Nucleophilic Attack of Siloxycarbenes on Carbonyl Groups. The Formation of Oxiranes

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Siloxycarbenes, formed by the photolysis of dimethyl- or diphenylsilacyclohexanone have been trapped as oxiranes or as the ring-opened hydrolysis products of oxiranes, with simple aldehydes and ketones such as acetaldehyde, or cyclohexanone. The reactions are interpreted as arising from the nucleophilic attack of the siloxycarbene on the carbonyl group. The structures of the oxiranes and their hydrolysis products have been established.

La photolyse de diméthyl- ou diphénylsilacyclohexanones fournit des siloxycarbènes qui réagissent avec les aldéhydes et les cétones simples comme l'acétaldéhyde et la cyclohexanone pour fournir des oxirannes ou les produits provenant d'une hydrolyse de ces hétérocycles. Ces produits proviendraient d'une attaque nucléophile du siloxycarbène sur les groupes carbonylés. On a bien établi la structure des oxirannes et de leurs produits d'hydrolyse.

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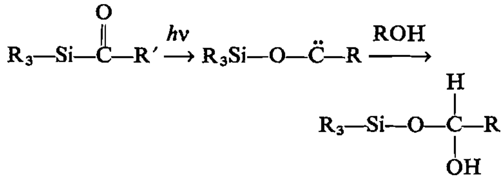
It has recently been shown that acylsilanes yield siloxycarbenes on photolysis which can be trapped with alcohols as mixed acetals (eq. 1)

[1]



$$R_3\text{—Si—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—R}' \xrightarrow{h\nu} R_3\text{Si—O—}\ddot{\text{C}}\text{—R} \xrightarrow{\text{ROH}} R_3\text{—Si—O—}\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}\text{—R}$$

(1). A cyclic siloxycarbene has also been trapped as a spirocyclopropane by reaction with diethyl fumarate (2). These and other studies suggest that siloxycarbenes display nucleophilic character.

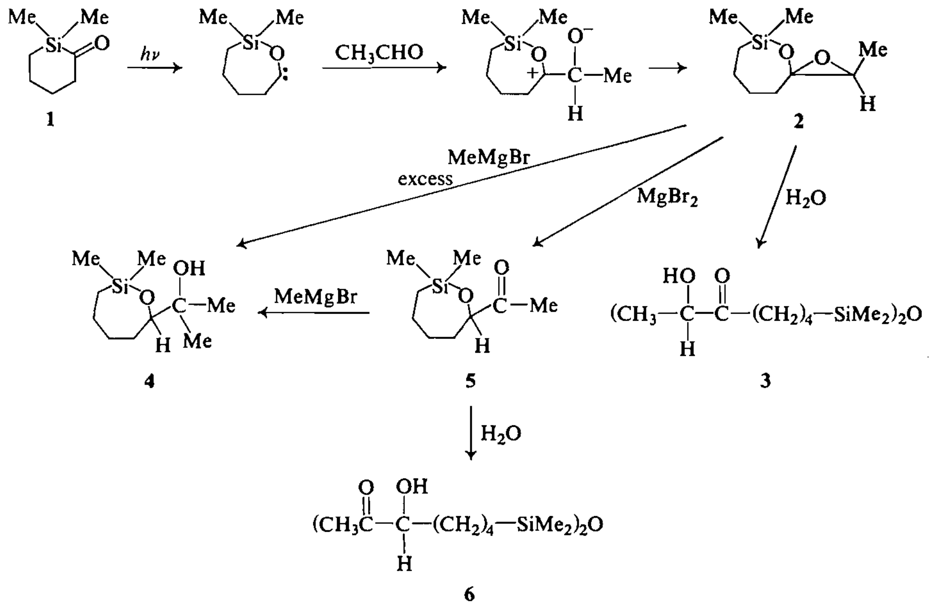
Additional support for this concept is now provided by the finding that siloxycarbenes, generated by photolysis of acylsilanes, will react with acetaldehyde or a simple ketone to give the oxirane, or compounds formally derivable therefrom, as reaction products.

Photolysis of 1,1-dimethyl-1-silacyclohexanone (**1**), in cyclohexane at 0° in the presence of excess acetaldehyde using a low pressure mercury floodlamp with λ_{max} about 360 nm gave the oxirane **2**, as a mixture of two isomers (Scheme 1). The mixture was unstable and hence the isomers could not be separated nor the mixture analyzed but the structures of the major components were confirmed by spectral data and derivatization reactions. The methyl group and hydrogen atom on the oxirane ring appeared as two sets of doublets and quartets in the ratio of 1 to 1.6, in the δ 1.2 and 2.8 p.p.m. regions of the n.m.r. spectra, compared with 1.3 and 3.0 p.p.m. for propylene oxide (3). The i.r. spectrum showed a doublet at 7.95–8.0 μ, corresponding to overlapping absorptions by the epoxide and Si—Me groups in the molecule.

Oxirane **2** slowly decomposed spontaneously, or rapidly in the presence of added water, being hydrolyzed to the acyloin **3**, which was characterized by analysis, the presence of a methyl doublet, hydrogen quartet and broad singlet in the n.m.r. spectrum, and OH, C═O, and SiOSi absorption in the i.r.

When treated with methylmagnesium bromide the carbinol **4** was formed almost quantitatively. This reaction appears surprising at first, but the isomerization of trisubstituted oxiranes in ring opening reactions is known to be facile (4). Further, treatment of the oxirane **2** with anhydrous magnesium bromide, a mild Lewis acid, gave the rearranged product, the methyl ketone **5**, in almost quantitative yield. This showed the expected carbonyl absorption at 5.82 μ. On treatment with methyl Grignard reagent, **5** also gave **4** as expected. On exposure to moisture **4** gave the acyloin **6**, isomeric to that given by **2**, as shown by the methyl ketone singlet at δ 2.13 p.p.m. together with the other expected spectral features.

The above data fully support the structure of **2** as that of the oxirane. While the reaction of carbenes with carbonyl groups is relatively



SCHEME 1

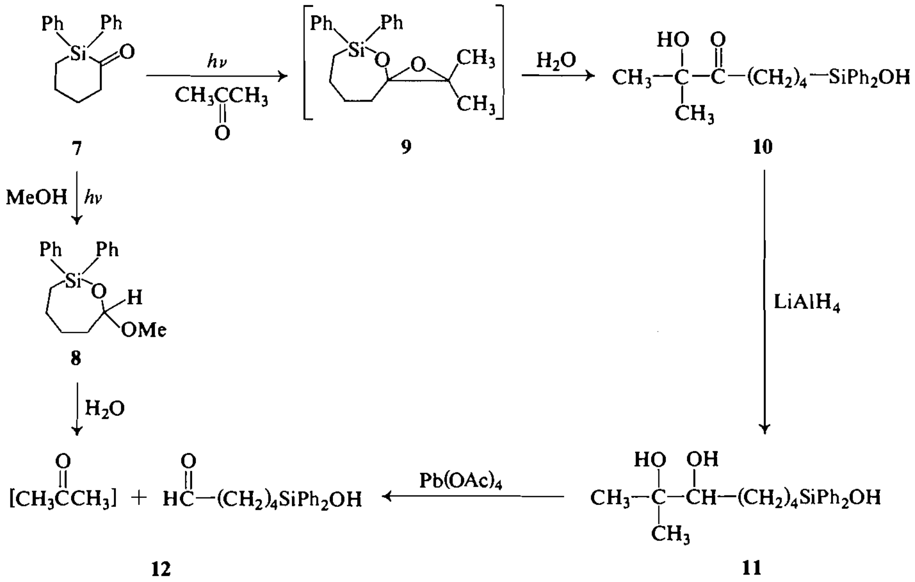
unknown, recent studies by Seyferth and Tronich (5) have shown that dihalocarbenes will form oxiranes only with highly fluorinated ketones such as hexafluoroacetone: the mechanism of this reaction has not been thoroughly established.

Attempts to trap the siloxycarbene using benzaldehyde were unsuccessful, and the fact that almost no decomposition of the acylsilane had occurred after 6 h irradiation, double that required for complete reaction with acetaldehyde, suggests that the benzaldehyde is acting as a quenching agent. Preliminary studies using pivaldehyde indicated that a mixture of products was formed. The n.m.r. data of the mixture could be interpreted as containing a mixture of the two diastereomeric oxiranes corresponding to **2**, with Me replaced by *t*-Bu.

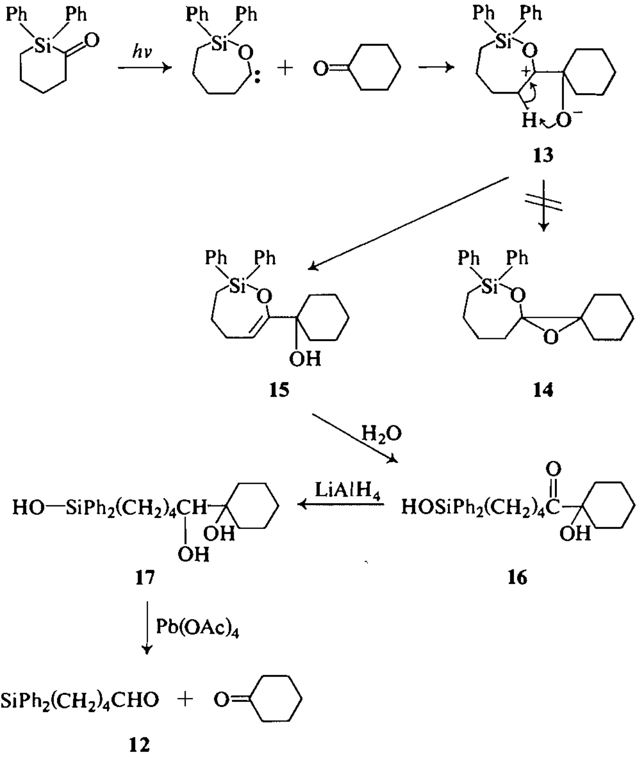
When diphenylsilacyclohexanone **7** was photolyzed in acetone, related behavior was observed (Scheme 2). The sole product isolated was the acyloin **10**, which is derivable at least formally from the oxirane **9**, which was not detected in this case. It seems probable that sufficient water to hydrolyze the oxirane (or other intermediate) was present in the excess acetone used as solvent.

The structure of **10** was confirmed by analysis, by the presence of Si—OH, C—OH, and C═O absorption in the i.r., by a six-proton singlet signal for the two methyl groups and by two sharp singlets (in DMSO) at δ 6.48 and 5.10 p.p.m. in the n.m.r. spectrum corresponding to the Si—OH and C—OH signals. Diphenylmethylsilanol also has OH absorption at 6.48 p.p.m. (6). The structure of **10** was further confirmed by its reduction to the diol–silanol **11**, which on cleavage with lead tetraacetate gave the known 5-diphenylhydroxysilylpentanal, **12** (7) which can be produced also by photolysis of **7** in damp ether, or by photolysis in methanol to give the acetal **8** which readily hydrolyzes to **12** on treatment with dilute acid.

A similar photochemical reaction appeared to take place when 2-butanone was used as the solvent for the diphenylsilacyclohexanone photolysis, as judged by the similar spectroscopic properties of the product isolated to those of **10**. However, somewhat different behavior was observed when cyclohexanone was employed as the solvent (Scheme 3). In addition to the acyloin **16** obtained in about 50% yield, a second compound, **15**, was obtained in 25% yield. This compound is isomeric with the oxirane, **14**, which would have been formed had ring closure of **13**, the dipolar product of nucleophilic addition to the carbonyl group, occurred. It is not clear why **15** is formed in this case instead of the



Scheme 2



Scheme 3

oxirane **14**, since molecular models do not suggest that **14** is unduly sterically hindered. Indeed, it is possible that **14** is formed and transformed into **15** during the course of the reaction or its work-up.

The structure of **16** was confirmed by its reduction to the silanol–diol **17**, which on cleavage with lead tetraacetate gave the known compound **12**, and cyclohexanone, isolated as the 2,4-dinitrophenylhydrazone. The structure of **15** was inferred from the presence of OH, Si—O—C, and C═C stretching absorption in the i.r., and the n.m.r. spectrum showed a single vinyl proton, as a triplet centered at 4.98 p.p.m. On treatment with acetone containing a drop of aqueous 5% hydrochloric acid, **15** was rapidly converted to **16**. This facile hydrolysis, observed before for siloxyalkenes (8), is consistent with **15** being the precursor of **16**, hydrolysis being accomplished by traces of water introduced with the cyclohexanone.

The reactions described above are all consistent with the photochemical generation, from an acylsilane, of a siloxycarbene which possesses nucleophilic character. While all acylsilanes readily undergo photolysis in polar reagents such as alcohols (1), within our limited experience cyclic acylsilanes appear to yield siloxycarbenes which react as nucleophilic carbenes more rapidly and cleanly with other kinds of electrophiles than do their acyclic analogs. The scope of this nucleophilic reactivity is being explored further.

Experimental

General

The n.m.r. spectra were run on either an A-60 or T-60 Varian spectrometer, using TMS as internal standard in most cases. The i.r. spectra were recorded on a Perkin–Elmer Model 237B instrument. Melting points and boiling points are uncorrected.

It was important to carry out the photolyses in the absence of oxygen, since in at least some cases its presence diverted the reaction and other products were formed.

The Oxirane 2 from Dimethylsilacyclohexanone 1 and Acetaldehyde

A solution of 1,1-dimethyl-1-silacyclohexan-2-one (9) (2.0 g, 0.014 mol), freshly distilled acetaldehyde (2 ml), and cyclohexane (80 ml) was placed in a vessel, flushed with nitrogen, sealed, and irradiated with a 100 W low pressure mercury floodlamp for about 3 h while being cooled in ice-water. The solution became colorless. After removal of the solvent by rotary evaporation, the residual liquid was distilled to give 1.1 g (43%) of colorless material, **2**, b.p. 35–36° (0.8 mm), 62–64° (2.5 mm). Freshly distilled material had the following spectral characteristics: i.r.; 7.0 (Si—Me), 9.3 (Si—O—C) μ; n.m.r.; δ (CCl_4), (isomer **1***a*, relative amount 1) 2.94 (Me—C*H*, q, *J* = 5.5 Hz, 1H), 1.13 (*Me*—CH, d, *J* = 5.5 Hz, 3H) and (isomer **1***b*, relative amount 1.6) 2.64 (Me—C*H*, q, *J* = 5.0 Hz, 1H), 1.22 (*Me*—CH, d, *J* = 5.0 Hz, 3H) together with 1.65 (CH_2, m), 0.73 (CH_2Si, poorly resolved t), 0.05 (Me_2Si, m) p.p.m. in relative ratio 6:2:6; δ (C_6H_6) (isomer **1***a*) 3.17 (*J* = 5.5 Hz, q), 1.00 (*J* = 5.5 Hz, d), and (isomer **1***b*) 2.65 (*J* = 5 Hz, q), 1.33 (*J* = 5 Hz, d) together with 1.73 (CH_2, m), 0.80 (s, CH_2, poorly resolved triplet), and 0.17 (three peak multiplet with separations of about 5 Hz due to nonequivalent Me groups on Si) p.p.m.

Formation of $(CH_3CHOHCO(CH_2)_4SiMe_2)_2O$ (3) by Hydrolysis of 1

When 0.5 g of **2** in ether was shaken with water for 30 min, or when exposed to air for 12 h, a pale-yellow liquid **3** was obtained on removal of the solvent, n_D^{21} 1.4597; i.r. (film) 2.7–3.2 (OH), 5.84 (C═O), 9.5 (SiOSi) μ; n.m.r. (CCl_4 with benzene as internal standard) δ 4.15 (C*H*OH, q, *J* = 7 Hz, 1H), 3.6 (OH, s (broad), 1H), 2.5 (CH_2CO, t (partially resolved) 2H), 2.0–0.9 (CH_2CH_2, m with d centered at δ 1.33, *J* = 7 Hz due to *CH_3*—CHOH, 7H), 0.7–0.3 (CH_2Si, m, 2H), 0.10 ($SiMe_2$, s, 6H) p.p.m.

Anal. Calcd. for $C_{18}H_{38}Si_2O_5$: C, 55.34; H, 9.80. Found: C, 55.34; H, 9.77.

Reaction of Oxirane 2 with Methylmagnesium Bromide

The oxirane produced from photolysis of 2.5 g (0.018 mol) of the acylsilane with acetaldehyde was added to excess methylmagnesium bromide in ether. After stirring for 15 min the reaction was worked-up rapidly with aqueous ammonium chloride solution to give 3.0 g (85%) of crude carbinol **4**. Distillation gave a colorless liquid in 50% yield, $n_D^{22.5}$ 1.4538; b.p. 54–55° (0.8 mm); i.r. (film) 2.7–3.1 (OH), 9.25 (Si—O—C) μ; n.m.r. (CCl_4 with benzene as internal standard) δ 3.3 (CH, m, 1H), 2.0–0.5 (CH_2 and OH, m, 9H), 1.1 (CMe_2, s (broad), 6H), 0.13 ($SiMe_2$, s, 6H) p.p.m.

Anal. Calcd. for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.48; H, 11.06.

Isomerization of Oxirane 2 to Siloxyketone 5

The photolysate from 3.0 g (0.021 mol) of **1** in acetaldehyde was poured into a solution of anhydrous magnesium bromide in ether (prepared from excess magnesium and 0.5 ml of 1,2-dibromoethane). The solution was stirred for 1 h and worked-up rapidly using aqueous ammonium chloride to give 3.45 g (91%) of pale-yellow liquid. Distillation gave 2.8 g (64%) of pure **5**, b.p. 85–88°/10 mm, n_D^{22} 1.4488; i.r. (film) 5.82 (C═O), 7.41 (COMe) μ; n.m.r. (CCl_4 with benzene as internal standard) δ 4.0 (C*H*COMe, m, 1H), 2.08 (MeCO, s, 3H), 2.1–0.5 (CH_2, m, 8H), 0.15 and 0.10 (Me_2Si, two s, 6H) p.p.m.

Anal. Calcd. for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found: C, 57.99; H, 9.96.

Formation of the Dimethylcarbinol 4 from Methyl Ketone 5 with Methyl Grignard Reagent

A solution of 0.5 g (0.0027 mol) of the ketone **5** was added to excess methylmagnesium bromide in ether. The solution was stirred for 15 min and then was rapidly worked-up with aqueous acid to give 0.52 g (85%) of material identical in all respects to the dimethylcarbinol **4** described above.

Hydrolysis of the Methyl Ketone 5 to Give Acyloin 6

Hydrolysis of **5** could be rapidly accomplished by shaking with water or with aqueous sodium hydroxide but exposure to air over a period of 4 weeks gave the purest product. The mixture, a pale-yellow liquid, n_D^{21} 1.4647 had i.r. (CCl_4) 2.85 (OH), 5.84 (C=O) μ; n.m.r. (CCl_4 with benzene as internal standard) δ 4.0 (C*H*OH, m (broad) 1H), 3.2 (OH, broad, 1H), 2.13 (MeCO, s, 3H), 1.4 (CH_2, m, 6H), 0.6 (CH_2Si, m, 2H), 0.06 (Me_2Si, s, 6H) p.p.m.

Anal. Calcd. for $C_{18}H_{38}Si_2O_5$: C, 55.34; H, 9.80. Found: C, 55.18; H, 10.04.

Photolysis of Dimethylsilacyclohexanone 1 in Benzaldehyde

Photolysis of 1.0 g of **1** in excess freshly redistilled benzaldehyde in cyclohexane was examined after 6 h. Spectra of the crude material indicated much **1** was still present and only traces of unidentified material (n.m.r. (CCl_4): δ 4.2, 3.8 p.p.m., both singlets of unequal intensity) were observed.

Photolysis of Dimethylsilacyclohexanone in Pivaldehyde

When the material obtained from a photolysis similar to the above but using pivaldehyde in place of benzaldehyde was examined, little **1** remained. The n.m.r. spectrum in CCl_4 showed absorptions at δ 3.4 (broad singlet), 1.10 and 0.90 (singlets), and 0.10 (m) assignable to the C—H, *t*-Bu, and Si—Me signals of a mixture of oxiranes like **2**, where *t*-Bu replaces Me on the three-membered ring. Other signals were also present indicating the presence of at least one other compound. The mixture could not be separated.

Photolysis of 1,1-Diphenylsilacyclohexane-2 in Methanol

Twenty-five milliliters of dry methanol (freshly distilled from MeOMgI) were placed in a flask and dry nitrogen was bubbled through for about 1/2 h to displace all the dissolved oxygen. Then 1.0 g (0.00377 mol) of 1,1-diphenylsilacyclohexanone-2 (**7**) was added in one lot and the 100 W mercury floodlamp was turned on. The solution was irradiated for 1/2 h while maintaining a constant flow of nitrogen. After this time the solution was blown over into a receiving flask with nitrogen and the photolysis flask was rinsed once with dry methanol. The methanol was removed under reduced pressure to give the cyclic acetal (**8**). The product was not absolutely pure as judged by the presence of a small carbonyl peak at 5.78 μ. It was distilled under high vacuum to give 0.404 g or 36% of **8**, b.p. 130–132° (0.04 mm) but little purification was obtained: i.r. (CCl_4) 3.51 (OMe), 7.0, 9.0 (Si—Ph) μ; n.m.r. (CCl_4) δ 7.10–7.75 (Ar, m, 10H), 4.80–5.00 (C*H*OMe, m, 1H), 3.23 (OMe, s, 3H), 0.91–2.15 (CH_2, m, 8H) p.p.m.

Anal. Calcd. for $C_{18}H_{22}SiO_2$: C, 72.46; H, 7.43. Found: C, 72.93; H, 7.47.

Hydrolysis of the Cyclic Acetal 8

To 0.40 g (0.00134 mol) of the cyclic acetal **8** (prepared in the above photolysis) in 20 ml of THF was added a solution consisting of 2 ml of a 1% solution of KOH in water and 10 ml of THF. After stirring for 15 min 5% HCl was added and the mixture was extracted with diethyl ether. The ether phase was washed with water, dried, and the solvent was then removed. The residue was chromatographed on silica gel using benzene, 50:50 benzene–chloroform, and then chloroform as eluents. Isolated in the benzene fractions was 0.12 g or 30% of the starting acetal. The aldehyde, 5-(diphenylhydroxysilyl)-pentanal, 2.5 g (68%), was eluted with benzene–chloroform and gave an i.r. spectrum identical to that of authentic material (**7**): n.m.r. (CCl_4) δ 9.44 (CHO, t, 1H), 6.80–7.70 (Ar, m, 10H), 1.90–2.34 ($COCH_2$ + OH, m, 3H), 0.81–1.80 (CH_2, m, 6H).

Photolysis of 1,1-Diphenylsilacyclohexanone-2 in Acetone Saturated with Nitrogen; Isolation of 10

Nitrogen was bubbled through a solution of 0.200 g (0.000753 mol) of 1,1-diphenylsilacyclohexanone-2 in 40 ml of dry acetone (freshly distilled from anhydrous $MgSO_4$) while maintaining the solution in the dark. After 15 min the lamp was started and the photolysis was continued for 2 h with a constant stream of nitrogen passing through the solution. An i.r. spectrum of a small aliquot taken 2 h after the start of the photolysis indicated that none of the starting acylsilane remained. The solution was collected under nitrogen in the conventional way and after removal of the solvent gave a residue which was purified by chromatography on silica gel. The majority of the material was eluted with chloroform to give 0.130 g (54%) of **10**: i.r. (CCl_4) 2.70 (Si—OH), 2.85 (C—OH), 5.85 (C=O), 7.0, 8.95 (Si—Ph) μ; n.m.r. (CCl_4), δ 7.18–7.67 (Ar, m, 10H), 3.60–3.82 (Si—OH + COH, broad, 2H), 2.13–2.50 (CH_2CO, m (broad), 2H), 1.0–2.02 (CH_2, m), with 1.19 (CMe_2, s, 6H) superimposed p.p.m.; (DMSO) δ 7.22–7.33 (Ar, m, 10H), 6.48 (Si—OH, s, 1H), 5.10 (C—OH, s, 1H) p.p.m.

Anal. Calcd. for $C_{20}H_{26}SiO_3$: C, 70.18; H, 7.66. Found: C, 70.15; H, 7.57.

Reduction of 10 with Lithium Aluminum Hydride

A mixture consisting of 0.089 g (0.000260 mol) of 7-(diphenylhydroxysilyl)-2-hydroxy-2-methylheptanone-3 (**10**) and 50 mg (0.00132 mol) of lithium aluminum hydride in 20 ml of dry ether was stirred for 20 min at room temperature. An aqueous solution of 5% HCl was added to destroy the excess lithium aluminum hydride and the mixture was then extracted with ether. The ether phases were dried and the solvent was removed under reduced pressure. An i.r. spectrum of the isolated material indicated that reduction had been complete (no carbonyl band). A total of 72 mg or 81% of the diol **11** was obtained; i.r. (CCl_4) 2.70 (Si—OH), 2.91, very broad (C—OH), 7.00, 8.96 (Si—Ph) μ.

Cleavage of 7-(Diphenylhydroxysilyl)-2-methylheptane-2,3-diol (11) with Lead Tetraacetate

A sample of lead tetraacetate was recrystallized from glacial acetic acid and dried under high vacuum. A mixture of 100 mg (0.000226 mol) of this purified material and 72 mg (0.000209 mol) of the above-produced 7-(diphenylhydroxysilyl)-2-methylheptane-2,3-diol in 75 ml of dry benzene was allowed to stand for $1\frac{1}{2}$ h. After this time the mixture was poured onto a saturated solution of sodium bicarbonate and was extracted with ether. The organic phases were washed with water and were then dried with $MgSO_4$. Evaporation of the solvents left an oily residue which gave spectra identical in every way to those of authentic 5-(diphenylhydroxysilyl)-pentanal (**12**) (7).

Photolysis of 1,1-Diphenylsilacyclohexanone-2 in Butanone-2 Saturated with Nitrogen

Purified butanone-2 was distilled from phosphorus pentoxide and a central cut was stored over Drierite for 2 days. After this time it was again distilled and a central cut was taken. The oxygen was displaced from a solution consisting of 0.200 g (0.000753 mol) of 1,1-diphenylsilacyclohexanone-2 in 30 ml of this purified solvent by bubbling nitrogen through the solution while maintaining it in the dark. An i.r. spectrum, taken 1 h after the beginning of the irradiation, indicated that no starting material remained. The solution was collected under nitrogen and the solvent was removed. Attempts to crystallize the residue from dry hexane failed. An i.r. spectrum of the material indicated that it was probably 8-(diphenylhydroxysilyl)-3-methyl-3-hydroxyoctanone-4. The n.m.r. spectra in CCl_4 and dimethyl sulfoxide confirmed this structure: i.r. (CCl_4) 2.70 (Si—OH), 2.85 (C—OH), 5.85 (C=O), 7.00, 9.00 (Si—Ph) μ; n.m.r. (CCl_4) δ 6.95–7.72 (Ar, m, 10H), 0.78–2.52 (complex), 1.12 (broad, possibly a singlet superimposed on band above) p.p.m.; n.m.r. (DMSO) δ 7.16–7.75 (Ar, m, 10H), 6.48 (Si—OH, s, 1H), 5.11 (C—OH, s, 1H) p.p.m.

Photolysis of 1,1-Diphenylsilacyclohexanone-2 in Oxygen-Free Cyclohexanone; Isolation of 15 and 16

Purified cyclohexanone was distilled at atmospheric pressure and a central cut retained. This cut was redistilled under nitrogen in "flamed out" apparatus and another central cut collected. A solution of 1.0 g (0.00377 mol) of 1,1-diphenylsilacyclohexanone-2 in 35 ml of this purified solvent was freed from oxygen and then was photolyzed for 8 h while a stream of nitrogen was constantly bubbled through the solution. The solution was collected after 8 h of irradiation and the solvent was removed by distillation under high vacuum. Two methods of purification of the residue were attempted. About half of the residue was distilled under high vacuum through a short column and three fractions boiling in the range 180–190 °C (0.05 mm) were collected. However, i.r. spectra of these fractions were all identical with the i.r. spectrum of the crude material indicating that no separation had occurred. Chromatography on silica gel collecting 75 ml fractions and using a series of solvents was more successful. With benzene as eluent, fractions 7 to 15 yielded compound **15** and after using 375 ml of chloroform, which eluted nothing, fractions 22 and 23 using ether as eluent gave compound **16**. The yields of **15** and **16** were approximately 25 and 51% respectively, as observed from a second experiment. Samples of **15** and **16** were pumped down under high vacuum at 100 °C for 18 h to prepare them for analysis. Both compounds were viscous oils. The cyclic siloxyalkene **15** had: i.r. (CCl_4) 2.76 (Si—OH), 6.01 (C=C) 7.00, 9.00 (Si—Ph) μ; n.m.r. (CCl_4) δ 7.20–7.65 (Ar, m, 10H), 4.97 (=CH, t, J = 7 Hz, 1H), 0.90–2.40 (m, 17H) p.p.m.

Anal. Calcd. for $C_{23}H_{28}SiO_2$: C, 75.77; H, 7.74. Found: C, 75.80; H, 7.82.

The hydrolysis product of **15**, the acyloin **16** had: i.r. (CCl_4); 2.70 (Si—OH), 2.85 (C—OH), 5.87 (C=O), 7.00, 8.97 (Si—Ph) μ; n.m.r. (CCl_4) δ 7.10–7.68 (Ar, m, 10H), 3.68–4.10 (C—OH + Si—OH, broad, 2H), 2.10–2.55 (CH_2CO—, m (broad), 2H), 0.82–1.95 (m, 16H) p.p.m.

Anal. Calcd. for $C_{23}H_{30}SiO_3$: C, 72.18; H, 7.90. Found: C, 72.62; H, 8.12.

Reduction of Acyloin 16 with Lithium Aluminum Hydride

A solution consisting of 120 mg (0.000314 mol) of compound **16** and 100 mg (0.00264 mol) of lithium aluminum hydride in 10 ml of dry ether was stirred for 1/2 h. A solution of 5% HCl was then added and the mixture was extracted with ether. The ether phases were dried and then evaporated to leave a residue whose i.r. spectrum indicated that reduction of the carbonyl group was complete. The yield of crude reduction product **17** was 112 mg or 93%: i.r. (CCl_4) 2.70 (Si—OH), 2.99 (C—OH, very broad), 7.00, 9.00 (Si—Ph) μ.

Treatment of 17 with Lead Tetraacetate

A solution consisting of 112 mg (0.000293 mol) of **17** as isolated from the experiment above and 129 mg (0.000293 mol) of freshly crystallized lead tetraacetate in 10 ml of dry benzene was stirred for 1/2 h at room temperature. It was then poured onto a saturated solution of sodium bicarbonate and was extracted with ether. After drying, the solvents were distilled from the products at atmospheric pressure. The flask containing the residue was then connected to a vacuum apparatus and all volatile material was collected in a cold trap. The volatile material (cyclohexanone + benzene) gave an i.r. spectrum (using benzene in the reference cell) which compared very favorably with an i.r. spectrum of authentic cyclohexanone. The 2,4-dinitrophenylhydrazone of this isolated ketone was prepared by the method of Parrick and Rasburn (10) by adding 2 ml of dimethyl sulfoxide and 100 mg of 2,4-dinitrophenylhydrazine followed by 1 drop of concentrated HCl to the residue. After 15 min the benzene was removed from the sample under reduced pressure and 0.049 g or 65% of the crystalline 2,4-dinitrophenylhydrazone of cyclohexanone was deposited. This material was filtered off, washed with dilute HCl, water, and then 95% ethanol, m.p. 161–163 °C, mixed m.p. with an authentic sample 162–163 °C. The non-volatile material consisted of 0.076 g or 91% of 5-(diphenylhydroxysilyl)-pentanal **12**, whose i.r. and n.m.r. spectra were identical to those of authentic material.

Hydrolysis of Siloxyalkene 15

A small sample of chromatographically pure **15** as isolated from the photolysis above was dissolved in acetone and about 5 drops of a 5% v/v HCl solution was added. After standing at room temperature for 1/2 h the sample was added to water and extracted with ether. The ether phases were dried and the solvents were then removed to leave a residue which gave an i.r. spectrum identical to that of authentic **16**. An n.m.r. spectrum taken in dimethyl sulfoxide confirmed the structure of the product.

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