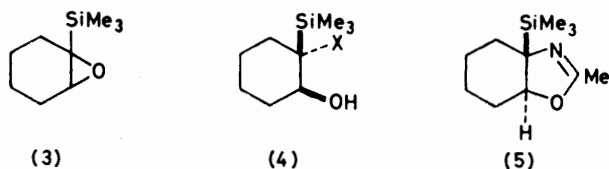


## Some Epoxide Ring-opening Reactions of $\alpha\beta$ -Epoxy-silanes

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Epoxide ring-opening of 1,2-epoxy-1-trimethylsilylcyclohexane (3) has given a range of the 2-substituted 2-trimethylsilylcyclohexanols (4; X = H, OH, OMe,  $\text{OCH}_2\text{CH}=\text{CH}_2$ , Br, I, SCN) in which attack by nucleophile has occurred at the carbon  $\alpha$  to silicon. The products (4) have been transformed into a number of functionalised silanes, including the silyl-episulphide (9). Other epoxides which have been less extensively studied are the conformationally biased epoxy-silanes (10) and (11), the eight-membered ring epoxy-silanes (17) and (21) and the two stereoisomeric 2,3-epoxy-3-trimethylsilylpentanes (26) and (29). Epoxide ring-opened adducts were obtained after treatment with  $\text{H}^+\text{-MeOH}$  in all cases except for compound (17), where the bicyclic alcohol (18) was formed by a transannular reaction.

STORK demonstrated, several years ago,<sup>1</sup> the synthetic equivalence between an  $\alpha\beta$ -epoxy-silane and an aldehyde or ketone, *i.e.* (1)  $\equiv$  (2), and sparked off interest in such epoxy-silanes. In the subsequent years their chemistry has been extensively explored,<sup>2-4</sup> particularly significant developments having been forthcoming from the work of Hudrlik<sup>2</sup> and Magnus<sup>3</sup> and their collaborators. Our interest in this area was indicated in a preliminary communication<sup>5</sup> and we now give details of that work and report on some extensions of it.



a; X = OMe  
b; X = OH  
c; X =  $\text{OCH}_2\text{CH}=\text{CH}_2$   
d; X = Br  
e; X = I  
f; X = SCN  
g; X = H  
h; X = NCS  
i; X = NHAc

Initial investigations were carried out with the cyclohexane (3). In this cyclic system, the stereochemistry of the product should provide useful information about the course of reaction. We find that under a variety of conditions, with catalysis by acid or other electrophile, preparatively useful yields of the epoxide ring-opened products are obtained. Thus, with sulphuric acid (5%) in aqueous acetone the glycol (4b) was obtained in 83% yield, sulphuric acid (5%) in methanol gave the ether (4a) (78%) together with a small amount of the glycol (4b), and with allyl alcohol-sulphuric acid the allyl ether (4c) was formed. The halohydrins (4d) and (4e) were produced in 90% and 70% yields, respectively, on treatment of compound (3) with aqueous solutions of the appropriate hydrogen halide. Similarly the hydroxy-thiocyanate (4f) was obtained (65%) from the cyclo-

hexane (3) and ethereal 'thiocyanic acid', and the *cis*-silyl alcohol (4g) (92%) was formed on reduction with lithium aluminium hydride in ether.

The alcohol (4g) was already known,<sup>6</sup> and the structure and stereochemistry of (4a) was confirmed by its ready Peterson elimination<sup>2a,7</sup> to give 1-methoxycyclohexene on treatment with sodium hydride in dimethylformamide (DMF). Structures of the other products (4) were assigned on the basis of spectroscopic data (see Experimental section). In no case was there any evidence, in the crude product from the ring-opening reactions, for the presence of regio- or stereo-isomers of the products (4), though the thiocyanate (4f) was accompanied by a small amount of the isomeric isothiocyanate (4h). Subsequent to the preliminary account of our work, Hudrlik *et al.*<sup>2d</sup> have also reported the stereospecific preparation of (4a), (4b), and (4d) from compound (3).

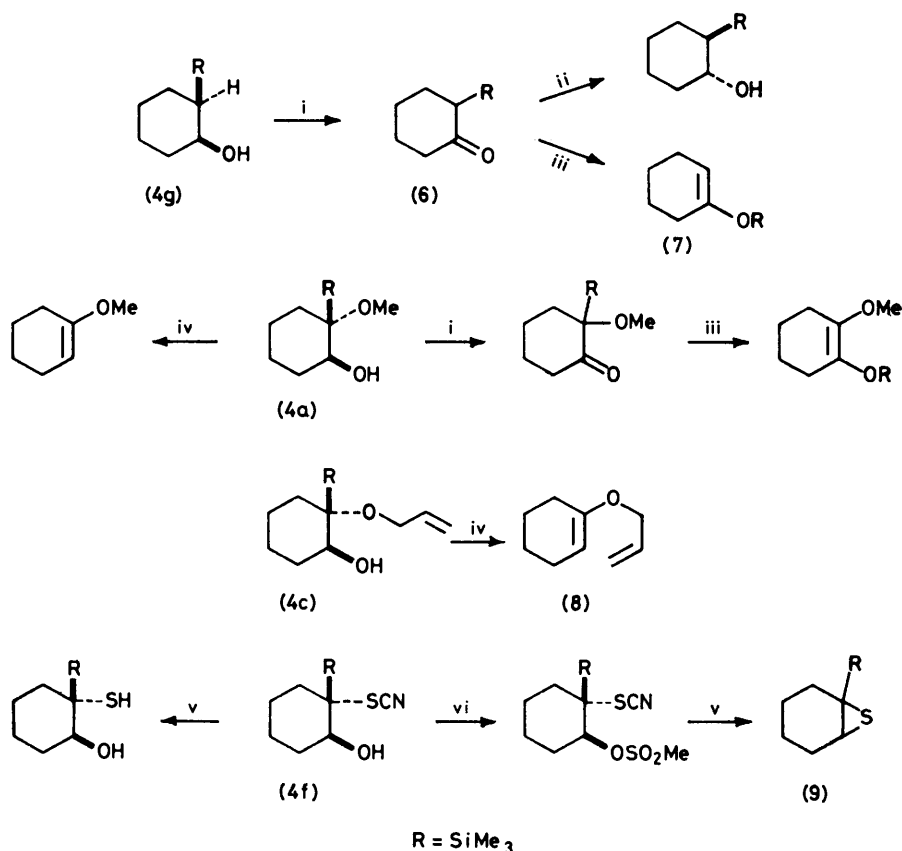
The acid-catalysed reaction of the epoxide (3) with acetonitrile did not give a simple ring-opened product as the major component; instead the oxazoline (5), a product of intramolecular capture of the intermediate nitrilium ion, was formed, accompanied by the hydroxy-amide (4i) as a minor product.

A number of relatively straightforward transformations were carried out on some of the adducts (4) to illustrate their potential as precursors of functionalised silanes, *etc.* These transformations are summarised in the Scheme. One or two points can be singled out for brief mention. The  $\alpha$ -silyl ketone (6) could be distilled unchanged below 98 °C; above that temperature it underwent 'Brook rearrangement'<sup>8</sup> into the silyl enol ether (7). The conversion of (4c) into the allyl vinyl ether (8) indicates the possible use of epoxy-silanes to generate such ethers preparatory to Claisen rearrangement. The hydroxy-thiocyanate (4f) has been transformed *via* the methane sulphonate into the novel silyl-episulphide (9).

It is clear from the above examples of reactions of the epoxy-silane (3) that there is a marked tendency for attack of nucleophile to occur at the carbon  $\alpha$  to silicon. It was therefore of interest to investigate the ring-opening of a conformationally biased epoxy-silane.

When the mixture of epoxysilanes (10) and (11), obtained by epoxidation of 4-*t*-butyl-1-trimethylsilylcyclohexene, was treated with lithium aluminium hydride in ether, the epoxide (10) reacted faster to give compound (12), the product of attack  $\alpha$  to silicon, by diaxial opening. The stereoisomeric epoxide (11) reacted with lithium triethylborohydride to give the silyl alcohol (13) in which diaxial opening had dominated, resulting in attack  $\beta$  to silicon.\* Opening with methanolic acid is less clear cut, although the *cis*-epoxide gave the ether (14), the *trans*-

methylsilylcyclo-octanol (9 : 1) was obtained. It is considered that the small amount of *trans*-silyl alcohol had been derived *via* rearrangement of the epoxide into 2-trimethylsilylcyclo-octanone which itself was shown to give a 1:1 mixture of the two stereoisomeric silyl alcohols on reduction with lithium aluminium hydride under the same conditions. Attempts to obtain epoxide ring-opened products from compound (17) under conditions of acid catalysis, *e.g.* sulphuric acid in methanol, gave the bicyclic alcohol (18). Apparently,



SCHEME Reagents: i,  $\text{CrO}_3$ -pyridine; ii, Li-liquid  $\text{NH}_3$ ; iii, heat; iv, NaH-DMF; vi,  $\text{LiAlH}_4$ - $\text{Et}_2\text{O}$ , then  $\text{H}_3\text{O}^+$ ; vi,  $\text{MeSO}_2\text{Cl}$ -pyridine

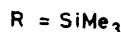
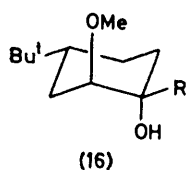
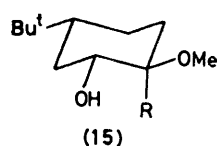
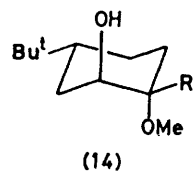
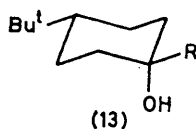
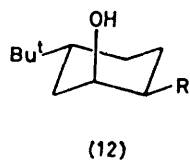
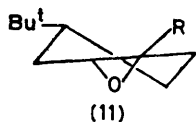
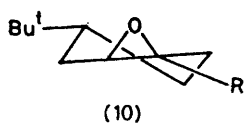
epoxide formed a mixture of two products tentatively considered to be the isomeric ethers (15) and (16) in the ratio 3 : 2, respectively. The opposing, directing effects of diaxial opening and attack  $\alpha$  to silicon are thus roughly balanced for this reaction.

We have also investigated the eight-membered ring epoxysilane (17) since it was of interest to find out how far the known reluctance of medium-ring compounds to suffer  $\text{S}_{\text{N}}2$  substitution might influence the mode of reaction. With lithium aluminium hydride [in tetrahydrofuran (THF)] a mixture of *cis*- and *trans*-2-tri-

transannular hydride migration can compete efficiently with attack by external nucleophile, and reaction is completed by transannular loss of the trimethylsilyl group: (19)  $\rightarrow$  (20)  $\rightarrow$  (18).

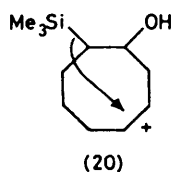
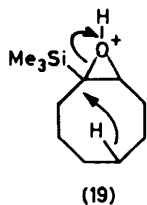
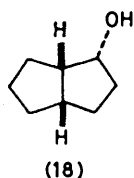
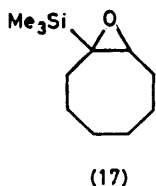
The unsaturated epoxysilane (21) was also studied to determine the competition between transannular double-bond participation and simple epoxide ring-opening. Treatment of (21) with sulphuric acid in methanol gave the methoxy-alcohol (22), obtained by nucleophilic attack of methanol  $\alpha$  to silicon, as the major product. An accompanying minor product was tentatively assigned the structure (23), considered to have been derived by transannular double-bond participation followed by carbonium ion rearrangement to give the aldehyde precursor of (23).

\* Paquette *et al.*<sup>9</sup> have reported that predominant attack  $\alpha$  to silicon occurs on reduction of the *trans*-epoxide (11) with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  (1 : 1). Apparently the more electrophilic hydride shows the greater tendency to be directed by the silicon.

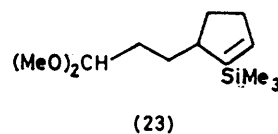
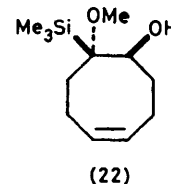
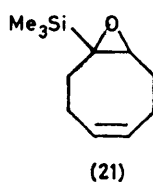


In the original work of Stork on  $\alpha\beta$ -epoxysilanes as carbonyl precursors, a mechanism involving cleavage of the  $\beta$  C-O bond was proposed,<sup>1</sup> *cf.* (24). Our results described above and those of other workers<sup>2</sup> suggested that  $\alpha$  C-O cleavage was more likely, followed by acid-catalysed *anti*-elimination of  $\text{Me}_3\text{SiOH}$ , *e.g.* (25). In the case of derivatives of type (4) such eliminations would be disfavoured stereoelectronically. It was therefore of interest to examine the reactions of an acyclic epoxysilane, suitably substituted to exist in diastereoisomeric forms, to see if intermediate epoxide ring-opened products could be isolated.

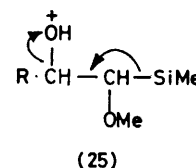
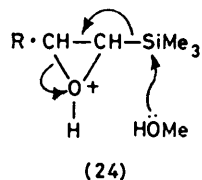
Treatment of the *Z*-epoxysilane (26) with sulphuric acid in methanol gave the adduct (27a) which was characterised and the stereochemistry corroborated by



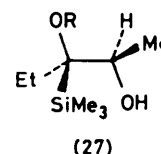
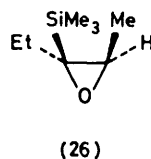
Peterson elimination to give the enol ether (28). Similarly, the diol (27b) was obtained from treatment of compound (26) with aqueous acid in THF. Isomeric adducts were obtained from the *E*-epoxysilane (29), but because they underwent more rapid elimination they were not fully characterised.



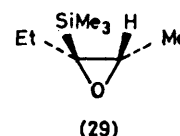
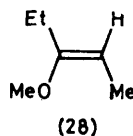
In summary, the experiments described above taken in conjunction with those of other workers<sup>2</sup> indicate the high susceptibility of  $\alpha\beta$ -epoxytrimethylsilanes to undergo attack by nucleophiles at the carbon  $\alpha$  to silicon under conditions of electrophilic catalysis. We believe that the



reactions are  $S_N2$  'borderline' type<sup>10</sup> displacements with the  $\alpha$ -trimethylsilyl group providing assistance, possibly by prior or concomitant co-ordination with the nucleophile, along the lines suggested for nucleophilic displacement on  $\alpha$ -silyl halides.<sup>11</sup> Apparently the triphenylsilyl group is less efficient in this respect.<sup>12</sup>



a; R = Me  
b; R = H



The availability of *cis*- and *trans*-2-trimethylsilylcyclooctanol, albeit as mixtures, presented the opportunity of testing the stereospecificity of the Peterson elimination in the somewhat demanding medium-ring system. Treatment of mixtures of the two alcohols with sodium

hydride in dimethyl sulphoxide gave *cis*- and *trans*-cyclo-octene in the same ratio as the *cis*- and *trans*-isomers in the precursor. Clearly the *syn*-elimination pathway is still followed, even for formation of the highly strained *trans*-cyclo-octene. It was not found possible to induce an *anti*-elimination to the *trans*-olefin, e.g. treatment of predominantly *cis*-2-trimethylsilylcyclo-octanol with methanesulphonyl chloride in triethylamine<sup>13</sup> (conditions under which *trans*-cyclo-octene was shown to be stable) gave only *cis*-cyclo-octene presumably by a *syn*-elimination pathway. Thus, even with trimethylsilyl as an electrofugal group, *anti*-elimination cannot be contrived and there is as yet no example of a substrate which gives *trans*-cyclo-octene by this mechanism.

#### EXPERIMENTAL

Instruments used were (i.r.) Perkin-Elmer 257, (<sup>1</sup>H n.m.r.) Perkin-Elmer R32 (90 MHz) and R24 (60 MHz) (CHCl<sub>3</sub> as internal standard for compounds containing Me<sub>3</sub>Si, otherwise Me<sub>2</sub>Si), and (g.l.c.) Pye 104.

1-Trimethylsilyl-7-oxabicyclo[4.1.0]heptane (3).—A mixture of 1-trimethylsilylcyclohexene<sup>14</sup> (30 g, 0.2 mol) and dichloromethane (60 ml) was stirred and cooled (ice-water). Peracetic acid (49% w/v; 60 ml, 0.46 mol), buffered with anhydrous sodium acetate (8.7 g), was added slowly during 1 h with further cooling. The mixture was stirred at 20 °C for 30 min. G.l.c. (15% Silicone oil, 150 °C) showed the reaction to be complete and sodium hydroxide solution (16% w/v; 250 ml) was slowly added until the mixture was pH 14. The organic layer was separated and the aqueous phase was extracted with ether (3 × 70 ml). The extracts were combined, washed with brine, and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave a colourless oil (36.5 g), which on distillation afforded the *bicycloheptane* (3) (27.4 g, 83%), b.p. 112–114 °C at 73 mmHg; g.l.c. showed largely one component (97.4%); δ (CCl<sub>4</sub>) 2.81 (1 H, 6-H), 1–2 (8 H, complex), and –0.05 (9 H, s, Me<sub>3</sub>Si); ν<sub>max</sub> (liquid film) 1 250 and 850 cm<sup>-1</sup> (C–Si) (Found: C, 63.6; H, 10.35. C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>Si requires C, 63.45; H, 10.65%).

*t*-2-Methoxy-2-trimethylsilylcyclohexan-*r*-1-ol (4a).—The silyl epoxide (3) (2.2 g, 13 mmol) was added to concentrated sulphuric acid (1 ml, 18 mmol) and dry methanol (20 ml) at 0 °C. After 5 min, sodium hydroxide solution (10% w/v; 20 ml), was added rapidly with further cooling. Water (20 ml) was added and the mixture was extracted with ether (3 × 15 ml). The combined ether extracts were washed with brine and dried (MgSO<sub>4</sub>). The ether was evaporated to give a white solid (2.5 g) which was chromatographed on a silica-gel column [ether–light petroleum (3 : 7) as eluant]. Fractions were collected and analysed by t.l.c. The major product was obtained from early fractions, R<sub>F</sub> 0.5 (2.03 g), and a minor product was obtained from later fractions, R<sub>F</sub> 0.2 (0.21 g). Both were recrystallised from light petroleum. The main product was the cyclohexanol (4a), m.p. 82–83 °C; δ (CCl<sub>4</sub>) 3.9 (1 H, t, 1-H), 3.3 (3 H, s, MeO), 2.1–1.2 (9 H, complex; 8 H, after D<sub>2</sub>O exchange), and 0.2 (9 H, s, Me<sub>3</sub>Si); ν<sub>max</sub> (Nujol mull) 3 400br (bonded OH), 1 250, and 850 cm<sup>-1</sup> (C–Si) (Found: C, 59.3; H, 10.95. C<sub>10</sub>H<sub>22</sub>O<sub>2</sub>Si requires C, 59.35; H, 10.95%). The minor product, m.p. 82–83 °C, was *c*-2-trimethylsilylcyclohexane-*r*-1,2-diol (4b) (8.7% yield), mixed m.p. 82–83 °C with authentic material (see below).

*t*-2-Allyloxy-2-trimethylsilylcyclohexan-*r*-1-ol (4c).—Con-

centrated sulphuric acid (0.7 ml, 13 mmol) was added in drops to the epoxysilane (3) (1.5 g, 9 mmol) in dry allyl alcohol (15 ml) at 0 °C. After warming to room temperature and stirring for 5 min, sodium hydroxide solution (10% w/v; 12 ml) was added rapidly with further cooling. Isolation with ether followed by chromatography on silica gel and crystallisation from light petroleum gave the *cyclohexanol* (4c) (1.2 g, 60% yield), m.p. 56–57 °C (Found: C, 62.5; H, 10.8. C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>Si requires C, 63.0; H, 10.6%); δ (CCl<sub>4</sub>) 6.0–5.6 and 5.3–4.9 (3 H, complex, CH<sub>2</sub>=CH), 3.9–3.8 (3 H, complex, OCH<sub>2</sub>, 1-H), 1.9–1.2 (9 H, complex, ring CH<sub>2</sub>, OH), and 0.1 (9 H, s, Me<sub>3</sub>Si).

*c*-2-Trimethylsilylcyclohexane-*r*-1,2-diol (4b).—Concentrated sulphuric acid (1 ml) was added to water (2 ml) and acetone (25 ml) at 0 °C. The silyl epoxide (3) (1 g, 5.8 mmol) was added and the mixture was stirred at 20 °C for 10 min. Sodium hydroxide solution (10% w/v; 20 ml) was added with cooling, followed by water (10 ml). The aqueous layer was extracted with ether and the ether extracts were combined, washed with water and brine, and dried (MgSO<sub>4</sub>). The ether was evaporated to give a white solid (0.92 g, 83%); g.l.c. (15% Silicone oil, 150 °C) showed largely one component (96%). Recrystallisation from ether–light petroleum afforded crystals of the *diol* (4b), m.p. 82–83 °C; δ (CCl<sub>4</sub>) 3.55 (1 H, t, 1-H), 2–1.1 (10 H, complex; 8 H, after D<sub>2</sub>O exchange), and 0.12 (9 H, s, Me<sub>3</sub>Si); ν<sub>max</sub> (Nujol mull) 3 390br (bonded OH), 1 245, and 845 cm<sup>-1</sup> (C–Si) (Found: C, 57.4; H, 10.6. C<sub>9</sub>H<sub>20</sub>O<sub>2</sub>Si requires C, 57.4; H, 10.7%).

*t*-2-Bromo-2-trimethylsilylcyclohexan-*r*-1-ol (4d).—The silyl epoxide (3) (1.5 g, 9 mmol) was added to aqueous hydrogen bromide (48% w/v; 10 ml, 80 mmol) with cooling, during 5 min. The reaction mixture was allowed to stand for 30 min and a solid separated. Anhydrous sodium carbonate (5 g, 50 mmol) was added cautiously with further cooling, followed by ether (20 ml). The precipitated solids were filtered off and washed with ether; the ether extracts were combined, washed with water, and dried (MgSO<sub>4</sub>). The ether was evaporated to give an oil (2.1 g, 94%), shown by g.l.c. (3% Silicone oil, 150 °C) to be largely one component. Recrystallisation from aqueous methanol afforded the *cyclohexanol* (4d) (1.5 g, 67%), m.p. 23–28 °C; δ (CCl<sub>4</sub>) 4.1 (1 H, t, 1-H), 2.5–1.3 (8 H, complex; 1 H, s, OH), and 0.25 (9 H, s, Me<sub>3</sub>Si) (Found: C, 43.1; H, 7.65. C<sub>9</sub>H<sub>18</sub>BrOSi requires C, 43.0; H, 7.6%).

*t*-2-Iodo-2-trimethylsilylcyclohexan-*r*-1-ol (4e).—The *iodohydrin* (4e) was similarly prepared from the epoxysilane (3) and aqueous hydrogen iodide. It had m.p. 36–38 °C (Found: C, 35.8; H, 6.25; I, 42.4. C<sub>9</sub>H<sub>18</sub>IOSi requires C, 36.25; H, 6.4; I, 42.55%); δ (CDCl<sub>3</sub>) 4.25 (1 H, br s, H-1), 2.2–1.5 (9 H, m), and 0.25 (9 H, s, SiMe<sub>3</sub>); ν<sub>max</sub> (film) 3 450 (OH), 1 250, and 850 cm<sup>-1</sup> (C–Si).

*t*-2-Hydroxyl-1-trimethylsilylcyclohexan-*r*-1-yl Thiocyanate (4f).—Perchloric acid (60% aqueous; 1.7 ml, 10 mmol) was added to a potassium thiocyanate solution (0.97 g in 10 ml water, 10 mmol) and the precipitate was filtered off. The filtrate was shaken with ether (20 ml) and the ethereal solution was washed with brine and dried (MgSO<sub>4</sub>). The epoxysilane (3) (0.8 g, 4.7 mmol) was added to the solution, which was set aside at 20 °C for 24 h. The solution was then washed successively with sodium carbonate solution (10 ml) and brine, and then dried (MgSO<sub>4</sub>). Evaporation gave a viscous oil (0.98 g) which showed three spots on t.l.c. (chloroform–methanol, 95 : 5), R<sub>F</sub> 0.5 (intense), 0.45, and 0.2 (weak). The components were separated on a silica-gel (50 g) column (chloroform as eluant). The major product

was distilled to give the *hydroxy-thiocyanate* (4f) (0.7 g, 65%), b.p. 112–114 °C at 0.3 mmHg (Found: C, 52.6; H, 8.35; N, 5.95; S, 14.2.  $C_{10}H_{19}NOSSi$  requires, C, 52.35; H, 8.35; N, 6.1; S, 14.0%);  $\delta$  ( $CDCl_3$ ) 4.1–3.9 (1 H, t, 2-H), 2.4–1.4 (9 H, complex, ring  $CH_2$  and OH), and 0.3 (9 H, s,  $Me_3Si$ );  $\nu_{max}$ . (film) 3 480br (OH), 2 150sh (S–C≡N), 1 250, and 850sh  $cm^{-1}$  (C–Si). The minor product (0.1 g, 9%),  $R_F$  0.45 was considered to be the corresponding isothiocyanate (4h);  $\delta$  ( $CDCl_3$ ) 0.2 (9 H, s,  $Me_3Si$ );  $\nu_{max}$ . (liquid film) 2 150–2 000br  $cm^{-1}$  (N=C=S). The third component,  $R_F$  0.2, was considered to be a trace of the diol (4b).

*c-2-Trimethylsilylcyclohexan-r-1-ol* (4g).—The silyl epoxide (3) (9 g, 53 mmol) was added during 40 min to a magnetically stirred slurry of lithium aluminium hydride (2.3 g, 61 mmol) in dry ether (50 ml), to maintain gentle reflux. After a further 10 min, g.l.c. (3% Silicone oil, 120 °C) showed that no starting material was present. Water (30 ml) was added cautiously, followed by hydrochloric acid (2M, 100 ml). The ether layer was separated and the aqueous layer extracted with ether (2 × 50 ml). The ether extracts were combined, washed with water, and dried ( $MgSO_4$ ). The ether was evaporated and an oil obtained which immediately crystallised to give a white solid (8.41 g, 92.4%); g.l.c. (10% PEGS, 95 °C) showed largely one component (96%), retention time 8.5 min, with no component at the longer retention time of *trans-2-trimethylsilylcyclohexan-1-ol* (see below). Recrystallisation of a sample from light petroleum gave white crystals of the cyclohexanol (4g), m.p. 57–58 °C (lit.,<sup>6</sup> m.p. 59–60 °C);  $\delta$  ( $CCl_4$ ) 4.18 (1 H, 1-H), 2–1.4 (8 H, complex), 1.1 (1 H, OH), 0.85–0.6 (1 H, m), and 0.08 (9 H, s,  $Me_3Si$ );  $\nu_{max}$ . (Nujol mull) 3 610 (free OH), 3 330br (bonded OH), 1 250, and 845  $cm^{-1}$  (C–Si) (Found: C, 62.75; H, 11.8. Calc. for  $C_9H_{20}OSi$ : C, 62.75; H, 11.7%).

*1-Methoxycyclohexene*.—Sodium hydride (0.5 g, 80% suspension in oil, 17 mmol) was washed with light petroleum. The methoxysilyl alcohol (4a) (0.6 g, 3 mmol) and dry dimethylformamide (DMF) (6 ml) were added and the mixture was stirred for 15 min. G.l.c. (15% Silicone oil, 150 °C) showed that no starting material (retention time, 10 min) was present and a product peak (retention time, 1.7 min) had appeared. The mixture was poured slowly onto crushed ice and the aqueous phase was extracted with light petroleum. The organic extracts were combined, washed with brine, and dried ( $MgSO_4$ ). The light petroleum was removed by distillation at atmospheric pressure and finally by use of a rotary evaporator at 20 °C. An oil was obtained (0.2 g) and g.l.c. showed largely one component (>98%), retention time 1.7 min;  $\delta$  ( $CCl_4$ ) 4.55 (1 H, vinyl proton), 3.5 (3 H, s, MeO), and 2.1–0.7 (complex);  $\nu_{max}$ . (liquid film) 2 990 (=CH) and 1 665  $cm^{-1}$  (C=C). This product was shown to be 1-methoxycyclohexene by comparison with an authentic sample.

*Allyl Cyclohex-1-enyl Ether* (8).—In a similar way the allyl ether (4c) (0.6 g) was converted into allyl cyclohexenyl ether (8) (0.19 g, 51%), b.p. 65–68 °C at 13 mmHg (lit.,<sup>15</sup> b.p. 75–78 °C at 16 mmHg);  $\delta$  ( $CCl_4$ ) 6.1–4.7 (3 H, complex,  $CH_2=CH$ ), 4.2–4.5 (1 H, t, 2-H), 3.7–4.0 (2 H, complex,  $OCH_2$ ), and 2.1–1.0 (8 H, complex, ring  $CH_2$ ).

*2-Trimethylsilylcyclohexanone* (6).—Dry pyridine (11 g, 0.14 mol) was stirred in dichloromethane (50 ml) at 0 °C. Dry chromium trioxide crystals (7 g, 70 mmol) were added in portions during 10 min and the resulting, dark red mixture was stirred for a further 15 min at 0 °C. *cis-2-Trimethylsilylcyclohexan-1-ol* (4g) (2 g, 12 mmol), dissolved in dichloromethane (15 ml), was added quickly and the

reaction mixture was stirred at 20 °C for 2 h. Ether (100 ml) was added, the precipitated complexes were filtered off, and the residues were washed with fresh ether. The combined ethereal solution was washed with water, evaporated to one quarter its volume, washed with more water, and dried ( $MgSO_4$ ). Evaporation gave a pale yellow oil (1.81 g, 85%); g.l.c. (3% Silicone oil, 90 °C) showed peaks at 20.2 (the silyl ketone), 5.9 (1-trimethylsilylcyclohexene), and 3.2 min (cyclohexanone), in the ratio 1:0.018:0.015. Distillation of a sample (0.8 g) (with oil-bath temperature <98 °C), afforded the *cyclohexanone* (6) (0.3 g), b.p. 55 °C at 0.65 mmHg;  $\delta$  ( $CCl_4$ ) 2.3–1.3 (9 H, complex) and –0.02 (9 H, s,  $Me_3Si$ );  $\nu_{max}$ . (liquid film) 1 688 (C=O), 1 253, and 850  $cm^{-1}$  (C–Si) (Found: C, 63.6; H, 10.6.  $C_9H_{18}OSi$  requires C, 63.45; H, 10.65%).

*Reduction of the Cyclohexanone (6) with Lithium–Ammonia*.—Ammonia (ca. 30 ml) was condensed into a nitrogen-filled flask; lithium (0.3 g, 43 mmol) was added with magnetic stirring and the solution turned blue. Crude cyclohexanone (6) (0.5 g, 3 mmol) was added during 10 min and the ammonia was allowed to reflux for 2 h. Methanol–water (1:1, 15 ml) was added cautiously to destroy the excess of lithium and the ammonia was left to evaporate for 12 h. Water and ether were added and the ether layer was separated. The aqueous layer was extracted with ether; the ether extracts were combined, washed with water, and dried ( $MgSO_4$ ). Evaporation gave a pale yellow oil (0.36 g); g.l.c. (10% PEGS, 85 °C) showed this to be largely the *trans- and cis-2-trimethylsilylcyclohexan-1-ols* in the ratio 11.75:1; relative retention times 1.15:1. A sample of the *trans*-alcohol was crystallised from light petroleum at low temperature, m.p. 41–44 °C (lit.,<sup>6</sup> m.p. 47–48 °C);  $\delta$  ( $CCl_4$ ) 3.6–3.3 (1 H, m, 1-H), 2.1–1.9 (8 H, complex; 1 H, OH), 0.75–0.55 (1 H, m, 2-H), and 0.05 (9 H, s,  $Me_3Si$ ).

*t-2-Methylsulphonyloxy-1-trimethylsilylcyclohexan-r-1-yl Thiocyanate*.—The dry silyl thiocyanate (4f) (0.5 g, 2 mmol) was dissolved in dry pyridine (20 ml) and methanesulphonyl chloride (1.0 ml, 13 mmol) was added in drops at 0 °C. The mixture was set aside at 20 °C for 24 h. A few drops of water were then added and the products were extracted into ether. The ether layer was washed with water and dilute sulphuric acid to remove the pyridine, and then washed with aqueous sodium carbonate and brine. After drying ( $MgSO_4$ ), evaporation of the solvent gave a brown solid which showed two spots on t.l.c. The two components were well separated by recrystallisation which gave the *thiocyanate* (0.3 g, 50%), m.p. 70–71 °C (Found: C, 42.9; H, 6.75; N, 4.65; S, 20.3.  $C_{11}H_{21}NO_3S_2Si$  requires C, 42.95; H, 6.9; N, 4.55; S, 20.85%);  $\delta$  ( $CDCl_3$ ) 5.0–4.7 (1 H, complex, 2-H), 3.1 (3 H, s,  $SO_2Me$ ), 2.5–1.5 (8 H, complex, ring  $CH_2$ ), and 0.3 (9 H, s,  $Me_3Si$ );  $\nu_{max}$ . ( $CCl_4$ ) 2 160sh (S–C≡N), 1 250, and 850  $cm^{-1}$  (C–Si). Evaporation of the mother liquor gave a brown oil considered to be mainly the corresponding isothiocyanate.

*t-2-Mercapto-2-trimethylsilylcyclohexan-r-1-ol*.—The silyl thiocyanate (4f) (0.5 g, 2.5 mmol) in dry ether (5 ml) was added in drops to lithium aluminium hydride (0.25 g, 6.6 mmol) in ether (80 ml) and the mixture was refluxed for 3 h. Water (2 ml) was added and then dilute hydrochloric acid (10 ml). The ether layer was separated, washed with brine, and dried ( $MgSO_4$ ). Evaporation of the solvent produced an unpleasantly smelling liquid (0.36 g) which was distilled to give the *mercapto-cyclohexanol* (0.22 g, 50%), b.p. 50–52 °C at 0.05 mmHg (Found: C, 52.5; H, 9.95; S, 15.95.  $C_9H_{20}OSSi$  requires C, 52.85; H, 9.85; S, 15.7%);  $\delta$  ( $CDCl_3$ )

3.75 (1 H, triplet, 1-H), 2.2—1.4 (9 H, 8 H after D<sub>2</sub>O exchange, complex, ring CH<sub>2</sub> and OH), 1.4 (1 H, s, SH), and 0.15 (9 H, s, Me<sub>3</sub>Si);  $\nu_{\max}$ . (liquid film) 3 480br (OH), 1 250, and 850 cm<sup>-1</sup> (C-Si).

1-Trimethylsilyl-7-thiabicyclo[4.1.0]heptane (9).—Methylsulphonyloxy thiocyanate (0.7 g, 2 mmol) in dry ether (10 ml) was added in drops to lithium aluminium hydride (0.35 g, 9 mmol) in ether (70 ml) and the mixture was refluxed for 1 h. Water (2 ml) was added and then dilute hydrochloric acid (10 ml). The ether layer was separated, washed with brine, and dried (MgSO<sub>4</sub>). Evaporation of the solvent followed by distillation gave the *thiaheptane* (9) (0.3 g, 70%), b.p. 32—35 °C at 0.4 mmHg (Found: C, 58.25; H, 9.95; S, 17.4. C<sub>9</sub>H<sub>18</sub>SSi requires C, 57.95; H, 9.75; S, 17.2%);  $\delta$ (CDCl<sub>3</sub>) 3.15—3.05 (1 H, quartet, 6-H), 2.4—1.0 (8 H, complex, ring CH<sub>2</sub>), and 0.03 (9 H, s, Me<sub>3</sub>Si);  $\nu_{\max}$ . 1 250 and 850 cm<sup>-1</sup> (C-Si).

Reaction of the Epoxide (3) with Acetonitrile and Sulphuric Acid.—The silyl epoxide (3) (3.0 g, 17.6 mmol) was added during 30 min with stirring to a solution of sulphuric acid (1.5 g) in acetonitrile (30 ml) at 0 °C. The mixture was left for 90 min and then basified with aqueous sodium hydroxide (2M, 19 ml). The acetonitrile was removed on the rotary evaporator and the residue was extracted with ether. The extract was washed with brine, dried, and the ether was removed on a rotary evaporator to leave a viscous liquid (2.35 g). Distillation at 1.3 mmHg gave 5 fractions (totalling 1.74 g). G.l.c. (PPE 150 °C) showed three components [retention time 1.9, 8.4 (90%), and 15.5 min]. Preparative g.l.c. (Silicone oil, 170 °C) isolated the second component, to give 2-methyl-3a-trimethylsilyl-trans-3a,4,5,6,7,7a-hexahydrobenzoxazole (5) as a viscous liquid (47% yield after distillation), b.p. 76—78 °C at 1.3 mmHg;  $\delta$ (CCl<sub>4</sub>) 3.28 (1 H, d of d, 7a-H), 2.1—0.8 (8 H, complex), 1.64 (3 H, s, Me), and -0.23 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\max}$ . (CCl<sub>4</sub>) 1 640 (C=N) and 1 380 cm<sup>-1</sup> (Me) (Found: C, 62.2; H, 9.9; N, 6.4. C<sub>11</sub>H<sub>21</sub>NOSi requires C, 62.5; H, 10.0; N, 6.65%). The impurity of retention time 15.5 min was *trans*-2-amino-2-trimethylsilyl cyclohexylacetate, by comparison with a pure sample (g.l.c.).

On addition of ether to the distillation residue a white solid appeared. This was recrystallised from ether to give *t*-2-acetamido-2-trimethylsilylcyclohexan-*r*-1-ol (4) (0.17 g), m.p. 134—136 °C;  $\delta$ (CDCl<sub>3</sub>) 5.45 (1 H, br s, NH), 5.15 (1 H, d, disappears with D<sub>2</sub>O, OH), 3.99 (1 H, d of d, 1-H), 1.99 (3 H, s, Me), 2.2—1.1 (8 H, complex), and 0.13 (9 H, s, SiMe<sub>3</sub>);  $\nu_{\max}$ . (CHCl<sub>3</sub>) 3 415br (H-bonded, OH and NH), 1 660, 1 510 (amide I and II), 1 255, and 855 cm<sup>-1</sup> (C-Si) (Found: C, 57.8; H, 10.2; N, 6.05. C<sub>11</sub>H<sub>23</sub>NO<sub>2</sub>Si requires C, 57.6; H, 10.1; N, 6.1%).

4-*t*-Butyl-1-trimethylsilyl-7-oxabicyclo[4.1.0]heptanes (10) and (11).—The epoxide mixture was prepared from 4-*t*-butyl-1-trimethylsilylcyclohexene by the method used for epoxidation of 1-trimethylsilylcyclohexene. It had b.p. 115—112 °C at 25 mmHg; g.l.c. (15% Carbowax, 130 °C) showed two components, retention times 13.5 and 14.5 min in the ratio 4 : 6, considered to be *c*-4- and *t*-4-*t*-butyl-*r*-1-trimethylsilyl-7-oxabicyclo[4.1.0]heptane,<sup>9</sup> respectively, by co-injection with a sample of the *t*-4-isomer (see below);  $\delta$ (CDCl<sub>3</sub>) 3.15—2.95 (1 H, m, 6-H), 2.2—0.9 (7 H, m), 0.8 (9 H, s, Bu<sup>t</sup>), and 0.0 (9 H, s, SiMe<sub>3</sub>) (Found: C, 69.0; H, 11.65. Calc. for C<sub>19</sub>H<sub>26</sub>OSi: C, 69.0; H, 11.6%).

Reduction of the Epoxides (10) and (11) with Lithium Aluminium Hydride.—The epoxide mixture (1.13 g) was heated under reflux with lithium aluminium hydride for 1 h.

The product was isolated with ether is the usual way and showed two major peaks on g.l.c., retention times 14.5 and 38 min (15% Carbowax, 130 °C). The faster-running component was isolated by preparative g.l.c. to give *t*-4-*t*-butyl-*r*-1-trimethylsilyl-7-oxabicyclo[4.1.0]heptane (11), m.p. 45 °C;  $\delta$ (CDCl<sub>3</sub>) 3.0 (1 H, d, 2-H), 2.15—0.9 (7 H, m), 0.8 (9 H, s, Bu<sup>t</sup>), and 0.0 (9 H, s, SiMe<sub>3</sub>) (Found: C, 68.6; H, 11.8. C<sub>13</sub>H<sub>26</sub>OSi requires C, 69.0; H, 11.5%). Isolation of the second compound by preparative layer chromatography (p.l.c.) gave, after sublimation, *t*-5-*t*-butyl-*c*-2-trimethylsilylcyclohexan-*r*-1-ol (12), m.p. 71 °C;  $\delta$ (CDCl<sub>3</sub>) 4.3—4.1 (1 H, br s, 1-H), 1.9—0.9 (7 H, m), 0.82 (9 H, s, Bu<sup>t</sup>), 0.7—0.2 (1 H, m, 2-H), and 0.01 (9 H, s, SiMe<sub>3</sub>).

Reduction of the Epoxide (11) with Lithium Triethylborohydride.—The epoxide (11) (0.09 g) in tetrahydrofuran (THF) (10 ml) with lithium triethylborohydride (1M in THF; 1.5 ml) was heated under reflux for 6 h until all the epoxide had been consumed (g.l.c.). After quenching with aqueous HCl the product was isolated with ether to give, after sublimation, *c*-4-*t*-butyl-1-trimethylsilylcyclohexan-*r*-1-ol (13) (0.07 g), m.p. 80—82 °C;  $\delta$ (CDCl<sub>3</sub>) 2.15 (1 H, s, OH), 1.85—1.1 (9 H, m), 0.85 (9 H, s, Bu<sup>t</sup>), and 0.0 (9 H, s, SiMe<sub>3</sub>) (Found: C, 68.2; H, 12.0. Calc. for C<sub>13</sub>H<sub>28</sub>OSi: C, 68.4; H, 12.35%). The compound was shown to be identical (g.l.c. and i.r.) with a sample kindly provided by Professor W. C. Still.<sup>16</sup>

1-Trimethylsilyl-9-oxabicyclo[6.1.0]nonane (17).—A solution of 1-trimethylsilyl-*cis*-cyclo-octene (12.2 g, prepared from 1-bromo-*cis*-cyclo-octene<sup>17</sup> using a procedure analogous to that used in the preparation of 1-trimethylsilylcyclohexene<sup>14</sup>) in methylene chloride (15 ml) was stirred and cooled (ice-water). Peracetic acid (49% w/v; 20 ml) containing anhydrous sodium acetate (2.9 g) was added in drops during 20 min. The mixture was stirred for a further 10 min and heated on a water-bath. After refluxing for 10 min, g.l.c. showed that all the starting material had been consumed. Aqueous sodium hydroxide (10%, 100 ml) was cautiously added to the cooled reaction mixture. The aqueous phase was separated and washed with ether. The extracts were combined, washed successively with saturated aqueous sodium hydrogencarbonate and brine, and then dried (MgSO<sub>4</sub>). The solvent was evaporated to give a colourless oil (12.5 g). Distillation yielded the epoxide (17) as a colourless oil (11.3 g, 85%), b.p. 52—54 °C at 0.5 mmHg (Found: C, 66.8; H, 11.2. C<sub>11</sub>H<sub>22</sub>OSi requires C, 66.6; H, 11.2%) shown by g.l.c. (Carbowax at 150 °C) to be one component (95%) (retention time, 6 min);  $\delta$ (CCl<sub>4</sub>) 2.9—2.8 (1 H, m, 8-H), 2.1—2.0 (2 H, m, 7-CH<sub>2</sub>), 1.4 (10 H, m), and 0.02 (9 H, m, SiMe<sub>3</sub>);  $\nu_{\max}$ . (liquid film) 2 920 and 2 860 (C-H), 1 247 and 840 cm<sup>-1</sup> (C-Si).

Reaction of the Epoxide (17) with Sulphuric Acid in Methanol.—The epoxysilane (17) (5.0 g) was added to a solution of sulphuric acid (10 ml) in methanol (90 ml) at 20 °C. An exothermic reaction occurred. The reaction mixture was evaporated to 50 ml and cautiously added to aqueous sodium carbonate and ether. The ether layer was separated, washed successively with aqueous sodium carbonate and brine, and then dried (MgSO<sub>4</sub>). The solvent was evaporated to give a colourless oil (2.4 g). A sample (0.9 g) was distilled to yield an oil (0.6 g), b.p. 82—85 °C at 20 mmHg; g.l.c. (Carbowax, 150 °C) showed this to be predominantly one component. The *p*-nitrobenzoate crystallised from aqueous ethanol, had m.p. 84—85 °C, undepressed on admixture with an authentic sample of the *p*-nitrobenzoate of *endo*-bicyclo[3.3.0]octan-2-ol (18).<sup>18</sup>

*c*-2-Trimethylsilylcyclo-octan-*r*-1-ol.—The epoxide (7) (3 g, 15 mmol) was added to a stirred slurry of lithium aluminium hydride (0.6 g, 16 mmol) in dry THF (30 ml). The mixture was refluxed for 48 h. G.l.c. showed that all the starting material had reacted. Water (30 ml) was added cautiously, followed by hydrochloric acid (2M, 30 ml). The organic layer was separated and the aqueous layer was washed with ether; the organic extracts were combined, washed with brine, and dried (MgSO<sub>4</sub>). Evaporation gave an oil (2.7 g, 89%) which solidified. G.l.c. (10% PEGA, 105 °C) showed two components of retention times 52 and 55.5 min, in the ratio 1 : 0.12, considered to be the *cis*- and *trans*-2-trimethylsilylcyclo-octan-1-ols, respectively. Three successive recrystallisations from light petroleum at -78 °C yielded the *cis*-alcohol, m.p. 58–61 °C;  $\delta(\text{CCl}_4)$  4.15–3.85 (1 H, m, 1-H), 2.0–1.3 (12 H, m), 1.25–1.1 (1 H, m, OH, disappears on D<sub>2</sub>O exchange), 1.05–0.85 (1 H, m, 2-H), and 0.13 (9 H, s, Me<sub>3</sub>Si);  $\nu_{\text{max}}$  (liquid film) 3 400br (OH), 1 240, and 840 cm<sup>-1</sup> (C–Si) (Found: C, 66.95; H, 11.6. C<sub>11</sub>H<sub>24</sub>OSi requires C, 66.95; H, 12.0%).

2-Trimethylsilylcyclo-octanone and its Reduction with Lithium Aluminium Hydride.—*cis*-2-Trimethylsilylcyclo-octan-1-ol (1 g, 5 mmol) was oxidised using chromium trioxide–pyridine, as for 2-trimethylsilylcyclohexanol, and gave an oil (1.1 g),  $\nu_{\text{max}}$  (film) 1 670 cm<sup>-1</sup>, shown by g.l.c. (10% PEGA, 150 °C) to contain the product and starting material in the ratio 5 : 1. Reduction of the crude trimethylsilylcyclo-octanone with lithium aluminium hydride in ether gave an oil which solidified. G.l.c. (10% PEGA, 105 °C) showed two components, retention times 52 and 55.5 min in the ratio 1 : 0.57, assigned as the *cis*- and *trans*-2-trimethylsilylcyclo-octan-1-ols, respectively. Allowing for the *cis*-alcohol present in the silyl ketone the corrected ratio of *cis*- to *trans*-alcohol, produced on reduction, was 1 : 0.8.

*Elimination Reactions of the 2-Trimethylsilylcyclo-octanols.*—(a) *With Sodium Hydride.* (i) A mixture of the silyl alcohols, *cis*- to *trans*-ratio 9 : 1, was treated with sodium hydride in dry dimethyl sulphoxide (2 h, 20 °C) and the product was isolated with ether after addition of water. G.l.c. analysis (1% AgBF<sub>4</sub>–TCEP, 60 °C) showed it to be the *cis*- and *trans*-cyclo-octenes in the ratio 9 : 1.

(ii) A similar elimination on a mixture of isomeric silyl alcohols, *cis*-*trans* 1 : 1, gave *cis*- and *trans*-cyclo-octene in the same ratio (1 : 1).

(b) *With Methanesulphonyl Chloride–Triethylamine.* Dry triethylamine (0.3 g) was added to the silyl alcohols (0.2 g, *cis*-*trans* 9 : 1) in methylene dichloride (25 ml) and, after cooling to -10 °C, a solution of methanesulphonyl chloride (0.14 g) in methylene dichloride (5 ml) was added with stirring. After 15 min at 0 °C, water and aqueous hydrochloric acid were added, the organic layer was separated, washed with aqueous sodium carbonate, and dried (MgSO<sub>4</sub>). G.l.c. analysis showed absence of the starting material and formation of *cis*-cyclo-octene. *trans*-Cyclo-octene was shown to be stable to the reaction conditions.

1-Trimethylsilyl-9-oxabicyclo[6.1.0]non-4-ene (21).—Peracetic acid (3.8 ml, 37% w/v, 16.6 mmol) buffered with sodium acetate (0.7 g) was added during 45 min to a stirred mixture of 1-trimethylsilyl-*cis*-*cis*-cyclo-octa-1,5-diene (3 g, 16.6 mmol, prepared from 1-bromo-*cis*, *cis*-cyclo-octa-1,5-diene<sup>19</sup> by a procedure analogous to that used for 1-trimethylsilylcyclohexene<sup>14</sup>) and sodium carbonate (1.1 g) in dichloromethane (50 ml). The temperature of the reaction mixture was maintained between 0 and 10 °C during

the addition (ice–salt bath). After the addition, g.l.c. (OV 17, 155 °C) showed two product peaks and a peak due to the starting vinyl-silane in the ratio 4 : 20 : 55, respectively. The mixture was stirred at 0 °C for a further 20 min. Sodium hydroxide (10% w/v) was added until the mixture was pH 14. The organic layer was separated and the aqueous layer extracted with dichloromethane (50 ml). The organic extracts were combined, washed with water and brine, and dried (MgSO<sub>4</sub>). Evaporation gave an oil (3.5 g) which on distillation gave two fractions. The first fraction (0.7 g, b.p. 85 °C at 15 mmHg) was shown by g.l.c. to consist of the starting vinyl-silane and the product mixture in a ratio of *ca.* 1 : 1. The second fraction (1.23 g, b.p. 102–108 °C at 15 mmHg) was shown by g.l.c. to consist of the two major products, 1-trimethylsilyl-9-oxabicyclo[6.1.0]non-4-ene (21) (identified by co-injection with an isolated sample) and 4-trimethylsilyl-9-oxabicyclo[6.1.0]non-4-ene in the ratio 5 : 1 (total estimated yield 48%). The former was isolated by preparative g.l.c. (15% Silicone oil, 180 °C), b.p. 118 °C at 25 mmHg (Found: C, 66.9; H, 10.1. C<sub>11</sub>H<sub>20</sub>OSi requires C, 67.3; H 10.25%);  $\delta(\text{CDCl}_3)$  5.6 (2 H, br s, 4- and 5-H), 2.9 (1 H, m, 8-H), 2.6–1.8 (8 H, m), and 0.05 (9 H, s, SiMe<sub>3</sub>).

*Reaction of a Mixture of the Epoxide (21) and 4-Trimethylsilyl-9-oxabicyclo[6.1.0]non-4-ene with Sulphuric Acid in Methanol.*—Concentrated sulphuric acid (0.5 ml, 9.4 mmol) was added to a stirred solution of the mixture of silyl epoxides (5 : 1, 2.55 g, 13 mmol) in dry methanol (100 ml) at 0 °C. The solution was stirred at 18 °C for 3 h. Sodium hydroxide solution (10% w/v) was added until the mixture was pH 14. The methanol was partially removed by evaporation and ether (50 ml) was added. The organic layer was separated and the aqueous layer was extracted with ether. The ethereal extracts were washed with water and brine and were dried (MgSO<sub>4</sub>). Evaporation gave a yellow oil (2.42 g), which showed three peaks on g.l.c. (3% Silicone oil, 138 °C), retention times 10.5, 16.5, and 19.5 min in the ratio 2 : 1 : 5.5, respectively. P.l.c. [light petroleum–ether (9 : 1) as eluant] gave three fractions. The fraction with *R*<sub>F</sub> 0.1 (0.38 g) corresponded to the g.l.c. peak with retention time 16.5 min on g.l.c. and was a yellow oil;  $\delta(\text{CDCl}_3)$  5.95 (1 H, m, 2-H), 3.6–3.0 (2 H, m, 5- and 6-H), 3.38 (3 H, s, OMe), 2.5–1.5 (8 H, m), and 0.08 (9 H, s, SiMe<sub>3</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  141.84 (s, C-1), 140.6 (s, C-1), 139.14 (d, C-2), 138.01 (d, C-2), 84.12 (d, C-5 or C-6), 83.48 (d, C-5 or C-6), 73.39 (d, C-5 or C-6), 72.69 (d, C-5 or C-6), 57.96 (q, OMe) 34.5, 33.36, 30.4, 29.48, 24.41, 24.09, 23.87, 23.49 (methylene carbons), and -1.7 (q, SiMe<sub>3</sub>);  $\nu_{\text{max}}$  (film) 3 480 (OH), 1 620 (C=C), 1 250, and 850 cm<sup>-1</sup> (C–Si), considered to be a mixture of *trans*-6-methoxy-1-trimethylsilylcyclo-oct-1-en-5-ol and *trans*-5-methoxy-1-trimethylsilylcyclo-oct-1-en-6-ol. The fraction with *R*<sub>F</sub> 0.23 (0.3 g) corresponded to the peak at 19.5 min on g.l.c. and was also a yellow oil. Distillation gave *t*-1-methoxy-*r*-1-trimethylsilylcyclo-oct-5-en-*c*-2-ol (22) as a yellow oil, b.p. 120 °C (bath) at 25 mmHg (Found: C, 63.4; H, 10.65. C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>Si requires C, 63.1; H, 10.6%);  $\delta(\text{CDCl}_3)$  5.65 (2 H, br s, 5- and 6-H), 4.25 (1 H, t, 2-H), 3.3 (3 H, s, OMe), 2.8, 1.8 (9 H, m), and 0.12 (9 H, s, SiMe<sub>3</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  131.92 (d, C-5 or C-6), 127.82 (d, C-5 or C-6), 79.16 (s, C-1), 74.47 (d, C-2), 51.54 (q, OMe), 32.6, 27.48, 24.63, 23.33 (methylene carbons), and -0.56 (q, SiMe<sub>3</sub>);  $\nu_{\text{max}}$  (film) 3 500 (OH), 1 660 (C=C), 1 250, and 850 cm<sup>-1</sup> (C–Si). The fraction with *R*<sub>F</sub> 0.36 (0.75 g), corresponding to the peak at 10.5 min on g.l.c., was distilled to give a yellow oil tentatively assigned the structure (23) (see Discussion),

b.p. 85 °C (bath) at 27 mmHg (Found: C, 64.35; H, 10.7.  $C_{13}H_{28}O_2Si$  requires C, 64.4; H, 10.8%) ;  $\delta(CDCl_3)$  5.85 (1 H, br s), 4.35 (1 H, t), 3.3 (6 H, s,  $2 \times OMe$ ), 2.5—1.2 (9 H, m), and 0.8 (9 H, s,  $SiMe_3$ ) ;  $\delta_C$  144.43 (superimposed s and d, olefinic carbons), 104.94 [d,  $HC(OMe)_2$ ], 52.73 (q, OMe), 47.93 (d, methine carbon), 35.36, 31.15, 30.56 (methylene carbons), and -1.48 (q,  $SiMe_3$ ) ;  $\nu_{max}$  (film) 1 590 (C=C), 1 250, and 850  $cm^{-1}$  (C-Si).

*Reaction of (Z)-2,3-Epoxy-3-trimethylsilylpentane (26) with Methanolic Sulphuric Acid.*—A solution of sulphuric acid (1.00 g) in methanol (5 ml) was made up and a portion (20  $\mu$ l) was added to the silyl epoxide (26) [1.0 g, 6.3 mmol; Z : E, 24 : 1; prepared by silylation<sup>14</sup> of 3-chloropent-2-ene<sup>20</sup> (Z : E, 7 : 3) followed by epoxidation using buffered peracetic acid in methylene chloride and spinning band distillation of the product (Found: C, 60.85; H, 11.45.  $C_8H_{18}OSi$  requires C, 60.7; H, 11.45%)] in methanol (4 ml) at 0 °C. G.l.c. showed the epoxide and a volatile product to be present in roughly equal amounts after 90 min. The mixture was basified with aqueous sodium hydroxide (2M) and water (20 ml) was added. Isolation of the product with ether gave an oil (1.05 g) which partly crystallised on standing. Two low-temperature crystallisations from light petroleum gave (2RS,3RS)-3-methoxy-3-trimethylsilylpentane-2-ol (27a) (0.49 g, 40%), m.p. 86 °C;  $\delta(CCl_4)$  3.90 (1 H, quintet, 2-H), 3.28 (3 H, s, OMe), 2.17 (1 H, d, OH), 2.03—1.7 (3 H, d, 1-H), 0.86 (3 H, t, 5-H), and 0.13 (9 H, s,  $SiMe_3$ ) ;  $\nu_{max}$  ( $CCl_4$ ) 3 570 (OH) and 1 095  $cm^{-1}$  (CO) (Found: C, 56.75; H, 11.65.  $C_9H_{22}O_2Si$  requires C, 56.8; H, 11.65%).

*Reaction of the Silyl Alcohol (27a) with Sodium Hydride.*—Sodium hydride (0.4 g, 80% suspension in oil) was washed with light petroleum to remove the oil and was treated, with stirring, with the methoxy-alcohol in dimethyl formamide (3 ml). After 2 h the mixture was added to ice and then water (15 ml) and carbon disulphide (1 ml) were added. The organic layer was removed, washed with water, and dried ( $CaCl_2$ ) to give a solution of (Z)- and (E)-3-methoxy-pent-2-enes (28) (Z : E, 95 : 5) identified by comparison (g.l.c. and n.m.r.) with an authentic sample.<sup>21</sup>

*Reaction of the Silyl Epoxide (26) with Sulphuric Acid in Aqueous THF.*—A solution of sulphuric acid (1.25 g) in water (0.5 ml) and THF (4.5 ml) was made and a portion (0.03 ml) was added to a solution of the silyl epoxide (26) (0.3 g, 1.9 mmol, Z : E, 24 : 1) in water (1.5 ml) and THF (5.5 ml). After 23 h g.l.c. (OV17, 118 °C) showed unchanged epoxide and a product, later shown to be (2RS,3RS)-3-trimethylsilylpentane-2,3-diol (27b), in the ratio 0.5 : 1. A further portion of the acid solution (0.2 ml) was added and after another 23 h g.l.c. showed the diol to be present in only slightly increased concentration and a volatile product considered to be pentan-2-one. No epoxide remained. Saturated aqueous sodium carbonate (2.5 ml), was added, the THF was removed on a rotary evaporator, and the residue extracted with ether. The

extract was washed with brine, dried, and evaporated leaving an oily residue which slowly crystallised. Sublimation gave the diol (27b) (0.12 g, 28%) as needles, m.p. 57.5—58 °C;  $\delta(CDCl_3)$  3.91 (1 H, q, 2-H), 2.44 (br, OH), 2.0—1.2 (complex, 4 H with the previous peak), 1.09 (3 H, d, 1-H), 0.87 (3 H, t,  $3 \times 5-H$ ), and 0.06 (9 H, s,  $SiMe_3$ ) (Found: C, 54.6; H, 11.6.  $C_8H_{20}O_2Si$  requires C, 54.5; H, 11.45%).

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#### REFERENCES

- G. Stork and E. Colvin, *J. Am. Chem. Soc.*, 1971, **93**, 2080; G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, 1974, **96**, 3682.
- (a) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, 1975, **40**, 2263; (b) P. F. Hudrlik, C-N. Wan, and G. P. Withers, *Tetrahedron Lett.*, 1976, 1449; (c) P. F. Hudrlik, R. N. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona, and J. P. Arcoleo, *Tetrahedron Lett.*, 1976, 1453; (d) P. F. Hudrlik, J. P. Arcoleo, R. H. Schwartz, R. N. Misra, and R. J. Rona, *Tetrahedron Lett.*, 1977, 591; (e) P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withers, *J. Am. Chem. Soc.*, 1977, **99**, 1993; (f) P. F. Hudrlik and C-N. Wan, *Synth. Commun.*, 1979, 333.
- D. Ayalon-Chass, E. Ehlinger, and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 1977, 772; F. Cooke and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 1977, 513; C. S. Burford, F. Cooke, E. Ehlinger, and P. Magnus, *J. Am. Chem. Soc.*, 1977, **99**, 4536.
- T. H. Chan, P. W. K. Lau, and M. P. Li, *Tetrahedron Lett.*, 1976, 2667; J. J. Eisch and J. O. Galle, *J. Am. Chem. Soc.*, 1976, **98**, 4646; J. C. Richer, M-A. Poirier, Y. Maroni, and G. Manuel, *Can. J. Chem.*, 1978, **56**, 2049; D. B. Boyd and G. A. Berchtold, *J. Org. Chem.*, 1979, **44**, 468; M. Obayashi, K. Utimoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2646.
- C. M. Robbins and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 1976, 697.
- W. K. Musker and G. L. Larson, *Tetrahedron Lett.*, 1968, 3481.
- D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.
- A. G. Brook, D. M. MacRae, and A. R. Bassindale, *J. Organomet. Chem.*, 1975, **86**, 185.
- W. E. Fristad, T. R. Bailey, and L. A. Paquette, *J. Org. Chem.*, 1978, **43**, 1620; *ibid.*, 1980, **45**, 3028.
- R. E. Parker and N. S. Isaccs, *Chem. Rev.*, 1959, **59**, 737; J. G. Buchanan and H. Z. Sable in 'Selective Organic Transformations,' ed. B. S. Thyagarajan, Wiley, New York, 1972, Vol. 2, p. 1.
- C. Eaborn and J. C. Jeffrey, *J. Chem. Soc.*, 1954, 4266.
- J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 1976, **41**, 2615.
- P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, 1975, **97**, 1464.
- A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev, *J. Gen. Chem. U.S.S.R. (Engl. Transl.)*, 1957, **27**, 1609.
- N. B. Lorette and W. L. Howard, *J. Org. Chem.*, 1961, **26**, 3112.
- W. C. Still, *J. Org. Chem.*, 1976, **41**, 3063.
- K. Schank and B. Eistert, *Chem. Ber.*, 1966, **99**, 1426.
- A. C. Cope, H. H. Lee, and H. E. Petree, *J. Am. Chem. Soc.*, 1958, **80**, 2849.
- G. L. Gr̄unewald and J. M. Grindel, *J. Med. Chem.*, 1976, **19**, 10.
- A. L. Henne and E. G. De Witt, *J. Am. Chem. Soc.*, 1948, **70**, 1548.
- E. Taskinen, *J. Chem. Thermodyn.*, 1974, **6**, 345.