Acylsilane Photolyses: 1,1-Diphenyl-1-Silacyclohexanone-2 in Cyclohexane

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Photolysis of the cyclic acylsilane 1,1-diphenyl-1-silacyclohexanone-2 yields 1,1-diphenyl-1-silacyclopentane and two dimeric products whose structures were established by chemical and spectroscopic methods. A mechanism involving a siloxycarbene intermediate which is trapped by a second acylsilane molecule, is proposed for the formation of the dimers.

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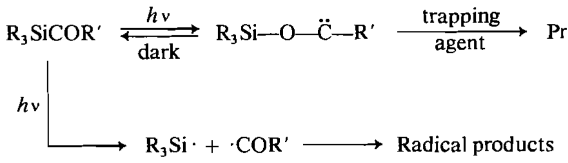
La photolyse de l'acylsilane cyclique, diphényl-1,1 sila-1 cyclohexanone-2, conduit au diphényl-1,1 sila-1 cyclopentane et à deux produits dimères dont les structures ont été établies par des méthodes chimiques et spectroscopiques. Pour la formation des dimères, on propose un mécanisme impliquant un intermédiaire siloxycarbène qui est piégé par une seconde molécule d'acylsilane. [Traduit par le journal]

Over the past few years we have been engaged in elaborating the photochemical behavior of acylsilanes (R_3SiCOR'). It has been shown that depending on the structure of the acylsilane and particularly on the solvent employed, two types of reaction can occur. These are (*i*) the photoisomerization of the acylsilane to a siloxycarbene which may revert back to acylsilane in a dark reaction if not trapped by a suitable reagent, and (*ii*) a radical type process which generally occurs less readily than reactions involving the siloxycarbene. Our findings are summarized in Scheme 1.

Most acylsilanes studied to date show this dual photochemical behavior. The photochemically formed siloxycarbenes insert into the polar bonds of protic solvents to give adducts (1), form cyclopropanes with suitably reactive alkenes (2), or form oxiranes (or their hydrolysis products) on reaction with certain carbonyl compounds (3). When photolyzed in halogenated solvents, acylsilanes yield radical type products (which may arise through exciplex formation (4)), including R_3SiCl and $R'COCl$ (5). More recently it was found that when acyclic acylsilanes such as acetyl- or phenylacetyltriphenylsilane were photolyzed in cyclohexane, a solvent unreactive towards silyl radicals or siloxycarbenes, a variety of products was obtained whose mode of formation was best explained as arising from the initial addition of silyl radicals to the carbonyl oxygen of a second molecule of acylsilane followed by normal radical behavior (6).

We now wish to report a new photochemical behavior of acylsilanes, namely photodimerization, which was observed when the cyclic acylsilane 1,1-diphenyl-1-silacyclohexanone-2 was photolyzed in cyclohexane. This investigation was actually one of the earliest studies in our laboratory of the photochemical behavior of acylsilanes (7), but because the structures of the two main products could not be assigned unambiguously from the available chemical and physical data, we deferred publication until the structures of the photodimers were confirmed recently by X-ray structure analysis by Nyburg *et al.* (8) of our department.

Irradiation of diphenylsilacyclohexanone **1** in



SCHEME 1

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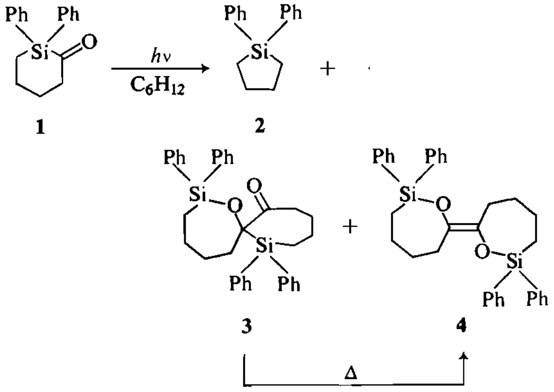
[1] Dow Corning Postdoctoral Fellow 1973–1975.

dry, oxygen-free, cyclohexane with a mercury spot lamp ($\lambda_{max} \simeq 360$ nm) gave three main products, 1,1-diphenyl-1-silacyclopentane, **2** (18–22%), and two dimers, **3** (20–53%) and **4** (9–12%), whose structures are given below.



The photolysis appeared to be quite clean and the low yield of isolated products in some cases was due more to the difficulty in isolating pure compounds than to the presence of significant amounts of unidentified products.

It was noted that **3** was thermally labile, the β-ketosilane functionality being quantitatively converted into the siloxyalkene functionality in **4** in less than 20 h at reflux in cyclohexane.[2] In accord with this observation, if the photolysis was carried out with cooling, higher yields of **3** (55%) were obtained, compared to the 20% isolated from photolysis at ambient temperature (35–40 °C). However, even at low temperatures, significant amounts of **4** were obtained and hence **4** is believed to arise, at least in part, directly as a result of the photolysis.

The diphenylsilacyclopentane may result from a Norrish type I cleavage to a diradical, followed by loss of carbon monoxide and ring closure. However, since none of the other types of products usually obtained from the photolysis of cycloalkanones were obtained (aldehydes, alkenes) and since none of the usual products resulting from silyl radicals were obtained (6), it is possible that the diphenylsilacyclopentane arose from a concerted extrusion of carbon monoxide.

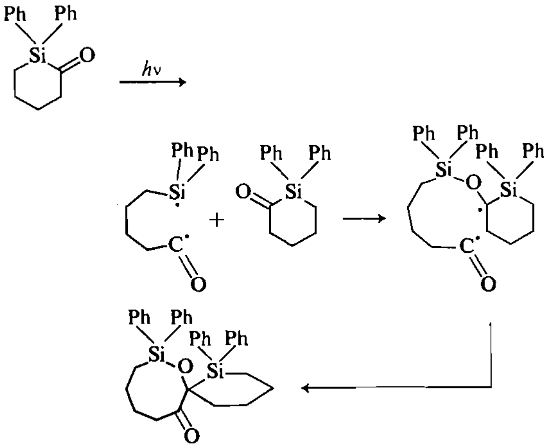
It seems unlikely that **3** (and **4**) arise from a radical process, since, by analogy with previous studies (6), the silyl radical resulting from cleavage of the acylsilane (Scheme 2) would be expected to attack the carbonyl oxygen of a second acylsilane molecule and the resulting diradical would then presumably close to the 8,6-spiro compound **3*b***, shown in Scheme 2; in fact the 7,7-spiro compound **3** (Scheme 1) is the observed product.

The formation of the dimeric products can be explained logically as arising from attack of a cyclic siloxycarbene, which is nucleophilic in character, on the carbonyl group of a second molecule of the silacyclohexanone, analogous to the observed addition reactions of siloxycarbenes with other carbonyl compounds such as acetaldehyde, acetone, and cyclohexanone (3). The resulting intermediate, **5**, could then react by any of the three routes shown in Scheme 3.

Unlike the reaction with acetaldehyde (3), there was no evidence obtained for the closure of the intermediate **5** to give the oxirane **6**. However a 1,2-migration of silicon to the electron deficient center in **5**, accompanied by reformation of the carbonyl group accounts for the formation of **3** (route *b*). Alternatively, the attack of the oxyanion center on the neighboring silicon atom, with displacement of electrons toward the electron deficient center, forming a carbon–carbon double bond, accounts for the formation of **4** directly from the intermediate (route *c*).

This behavior attributed to **5**, reacting by routes *b* and *c*, follows closely the behavior of the intermediate formed between acylsilanes and diazomethane, where β-ketosilanes and siloxyalkenes are likewise formed competitively (10, 11).

Other routes to **3** and **4** can be envisioned but



3*b*

SCHEME 2

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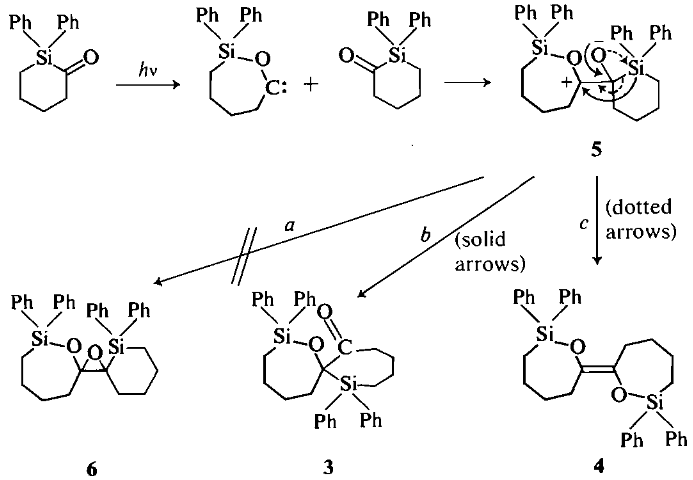
[2] This was the first observed case of a β-ketosilane to siloxyalkene thermal rearrangement (9, 10).

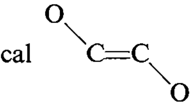


SCHEME 3

appear less likely. Thus **3** could arise by direct insertion of the siloxycarbene into the silicon–acyl bond of the second acylsilane molecule but this is unprecedented. Compound **4** could arise by direct coupling of two siloxycarbenes but the probable concentration of siloxycarbene in the system makes the formation of **4** in significant amounts by this route unlikely.

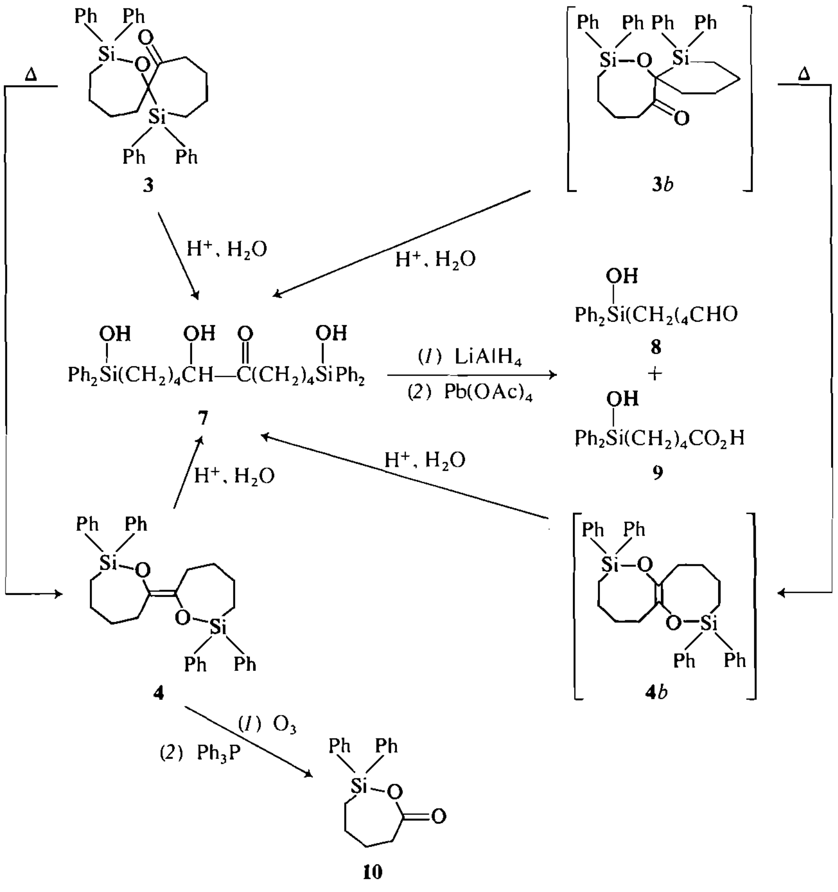
Therefore it appears that the photodimers formed in the photolysis of diphenylsilacyclohexanone in cyclohexane arise from siloxycarbenes, in contrast to the behavior of acyclic acylsilanes whose photolysis in cyclohexane led to radical-derived products (6). A similar tendency for cyclic acylsilanes to react via siloxycarbenes under conditions where acyclic acylsilanes are either unreactive or react by radical pathways has been observed previously (in reactions with C=C and C=O) but it is not yet clear whether this difference arises because the cyclic siloxycarbenes are more reactive, are more readily formed, or are longer-lived than their acyclic counterparts.

The structures of products **3** and **4** were originally assigned partly on the preceding mechanistic arguments and also on the basis of chemical and spectroscopic data. Thus **3** was believed to be a β-ketosilane by virtue of the relatively long wavelength carbonyl absorption at 5.90 μm (11). No other functional groups appeared to be present. Hydrolysis of **3** gave a compound formulated as **7** (Scheme 4), containing silanol and α-hydroxyketone groups. Isolation of such a product fails to distinguish between **3** and **3*b***, whose possible modes of formation were described earlier in Schemes 2 and 3. The identity of **7** was confirmed by its reduction to the diol and cleavage with lead tetraacetate to give the known 5-(diphenylhydroxysilyl)pentanal, **8**, and the related acid, **9** (12).

Compound **4** (or its possible alternative **4*b***) derived either directly from the photolysis or indirectly by the thermolysis of **3** (or **3*b***) showed no OH, C=O, or C=C i.r. absorption although its Raman spectrum showed a band at 5.93 μm (symmetrical  $\mathrm{OC{=}CO}$). Mild acid hydrolysis of this dimer similarly gave **7** but this fact again failed to distinguish unambiguously between the possible structures **4** and **4*b***.

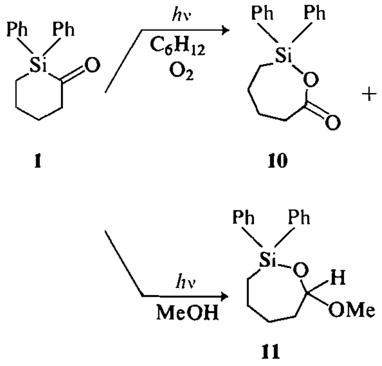
In an attempt to distinguish **4** from **4*b*** the compound was treated with ozone, followed by careful anhydrous work-up using triphenylphosphine to destroy the ozonide. The product isolated, contaminated with some triphenylphosphine oxide, was the silalactone **10**, expected from **4**. However, the possibility that the macrocyclic bis-lactone derivable from **4*b*** might have broken down to give **10** during work-up could not be ruled out.

Numerous other attempted structure-proving reactions, including reduction, and reaction with methylmagnesium iodide, failed to distinguish between the possible pairs of isomers and hence it was necessary to confirm the proposed structures for **3** and **4** by X-ray diffraction techniques.



SCHEME 4

The silalactone **10** was also formed in significant yield along with silacyclopentane **2** when the cyclic acylsilane **1** was photolyzed in cyclohexane saturated with oxygen. When **1** was photolyzed in methanol, the cyclic acetal **11**, expected from trapping of the siloxycarbene (1), was obtained.



One major question remaining is the apparent ease (80 °C, <20 h) with which the β-ketosilane **3** rearranges to siloxyalkene **4**. Other than this case, the most facile β-ketosilane–siloxyalkene rearrangement known is that of triphenylsilylacetophenone, which required about 18 h at 100 °C for complete rearrangement; only 10% rearrangement occurred in 18 h at 80 °C (13). It is known that incorporation of a β-ketosilane functionality into a seven-membered ring considerably reduces the ease of thermal rearrangement compared to acyclic systems. For example, 1,1-dimethyl-1-silacycloheptanone-3 rearranged about 5 times more slowly than trimethylsilylacetone and 170 times more slowly than triphenylsilylacetophenone (13). This appears to be reasonable since models suggest that approach of the carbonyl oxygen to the β-silicon atom is more difficult in the cyclic system. The difficulty of such an approach in the spiro compound **3** appears to be even more pronounced. Therefore, the observed ease of rearrangement of **3** suggests that the α-siloxy functionality is playing an important role, not yet understood, in facilitating the β-ketosilane to siloxyalkene rearrangement; the fact that the siloxy-silicon atom of **3** is somewhat closer (3.02 Å) to the carbonyl oxygen than is the β-silicon atom with which bonding ultimately occurs (3.77 Å) is probably of some relevance.

Experimental

The synthesis of 1,1-diphenyl-1-silacyclohexanone-2 has been described previously (12).

Photolyses were carried out in Pyrex flasks using a Westinghouse PAR 38 100 W mercury spot lamp. Solvents were carefully dried by standard methods and photolysis solutions were deoxygenated by bubbling dry nitrogen through them. The extent of photolyses was determined by withdrawing small samples and following the disappearance of the carbonyl absorption of the acylsilane at 6.08 μm.

Nuclear magnetic resonance spectra were recorded on a Varian A60 instrument, i.r. spectra on a Beckman IR8. Column chromatography used Grace activated silica gel, grade 923, 100–200 mesh. Melting points are uncorrected.

Photolysis of 1 in Cyclohexane

This reaction was carried out many times and variations in the conditions and work-up procedure significantly affected the results. The isolations of the three photolysis products are described separately.

Photolysis at 0 °C. Isolation of Dimer 3, 2,2,8,8-Tetraphenyl-1-oxa-2,8-disilaspiro[7.7]tridecanone-13

A solution of 4.4 g of **1** in 80 ml of cyclohexane, cooled to 0 °C in an ice bath, was irradiated for 8 h. The solution was evaporated to dryness at reduced pressure without heating and the residue was dissolved in 30 ml of dry hexane. The solution was stored at room temperature for 20 h to give 2.41 g (54.8%) of dimer **3** as white crystals. The product was recrystallized by dissolving it in a minimum of cold dichloromethane and reprecipitating it with hexane; m.p. 152–154 °C; i.r. (CCl_4) 5.90 (Si—C—C=O) 7.0, 9.0 μm (Si—Ph); n.m.r. ($CDCl_3$) δ 7.0–7.85 (m, 20H, Ph), 2.15–2.96 (broad, 2H, CH_2CO), 0.85–2.1 p.p.m. (m, 14H, ring protons).

Mol. Wt. Calcd. for $C_{34}H_{36}O_2Si_2$: 532. Found (osmometry): 544.

Anal. Calcd. for $C_{34}H_{36}O_2Si_2$: C, 76.65; H, 6.76. Found: C, 76.93; H, 6.83.

Photolysis at 15 °C; Isolation of Dimer 4, trans-7,7′-Bicyclo(2,2-diphenyl-1-oxa-2-silacycloheptylidene)

Photolysis of 2.0 g of **1** in cyclohexane cooled by a cold finger condenser (solution temperature *ca.* 15 °C) followed by crystallization from hexane, as above, gave a total of 1.06 g (53%) of dimer **3**. The mother liquor was then evaporated to dryness and the oily residue was taken up in a small amount of diethyl ether. This solution was stored at −20 °C to yield 0.17 g (9%) of dimer **4**. This compound, which was more readily obtained from thermolysis of **3** (see below), had the following properties: m.p. 149–151 °C; i.r. (CCl_4) 7.0, 9.0 μm (Si—Ph); Raman (powder) 5.93 μm (O—C=C—O); n.m.r. ($CDCl_3$) δ 7.2–7.75 (m, 20H, Ph), 2.3–2.6 (m, 4H, CH_2—C=C—CH_2), 1.1–2.0 p.p.m. (m, 12H, ring protons).

Mol. Wt. Calcd. for $C_{34}H_{36}O_2Si_2$: 532. Found (osmometry): 527.

Anal. Calcd. for $C_{34}H_{36}O_2Si_2$: C, 76.65; H, 6.76. Found: C, 76.78; H, 6.93.

Photolysis at Ambient Temperature; Isolation of 2, 1,1-Diphenyl-1-silacyclopentane

Following the photolysis of 4.3 g (0.016 mol) of **1** in cyclohexane at ambient temperature (solution temperature *ca.* 40 °C) and crystallization of dimer **3** (1.06 g, 25%) from petroleum ether (b.p. 60–70 °C) the residual product was distilled. This afforded 0.70 g (18%) of 1,1-diphenyl-1-silacyclopentane, b.p. 115–120 °C/0.2 Torr, which was identified by comparison with the authentic material (14).

Thermal Rearrangement of 3 to 4

A solution of 1.06 g of **3** in 50 ml of cyclohexane was refluxed for 20 h by which time the i.r. carbonyl absorption of **3** (5.90 μm) had disappeared. Removal of solvent gave a solid which was washed twice with cold ether to give 0.92 g (90%) of **4**, m.p. 150–150.5 °C, identical to the material obtained from the photolysis. An additional 0.06 g (total yield 93%) was crystallized from the ether washings.

Hydrolysis of 3 with Aqueous Acid; Isolation of 7

A solution of 0.5 g (0.96 mmol) of **3** in 25 ml of acetone containing 10 drops of 5% aqueous hydrochloric acid was stirred at room temperature for 2 days. The acetone was evaporated and the residue was extracted with ether and water. The organic product was chromatographed on silica gel. Elution with ether gave an oil which was identified as pure **7** (0.53 g, 97%) on the basis of the following data: i.r. (CCl_4) 2.70 (Si—OH), 2.90 (broad, C—OH), 5.85 (C=O), 7.0, 9.0 μm (Si—Ph); n.m.r. (DMSO) δ 6.48 (s, 2H, SiO*H*), 5.10 p.p.m. (d, 1H, CHO*H*).

Anal. Calcd. for $C_{34}H_{40}O_4Si_2$: C, 71.80; H, 7.09. Found: C, 72.02; H, 7.01.

Reduction and Cleavage of 7 to 8, 5-(Diphenylhydroxysilyl)pentanal

To 0.25 g (0.44 mmol) of **7**, obtained as above, in ether solution was added 0.20 g (5.3 mmol) of lithium aluminum hydride. After 18 h at reflux, normal aqueous work-up yielded material having both Si—H (i.r. 4.7 μm) and Si—OH groups present. The Si—H function was hydrolyzed to SiOH by brief treatment of the product in aqueous alkaline ethanol. Work-up gave an oil (0.26 g, 96%) presumed to be the expected bis(diphenylhydroxysilyl)-diol; i.r. (CCl_4) 2.70 (Si—OH) 2.98 μm (broad, strong, C—OH).

To 0.14 g (0.25 mmol) of the above in 25 ml of benzene was added 0.13 g (0.29 mmol) of freshly recrystallized lead tetraacetate. After 18 h at room temperature saturated aqueous sodium bicarbonate was added and the solution was extracted with ether to give a mixture of 5-(diphenylhydroxysilyl)pentanal, **8**, and the corresponding acid, **9**. The acid was removed by extraction with sodium bicarbonate to give 0.066 g (39%) of the pure aldehyde, the spectra of which were identical to those of the authentic material (12).

Acidification of the sodium bicarbonate solution and extraction with ether afforded 0.053 g (31%) of 5-(diphenylhydroxysilyl)pentanoic acid, **9**, m.p. 102–104 °C, which was identified by mixture m.p. with the authentic material (12).

A control experiment showed that the aldehyde, **8**, was partly converted by lead tetraacetate into the acid, **9**, under the conditions of the reaction.

Hydrolysis of Dimer 4

Hydrolysis of dimer **4** in dilute aqueous acidic acetone for 4 days at room temperature gave the hydroxyketone, **7** (identical to the above), in almost quantitative yield.

Ozonolysis of Dimer 4; Isolation of Silalactone 10

A solution of 1.12 g (2.11 mmol) of **4** in cyclohexane was treated with ozone under anhydrous conditions. Following completion of the reaction 0.53 g (2.11 mmole) of pure dry triphenylphosphine was added and the solution was concentrated and then distilled under vacuum (175–187 °C/0.05 Torr) to give a mixture of 5-(diphenylhydroxysilyl)pentanoic acid lactone, **10**, and triphenylphosphine oxide which were identified spectroscopically.

The mixture was hydrolyzed with dilute acid and the resultant product was chromatographed. Elution with chloroform yielded 0.23 g (37%) of triphenylphosphine oxide, m.p. 155–157 °C, and 0.29 g (21%) of 5-(diphenylhydroxysilyl)pentanoic acid, **9**, m.p. 102–102.5 °C.

Photolysis of 1 in the Presence of Oxygen

The acylsilane **1** (2.55 g, 9.58 mmol) was irradiated in 40 ml of cyclohexane through which oxygen was bubbled. After completion of the photolysis (6 h) the solvent was removed and the residue (i.r. 5.76 μm) was distilled to give 0.40 g (18%) of 1,1-diphenyl-1-silacyclopentane, **2**, (102–112 °C/0.03 Torr), and 0.72 g (27%) of lactone **10** (180–185 °C/0.25 Torr).

The above lactone was hydrolyzed in wet ether to give crystalline 5-(diphenylhydroxysilyl)pentanoic acid (73% yield) which was identified by mixture m.p. with authentic material.

Preparation of 5-(Diphenylhydroxysilyl)pentanoic Acid Lactone, 10

A solution of 0.75 g of the acid, **9**, in 25 ml of acetic anhydride was slowly distilled at atmospheric pressure until the acetic acid and anhydride were largely removed. The residue was distilled to give 0.33 g (47%) of the expected lactone, **10**; b.p. 150–152 °C/0.005 Torr; n_D^{25} 1.5814; i.r. (CCl_4) 5.76 μm (C=O); n.m.r. (CCl_4) δ 7.2–7.7 (m, 10H, Ph), 1.21–2.24 p.p.m. (m, 8H, ring protons).

Anal. Calcd. for $C_{17}H_{18}O_2Si$: C, 72.3; H, 6.38. Found: C, 71.9; H, 6.30.

This lactone slowly hydrolyzed to the acid, **9**, in moist air.

Photolysis of 1 in Methanol; Formation of 11

The photolysis of a solution of 1.0 g of **1** in 25 ml of methanol was complete in 0.5 h. Removal of the solvent gave an oil, the spectra of which indicated it to consist of over 95% of the cyclic acetal, **11**, contaminated with the corresponding open-chain aldehyde. Distillation gave a sample of pure acetal (0.40 g, 36%); b.p. 130–132 °C/0.04 Torr; i.r. (CCl_4) 3.51 (OCH_3), 7.0, 9.0 μm (SiPh); n.m.r. (CCl_4) δ 7.1–7.75 (m, 10H, Ph), 4.9 (broad, t, 1H, O—CH—O), 3.23 (s, 3H, OCH_3), 0.91–2.15 p.p.m. (m, 8H, ring protons).

Anal. Calcd. for $C_{18}H_{22}O_2Si$: C, 72.43; H, 7.43. Found: C, 72.70; H, 7.48.

This acetal was readily converted to the aldehyde, **8**, in aqueous alkaline tetrahydrofuran.

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