylthiomethoxy-*r*-1-trimethylsilylcyclohexane (11) (5.6 g, 19.3 mmol) was added to 10% methanolic potassium hydroxide (60 ml) and the mixture was stirred at 50 °C for 18 h. The mixture was then poured into water (200 ml) and ether (200 ml). The aqueous layer was extracted with further ether (3 × 60 ml), and the combined ether extracts were then washed with brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave an oil (4.2 g) which eventually solidified. The solid was recrystallised from light petroleum (b.p. 40–60 °C) to give the *cis*- $\beta$ -hydroxy silane (12) (3.7 g, 80%), m.p. 74–75 °C (Found: C, 53.05; H, 9.75; S, 12.75. C<sub>11</sub>H<sub>24</sub>O<sub>2</sub>SSi requires C, 53.2; H, 9.75; S, 12.9%);  $\delta(\text{CDCl}_3)$  4.7 (2 H, ABq, OCH<sub>2</sub>S), 4.05 (1 H, m, *W*<sub>H</sub> 16 Hz, 1-H), 2.75 (1 H, br

s, D<sub>2</sub>O exch., OH), 2.3 (3 H, s, SMe), 1.2–2.2 (8 H, complex), and 0.28 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\max.}(\text{CHCl}_3)$  3 480br (OH), 1 330, 1 070, and 840 cm<sup>-1</sup> (C–Si).

**Reactions of *t*-2-Methylthiomethoxy-*c*-2-trimethylsilylcyclohexan-*r*-1-ol (12).**—(a) *With potassium hydride in THF.* Potassium hydride (20% dispersion in oil; 0.65 g, 3.3 mmol) was washed under nitrogen with light petroleum (b.p. 30–40 °C, 3 × 5 ml) after which dry THF (12 ml) was added and the mixture cooled to 0 °C. The *cis*- $\beta$ -hydroxy silane (12) (0.5 g, 2.0 mmol) in dry THF (2 ml) was then added, with stirring under nitrogen, and the mixture became yellow soon after the addition. After 10 min, g.l.c. (silicone oil; 150 °C) indicated one main component, *R*<sub>t</sub> 4 min, and the reaction mixture was slowly poured into water (20 ml) and ether (20 ml). The aqueous layer was extracted with further ether (2 × 20 ml), and the combined ether extracts were then washed with brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave an oil (0.36 g). Short-path distillation at 1.5 mmHg and 100–120 °C gave 1-methylthiomethoxycyclohexene (13) (0.23 g, 90%) as a colourless oil (Found: C, 60.85; H, 8.8; S, 19.95. C<sub>8</sub>H<sub>14</sub>OS requires C, 60.7; H, 8.9; S, 20.25%);  $\delta(\text{CDCl}_3)$  4.75 (2 H, s, OCH<sub>2</sub>S), 4.65 (1 H, m, 2-H), 2.15 (3 H, s, SMe), and 1.3–2.2 (8 H, complex);  $\nu_{\max.}$  (liquid film) 3 080 (=C–H), 1 670 (C=C), 1 380, 1 150, and 1 009 cm<sup>-1</sup>. Immediately after isolation the enol ether (13) showed a single symmetrical peak on g.l.c. (silicone oil; 150 °C) but decomposed with time to give a mixture of products on g.l.c., the predominant component being cyclohexanone.

(b) *With Potassium *t*-Butoxide in DMSO.* To a solution of potassium *t*-butoxide (0.45 g, 4.0 mmol) in dry DMSO (15 ml) at 15 °C was added with stirring, the *cis*- $\beta$ -hydroxy silane (12) (0.5 g, 2.0 mmol) in dry DMSO (5 ml); the mixture became red following the addition. After 2 h, g.l.c. (silicone oil; 150 °C) indicated one main component, *R*<sub>t</sub> 8.5 min, and the reaction mixture was poured into water (40 ml) and light petroleum (b.p. 40–60 °C; 40 ml). The aqueous layer was extracted with more light petroleum (2 × 20 ml) and the combined petroleum extracts were washed with brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave an oil (0.28 g). Short-path distillation at 0.9 mmHg and 120–140 °C gave *trans*-2-methylthiomethoxycyclohexanol (16) (0.25 g, 71%) as a colourless oil (Found: C, 54.25; H, 9.3; S, 18.35. C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>S requires C, 54.5; H, 9.15; S, 8.2%);  $\delta_{\text{H}}(\text{CDCl}_3)$  4.65 (2 H, ABq, OCH<sub>2</sub>S), 3.4 (2 H, m, 1-H and 2-H), 2.9 (1 H, br s, D<sub>2</sub>O exch., OH), 2.2 (3 H, s, SMe), and 0.9–2.1 (8 H, complex);  $\nu_{\max.}$  (liquid film) 3 440 (br, OH), 1 500, 1 070, and 845 cm<sup>-1</sup>;  $\delta_{\text{C}}$  (CDCl<sub>3</sub> solvent and reference) 81.8 (d, C-1), 73.6 (t, OCH<sub>2</sub>S), 73.5 (d, C-2), 32.4 (t), 29.4 (t), 24.1 (t), 23.8 (t), and 14.0 (q, SMe).

***trans*-2-Acetoxy-1-methylthiomethoxycyclohexane.**—To a mixture of dry DMSO (42 ml), glacial acetic acid (12 ml), and acetic anhydride (28 ml) was added, with stirring, *trans*-2-acetoxycyclohexanol<sup>13</sup> (2.3 g, 14.6 mmol). The mixture was left to stand at 18 °C for 48 h and was then slowly poured into saturated aqueous sodium hydrogencarbonate (250 ml). The mixture was extracted with chloroform (3 × 100 ml) and the combined extracts were then washed consecutively with water, saturated aqueous sodium carbonate, and brine, and then dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by distillation gave the methylthiomethyl ether (2.8 g, 89%), b.p. 85–90 °C at 0.01 mmHg (Found: C, 55.3; H, 8.05; S, 14.3. C<sub>10</sub>H<sub>18</sub>O<sub>3</sub>S requires C, 55.0; H, 8.3; S, 14.7%);  $\delta(\text{CDCl}_3)$  4.7 (2 H, s, OCH<sub>2</sub>S), 4.7 (1 H, m, 2-H), 3.6 (1 H, m, 1-H), 2.0 (3 H, s, SMe), 2.1 (3 H, s, COMe), and 1.2–2.2 (8 H, complex);  $\nu_{\max.}$  (liquid film) 1 740 (C=O), 1 370, 1 240, and 1 070 cm<sup>-1</sup>.

***trans*-2-Methylthiomethoxycyclohexanol (16).**—*trans*-2-Acetoxy-1-methylthiomethoxycyclohexane (1.7 g, 7.8 mmol)

was added to 10% methanolic potassium hydroxide (40 ml) and the mixture was stirred at 18 °C for 20 h. Water (80 ml) was then added and the mixture was extracted with ether (3 × 50 ml). The combined ether layers were then washed with brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by short-path distillation at 0.9 mmHg and 120–140 °C gave the alcohol (16) (0.82 g, 60%) which had identical n.m.r. and i.r. spectroscopic data to the product from the reaction of the *cis*- $\beta$ -hydroxy silane (12) with potassium *t*-butoxide in DMSO, and gave rise to a peak with the same *R*<sub>t</sub>, 8.5 min on g.l.c. (silicone oil; 150 °C), shown by co-injection.

***c*-2-Methylthiomethoxy-*t*-2-trimethylsilylcyclohexan-*r*-1-ol (8).**—*t*-2-Acetoxy-1-methylthiomethoxy-*r*-1-trimethylsilylcyclohexane (7) (3.9 g, 13.4 mmol) was hydrolysed as for the isomeric acetate (11) to give the *trans*- $\beta$ -hydroxy silane (8) (2.4 g, 72%), m.p. 58–61 °C (Found: C, 52.8; H, 9.55; S, 12.8. C<sub>11</sub>H<sub>24</sub>O<sub>2</sub>SSi requires C, 53.2; H, 9.75; S, 12.9%);  $\delta(\text{CDCl}_3)$  4.55 (2 H, s, OCH<sub>2</sub>S), 3.5 (1 H, m, *W*<sub>H</sub> 17.5 Hz, 1-H), 2.25 (3 H, s, SMe), 1.0–2.1 (9 H, complex, 8 H after D<sub>2</sub>O exch.), and 0.2 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\max.}(\text{CHCl}_3)$  3 470br (OH), 1 340, 1 070, and 840 cm<sup>-1</sup> (C–Si).

**Reactions of *c*-2-Methylthiomethoxy-*t*-2-trimethylsilylcyclohexan-*r*-1-ol (8).**—(a) *With methanesulphonyl chloride.* To a solution of the *trans*- $\beta$ -hydroxy silane (8) (0.29 g, 1.17 mmol) in dry pyridine (5 ml) at 0 °C was added, with stirring, methanesulphonyl chloride (108  $\mu$ l, 0.16 g, 1.38 mmol). The mixture was allowed to warm slowly to 18 °C and stirring was continued at 18 °C for 18 h. Water (4 drops) was added followed after 5 min by further water (15 ml) and ether (15 ml). The aqueous layer was extracted with ether (2 × 10 ml), and the combined ether extracts were washed with 2M-HCl (15 ml), saturated aqueous sodium hydrogencarbonate, and brine, and then dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by short-path distillation at 1.5 mmHg and 100–130 °C gave 1-methylthiomethoxycyclohexene (13) (0.18 g, 94%), identified by comparison of n.m.r. and i.r. spectra and co-injection on g.l.c. (silicone oil; 150 °C) with the authentic sample produced by reaction of the *cis*- $\beta$ -hydroxy silane (12) with potassium hydride in THF.

(b) *With potassium *t*-butoxide in DMSO.* To a solution of potassium *t*-butoxide (0.41 g, 3.6 mmol) in dry DMSO (12 ml) at 17 °C was added, with stirring, the *trans*- $\beta$ -hydroxy silane (8) (0.45 g, 1.8 mmol) in dry DMSO (4 ml); the mixture gradually became dark red. After 1.5 h, g.l.c. (silicone oil; 150 °C) indicated one main component, *R*<sub>t</sub> 7.5 min, and the reaction mixture was poured into water (30 ml) and light petroleum (b.p. 40–60 °C; 30 ml). The aqueous layer was extracted with light petroleum (b.p. 40–60 °C; 30 ml). The aqueous layer was extracted with light petroleum (2 × 15 ml) and the combined petroleum layers were then washed with brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave an oil (0.3 g). Short-path distillation at 1.5 mmHg and 100–120 °C gave *cis*-2-methylthiomethoxycyclohexanol (15) (0.23 g, 79%) as a colourless oil (Found: C, 54.25; H, 8.9; S, 18.4. C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>S requires C, 54.5; H, 9.15; S, 18.2%);  $\delta_{\text{H}}(\text{CDCl}_3)$  4.6 (2 H, ABq, OCH<sub>2</sub>S), 3.7 (2 H, m, 1-H and 2-H), 2.3 (1 H, s, OH, D<sub>2</sub>O exch.), 2.1 (3 H, s, SMe), and 1.0–2.0 (8 H, complex);  $\nu_{\max.}$  (liquid film) 3 470 (br, OH), 1 500, 1 070, and 980 cm<sup>-1</sup>;  $\delta_{\text{C}}$  (CDCl<sub>3</sub> solvent and reference) 76.3 (d, C-1), 72.7 (t, OCH<sub>2</sub>S), 68.6 (d, C-2), 30.4 (t), 26.4 (t), 22.2 (t), 21.0 (t), and 13.8 (q, SMe).

***t*-2-Acetoxy-1-methylthiomethoxy-*r*-1-trimethylsilylcyclooctane (20).**—*c*-2-Acetoxy-1-trimethylsilylcyclooctan-*r*-1-ol (19) (3 g, 11.6 mmol) was added to a mixture of dry DMSO (34 ml), glacial acetic acid (9 ml), and acetic anhydride (23 ml). The mixture was left at 18 °C for 40 h and isolation with chloroform

in the usual way followed by short-path distillation at 0.01 mmHg and 120–130 °C gave the *methylthiomethyl ether* (**20**) as a colourless oil (2.7 g, 72%) (Found: C, 56.65; H, 9.6; S, 9.7.  $C_{15}H_{30}O_3SSi$  requires C, 56.55; H, 9.5; S, 10.05%;  $\delta(CDCl_3)$  4.9 (1 H, d,  $J$  8 Hz, 2-H), 4.6 (2 H, s,  $OCH_2S$ ), 2.2 (3 H, s, SMe), 2.0 (3 H, s, COMe), 1.2–2.2 (12 H, complex), and 0.2 (9 H, s, SiMe);  $\nu_{max.}$  (liquid film) 1 735 (C=O), 1 379, 1 245, 1 043, and 840  $cm^{-1}$  (C–Si).

*c-2-Methylthiomethoxy-t-2-trimethylsilylcyclo-octan-r-1-ol* (**21**).—*t-2-Acetoxy-1-methylthiomethoxy-r-1-trimethylsilyl cyclo-octane* (**20**) (1.27 g, 3.99 mmol) was hydrolysed with 10% methanolic potassium hydroxide (20 ml) in the usual way. Isolation with ether gave the *trans- $\beta$ -hydroxy silane* (**21**) (0.80 g, 73%) as an oil which eventually solidified to give a sticky solid, m.p. 38–43 °C after recrystallisation from light petroleum (b.p. 30–40 °C) (Found: C, 56.3; H, 10.45; S, 11.3.  $C_{13}H_{28}O_2SSi$  requires C, 56.45; H, 10.2; S, 11.6%;  $\delta(CDCl_3)$  4.65 (2 H, s,  $OCH_2S$ ), 3.95 (1 H, br d,  $J$  9 Hz, sharpened on  $D_2O$  exch., 2-H), 2.6 (1 H, br d,  $D_2O$  exch., OH), 1.2–2.2 (12 H, complex), and 0.3 (9 H, s, SiMe<sub>3</sub>);  $\nu_{max.}$  (CHCl<sub>3</sub>) 3 580 (OH), 1 450, 1 050, and 850  $cm^{-1}$  (C–Si).

Recrystallisation of this low melting point solid was difficult and usually gave poor recovery of material that was spectroscopically not of better quality than the crude product. In general, purification was brought about by removal of volatile impurities under high vacuum (0.01 mmHg) using an oil pump.

*Reaction of c-2-Methylthiomethoxy-t-2-trimethylsilylcyclo-octan-r-1-ol* (**21**) with Potassium Hydride in THF.—Potassium hydride (20% dispersion in oil; 0.31 g, 1.5 mmol) was washed under nitrogen with light petroleum (b.p. 30–40 °C, 3 × 5 ml) then dry THF (4 ml) was added and the mixture was cooled to 0 °C. The *trans- $\beta$ -hydroxy silane* (**21**) (0.28 g, 1.0 mmol) in dry THF (1 ml) was then added under nitrogen. The mixture was stirred at 0 °C for a further 20 min and then poured into water (20 ml) and light petroleum (b.p. 40–60 °C; 15 ml). The aqueous layer was extracted with further light petroleum (2 × 15 ml) and the combined organic layers were washed with brine and then dried (MgSO<sub>4</sub>). Evaporation of the solvent using a cold water bath gave an oil (0.26 g) considered to contain mainly 1-methylthiomethoxy-*trans*-cyclo-octene (**23**),  $\delta(CDCl_3)$  4.93 (1 H, dd,  $J$  4, 12.5 Hz, 2-H), 4.88 (2 H, s,  $OCH_2S$ ), 2.17 (3 H, s, SMe), and 0.8–2.6 (12 H, complex);  $\nu_{max.}$  (liquid film) 3 020 (=C–H), 1 660 (C=C), 1 450, 1 257, 1 045, and 843  $cm^{-1}$ .

The *trans*-enol ether (**23**) was unstable and isolation of the compound pure by distillation or chromatography was not possible. It had a half-life of ca. 40 min at 15 °C and isomerized to 1-methylthiomethoxy-*cis*-cyclo-octene (Found:  $M^+$ , 186.1078.  $C_{10}H_{18}OS$  requires  $M$ , 186.1078);  $\delta(CDCl_3)$  4.78 (2 H, s,  $OCH_2S$ ), 4.53 (1 H, t,  $J$  7.5 Hz, 2-H), 2.17 (3 H, s, SMe), and 0.8–2.6 (12 H, complex);  $\nu_{max.}$  (liquid film) 3 062 (=C–H), 1 665 (C=C), 1 465, 1 260, 1 152, and 1 080  $cm^{-1}$ ;  $m/z$  186 ( $M^+$ , 2%), 139 ( $M^+ - SMe$ , 11), 61 (CH=SMe<sup>+</sup>, 100), 55 (14), 41 (16), and 39 (10).

The isomerization of the *trans*-enol ether (**23**) to the *cis*-isomer could be followed by n.m.r. and i.r. spectroscopy. Complete conversion took place on g.l.c. (3% silicone oil; 140 °C) such that even samples containing the mainly *trans*-isomer gave a single peak of  $R$ , 15.9 min corresponding to *cis*-isomer. The latter was also unstable and decomposed slowly with time to cyclo-octanone; isolation of the *cis*-isomer pure was thus not possible, and mass spectroscopic data were obtained using g.l.c.–mass spectroscopy.

*c-2-Acetoxy-1-methoxy-r-1-trimethylsilylcyclohexane* (**14**).—To a slurry of Raney nickel (2 g) in ethanol (8 ml) was added,

with vigorous stirring, *c-2-acetoxy-1-methylthiomethoxy-r-1-trimethylsilylcyclohexane* (**11**) (0.2 g, 0.69 mmol). The mixture was stirred at 70–80 °C for 1 h and then cooled and filtered through Celite. The Celite pad was washed with ethanol (3 × 10 ml), and then the combined ethanol solutions were partitioned between water (50 ml) and light petroleum (b.p. 40–60 °C; 30 ml). The aqueous layer was extracted with light petroleum (3 × 10 ml) and the combined petroleum layers were then washed with brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by short-path distillation at 0.01 mmHg and 80–100 °C gave the *methoxy acetate* (**14**) (0.15 g, 89%) (Found: C, 58.85; H, 10.0.  $C_{12}H_{24}O_3Si$  requires C, 59.0; H, 9.9%;  $\delta(CDCl_3)$  5.2 (1 H, m,  $W_H$  12 Hz, 2-H), 3.3 (3 H, s, OMe), 2.1 (3 H, s, COMe), 1.2–2.1 (8 H, complex), and 0.2 (9 H, s, SiMe<sub>3</sub>);  $\nu_{max.}$  (liquid film) 1 740 (C=O), 1 370, 1 230, 1 080, and 840  $cm^{-1}$  (C–Si).

*t-2-Acetoxy-1-methoxy-r-1-trimethylsilylcyclo-octane*.—To a slurry of Raney nickel (13 g) in benzene (30 ml) was added with vigorous stirring, *t-2-acetoxy-1-methylthiomethoxy-r-1-trimethylsilylcyclo-octane* (**20**) (1.3 g, 4.09 mmol). The mixture was stirred at 25–30 °C for 1 h and then filtered through Celite. The Celite pad was washed with benzene (2 × 20 ml) and the combined filtrate and washings were then washed with water and brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by short-path distillation at 0.01 mmHg and 110–120 °C gave the *methoxy acetate* (1.05 g, 94%) (Found: C, 61.8; H, 10.4.  $C_{14}H_{28}O_3Si$  requires C, 61.7; H, 10.35%;  $\delta(CDCl_3)$  4.9 (1 H, d,  $J$  8 Hz, 2-H), 3.35 (3 H, s, OMe), 2.1 (3 H, s, COMe), 1.3–2.3 (12 H, complex), and 0.2 (9 H, s, SiMe<sub>3</sub>);  $\nu_{max.}$  (liquid film) 1 745 (C=O), 1 367, 1 245, 1 080, and 843  $cm^{-1}$  (C–Si).

*c-2-Methoxy-t-2-trimethylsilylcyclo-octan-r-1-ol* (**22**).—*t-2-Acetoxy-1-methoxy-r-1-trimethylsilylcyclo-octane* (0.69 g, 2.54 mmol) was added to 10% methanolic potassium hydroxide (10 ml) and the mixture was stirred at 45 °C for 16 h. The mixture was then poured into water (30 ml) and ether (25 ml). The aqueous layer was re-extracted with ether (3 × 15 ml), and the combined ether extracts were washed with brine (2 × 15 ml) and dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by short-path distillation at 0.005 mmHg and 115–125 °C gave the *trans- $\beta$ -hydroxy silane* (**22**) (0.46 g, 79%) (Found: C, 62.4; H, 11.45.  $C_{12}H_{26}O_2Si$  requires C, 62.55; H, 11.35%;  $\delta(CDCl_3)$  3.9 (1 H, dd,  $J$  9.7, 7.8 Hz, collapses to d,  $J$  7.8 Hz on  $D_2O$  exch., 2-H), 3.35 (3 H, s, OMe), 2.75 (1 H, d,  $J$  9.7 Hz,  $D_2O$ , exch., OH), 1.2–2.2 (12 H, complex), and 0.2 (9 H, s, SiMe<sub>3</sub>);  $\nu_{max.}$  (liquid film) 3 660, 3 460 (OH), 1 448, 1 249, 1 080, and 845  $cm^{-1}$  (C–Si).

The distilled product eventually solidified to give a sticky solid, m.p. 49–52 °C after recrystallization from light petroleum (b.p. 40–60 °C). The recovery of material after recrystallization was poor and on the basis of its n.m.r. and i.r. spectra, its quality was not significantly improved from that of the distilled product. In general, the distilled material was used for subsequent reactions.

*Reaction of c-2-Methoxy-t-2-trimethylsilylcyclo-octan-r-1-ol* (**22**) with Potassium Hydride in THF.—Potassium hydride (20% dispersion in oil; 0.26 g, 1.3 mmol) was washed under nitrogen with light petroleum (b.p. 30–40 °C; 3 × 4 ml) then dry THF (3.5 ml) was added and the mixture was cooled to 0 °C. To this was added the *trans- $\beta$ -hydroxy silane* (**22**) (0.2 g, 0.87 mmol) in dry THF (1 ml) under nitrogen. The mixture was stirred at 0 °C for a further 30 min and was then poured into water (15 ml) and light petroleum (b.p. 30–40 °C; 15 ml). The aqueous layer was extracted with light petroleum (2 × 12 ml) and the combined organic layers were washed with brine and dried (MgSO<sub>4</sub>). Evaporation of the solvent using a cold water bath gave an oil

(0.11 g) considered to contain mainly 1-methoxy-*trans*-cyclooctene (**25**),  $\delta(\text{CDCl}_3)$  4.63 (1 H, dd,  $J$  4.3, 12.3 Hz, 2-H), 3.57 (3 H, s, OMe), and 0.85–2.58 (12 H, complex);  $\nu_{\text{max}}$  (liquid film) 3 040 (=C–H), 1 660 (C=C), 1 450, 1 360, and 1 160  $\text{cm}^{-1}$ .

The *trans*-enol ether (**25**) was unstable and isolation of a pure sample by distillation or chromatography was not possible. It isomerized with time to give 1-methoxy-*cis*-cyclooctene.<sup>14</sup> Even freshly prepared samples containing mainly the *trans*-enol ether (**25**) gave only a single main peak, of  $R_f$  6.4 min on g.l.c. (silicone oil; 170 °C) which corresponded to the *cis*-isomer as shown by co-injection. The isomerization of (**25**) was followed by n.m.r., spectra of separate samples of freshly prepared *trans*-enol ether (**25**) in  $\text{CDCl}_3$  and  $\text{CCl}_4$  solutions being recorded at intervals.

*Note added in proof.* A recent paper<sup>15</sup> describes the hydroxylation of vinylsilanes by osmium tetroxide and the conversion of the glycols obtained into silyl enol ethers.

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