REACTION OF DIMETHYLSILYLENE WITH CYCLOOCTENE OXIDE

WILLIAM F. GOURE and THOMAS J. BARTON*

Department of Chemistry, Iowa State University, Ames, Iowa 50011 (U.S.A.)

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Summary

The deoxygenation of cyclooctene oxide with both thermally and photo-chemically generated dimethylsilylene is described. Four mechanistic possibilities are considered; two involving initial silaoxetane formation, and two involving ylide ($\supset$Si$^-$—O$^+\subset$) formation. It is concluded that ylide formation must be favored. However, whether this ylide actually extrudes dimethylsilanone ($Me_2Si=O$), or simply acts as a "silanone transfer agent" cannot be conclusively determined from the data.

The recent report by Tzeng and Weber [1] of the reaction of dimethyl-silylene and vinyl epoxides prompts us to tardily report our investigations [2] of the oxidation of dimethylsilylene by cyclooctene oxide. This study is part of a program of synthesis and investigation of the chemistry of small rings containing a silicon—oxygen bond.

Since our initial proposal [3] that silenes ($R_2Si=CR_2'$) cycloadd to the carbonyl group of ketones and aldehydes to form silaoxetanes ($\underline{I}$), which under our conditions ($>400°C$, gas phase) underwent decomposition to a silanone ($\underline{II}$) and an olefin, this route has become one of the standard tests for silene intermediacy. However, it is our belief that under the much milder reaction conditions employed in several more recent studies, such facile decomposition of $\underline{I}$ is an unreasonable thermodynamic expectation.


$$(I) \qquad\qquad (II)$$
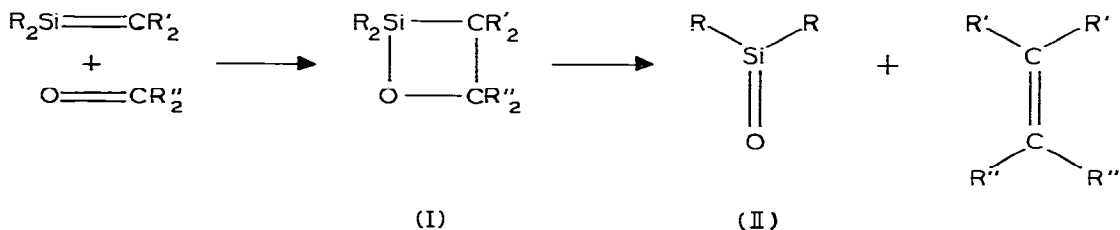
Thus, we have been particularly interested in obtaining a silaoxetane ring,

34

and exposing it to a variety of thermal and photochemical conditions. Both the established ability of silylenes to insert into strained rings [4], and the considerable strength of the silicon—oxygen bond, suggested that insertion of silylenes into epoxides to form silaoxetanes was a reasonable expectation.
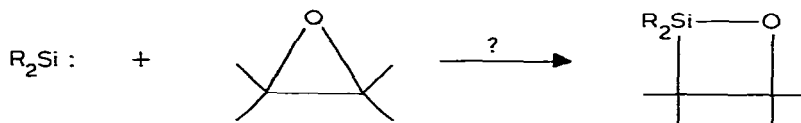

To maximize our chances of actually isolating a silaoxetane, the mildest known thermal generator of dimethylsilylene, hexamethylsilirane (III) [5] was chosen for the initial studies. Heating a benzene solution of III and an excess of cyclooctene oxide at 84°C for 12 h led to formation of tetramethylethylene and octamethyl-2,5-disiloxacyclopentane, the usual products from thermolysis of III, along with a 48% yield of cyclooctene (Scheme 1). Cyclooctene oxide

SCHEME 1
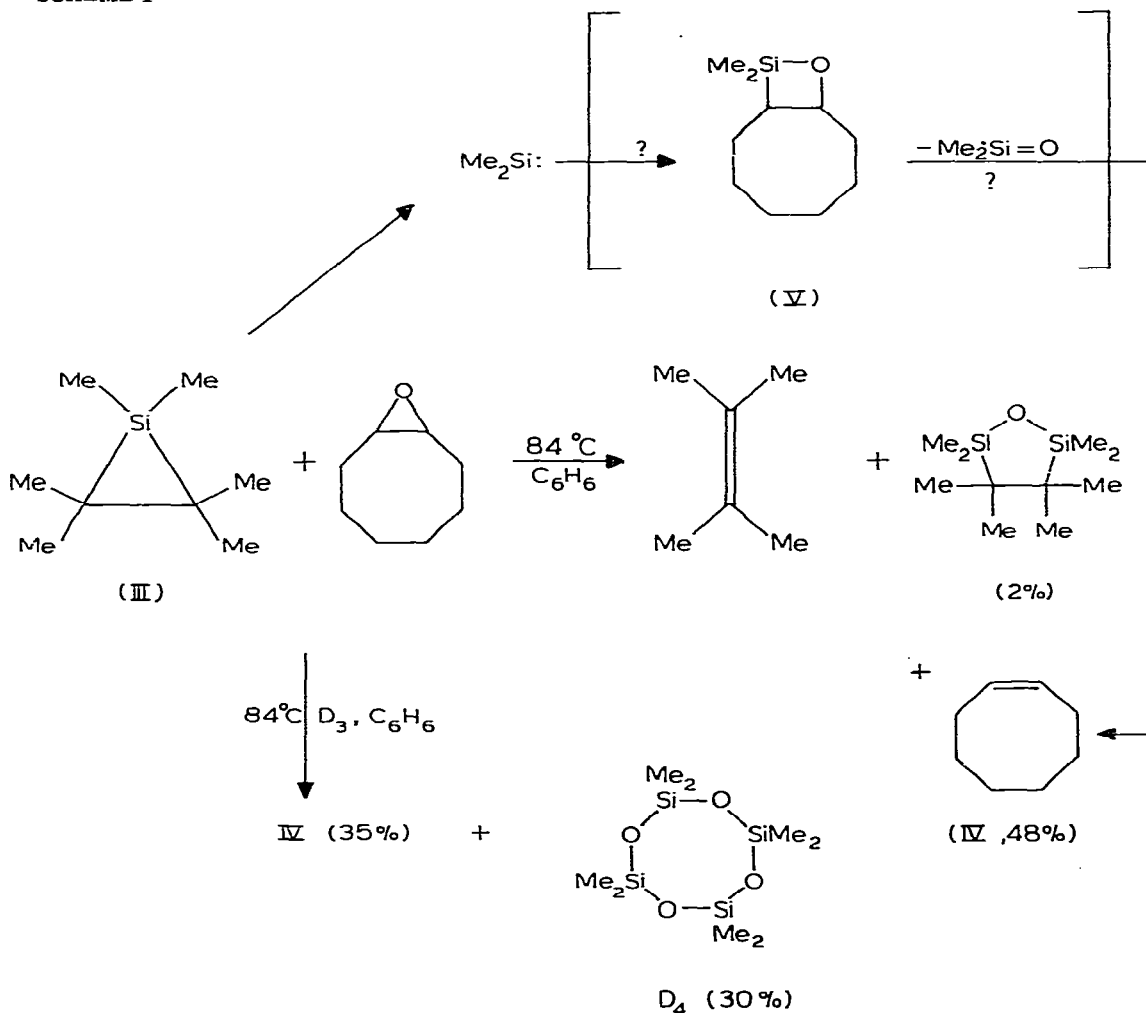
was independently shown not to arise from thermolysis of cyclooctene oxide under these conditions. Thus, these results are in keeping with the desired insertion of dimethylsilylene into the epoxide to form silaoxetane V, which extruded dimethylsilanone to afford cyclooctene. Inclusion of hexamethylcyclotrisiloxane (D_3) in the reaction mixture resulted in formation of octamethylcyclotetrasiloxane (D_4) in a yield of 30%. Insertion of dimethylsilanone into D_3 to form D_4 has often been used as a test for silanone intermediacy [e.g., 6].

SCHEME 2
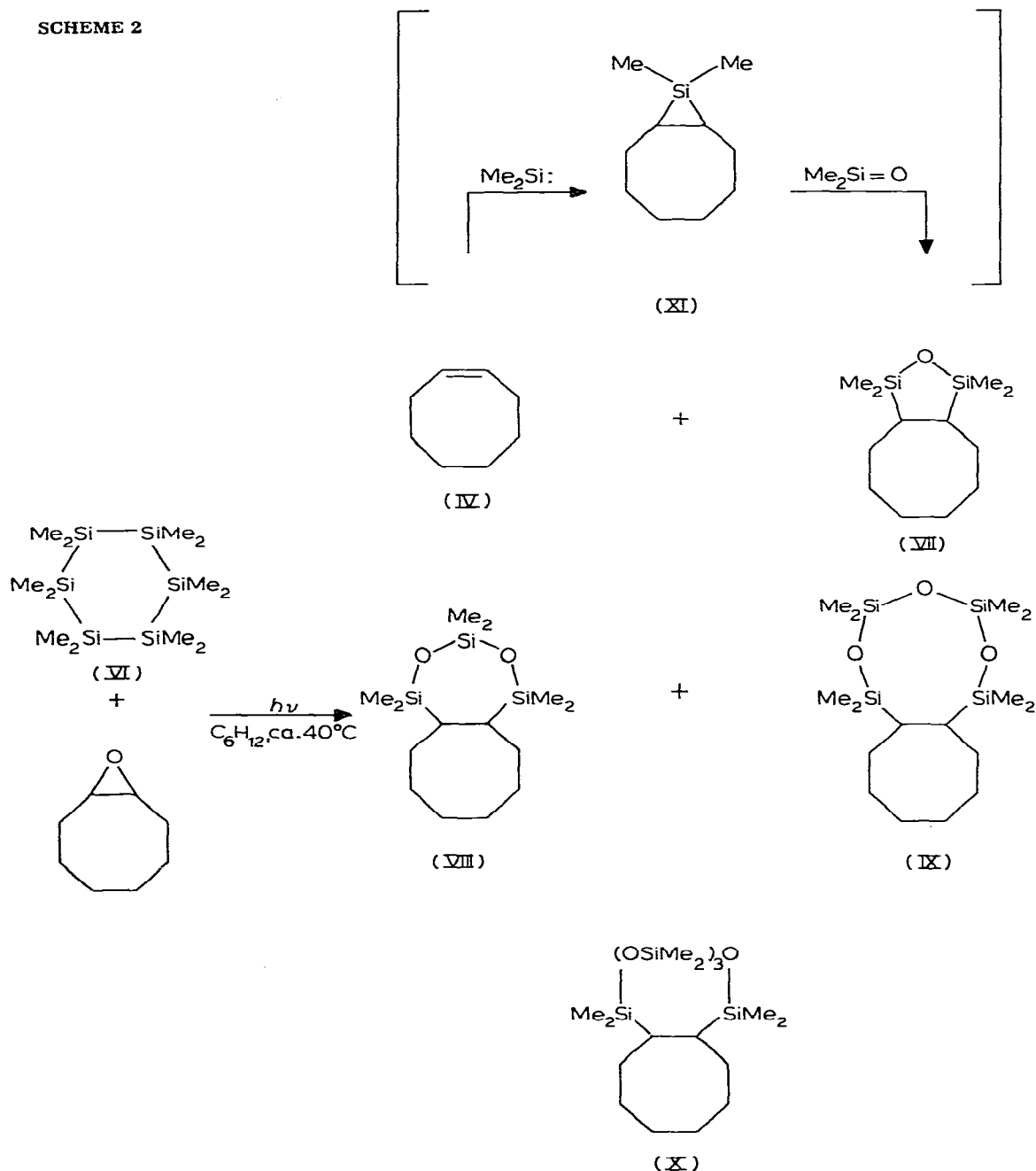
Thus, if silaoxetane V is formed in the above reactions, it is either too unstable or too reactive to survive. To lower the thermal requirements for dimethylsilylene generation, we turned to photolysis of dodecamethylcyclohexasilane (VI) [7]. Irradiation (450 W Hanovia through quartz) of a cyclohexane solution of VI and cyclooctene oxide afforded a 62% yield of cyclooctene after 2 h. Continued irradiation resulted in the gradual disappearance of cyclooctene, and the formation of cyclic siloxanes VII, VIII, IX, and X (Scheme 2 and Table 1). An economical explanation for both the decrease in cyclooctene and the appearance of these cyclic siloxanes is insertion of dimethylsilylene into the π-bond of cyclooctene to form silirane XI [8], followed by sequential insertions of dimethylsilanone. ·

The involvement of dimethylsilanone in this reaction was further suggested by the observation that addition of D_3 to the reaction mixture eliminated the secondary products VII—X, and afforded high yields of D_4 and significant amounts of $\overset{\cdot}{D_5}$. The only other new product observed was XII, the known adduct of dimethylsilylene and D_3 (Scheme 3 and Table 2).

SCHEME 3

(XII)
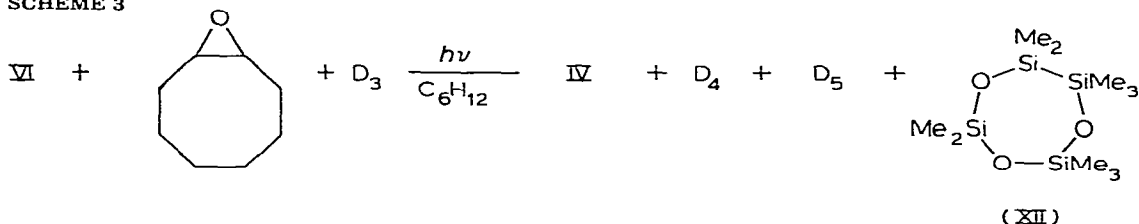
If indeed these reactions involve the intermediacy of dimethylsilanone, the results still do not require that it originate from decomposition of silaoxetane V. Reaction of dimethylsilylene and epoxide could equally well proceed by formation of ylide XII, followed by extrusion of dimethylsilanone (Scheme 4). As we find it difficult to believe that V would be so thermally unstable as to extrude silanone under our conditions, the ylide route appears more attractive. However, this is only true if dimethylsilanone is actually involved in our reactions, and that must be questioned. It is possible that a silaoxetane could serve as a "silanone transfer agent", as shown in Scheme 4, to produce cyclooctene. We discard this route since the other product, disiloxane XIV, is never observed.

TABLE 1

PHOTOLYSIS OF VI AND CYCLOOCTENE OXIDE

Irradiation time (h)	Yield (%) [a]				
	IV	VII	VIII	IX	X
2	62	—	—	—	—
12	44	<1	4	2	—
18	16	—	5	·2	2

[a] Yields are obtained by calibrated GC and are based on reacted epoxide.

TABLE 2

PHOTOLYSIS OF VI AND CYCLOOCTENE OXIDE WITH ADDED D$_3$

Irradiation time (h)	Yield (%) [a]			
	IV	D$_4$	D$_5$	XII
2	76	73	<2	—
12	22	60	8	9

[a] Yields (GC) of IV, D$_4$ and D$_5$ are based on reacted epoxide. The yield of XII is based on reacted D$_3$.

Although the polarity of ylide XIII is opposite that required for a direct inser-

SCHEME 4

(Ⅴ)

(ⅩⅢ)

(ⅩⅣ)

(Ⅳ)
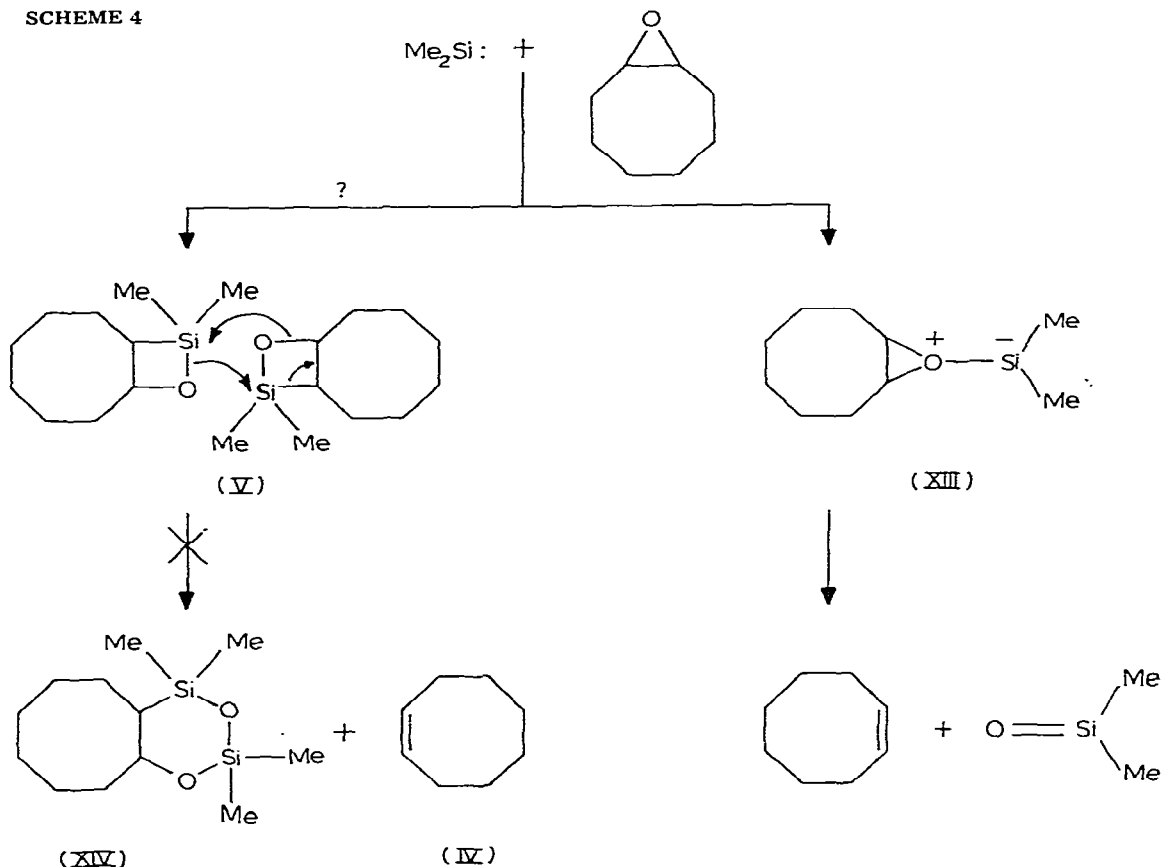
not observed

tion into a Si—O bond, it is possible that XIII could act as a "silanone transfer agent". As illustrated in Scheme 5, such a transfer would be initiated by nucleophilic attack by the silyl anion of XIII on silicon in a siloxane. Decomposition of 1,3-ylide XV in either a stepwise or concerted fashion could yield the formal product of silanone insertion and cyclooctene. Such a route has the added advantage of explaining the absence of the expected oligomers of

dimethylsilanone (e.g., D_3 and D_4) in the untrapped reactions. Thus, the data

SCHEME 5

(XV)
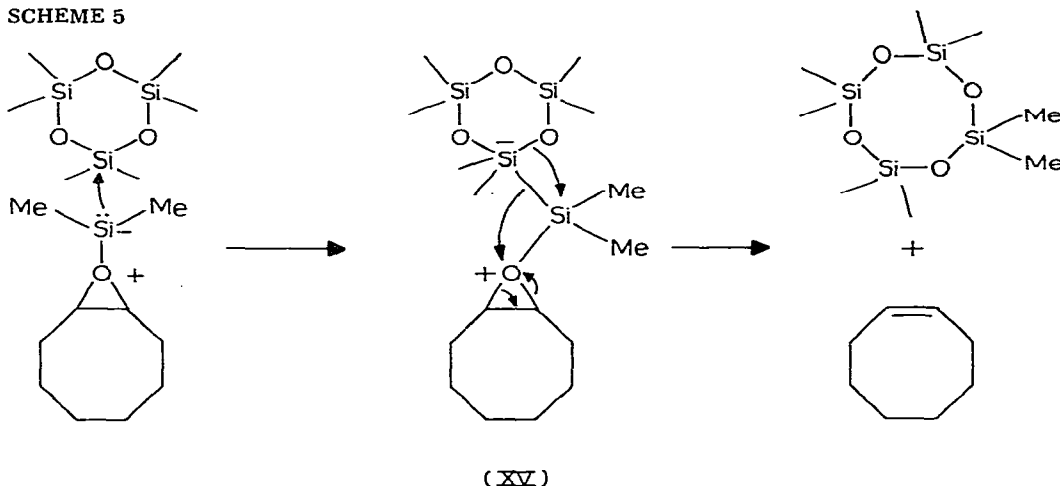
will not allow absolute distinction between extrusion of dimethylsilanone from ylide XIII, and "silanone transfer" from ylide XIII. It should also be noted that nothing in our data demands that free dimethylsilylene be involved in these reactions. Coordination of epoxide and VI (or photoexcited VI) may well precede the loss of "dimethylsilylene". Indeed, it is our qualitative observation that the disappearance of VI is accelerated by the presence of epoxide.

It is interesting to note that Tzeng and Weber [1] have likewise interpreted the reaction of dimethylsilylene and vinyl epoxides to proceed through an ylide intermediate (XVI), which rearranges in a stepwise fashion. This proposal is not without ambiguity since the possibility of initial silylene addition to the π-bond was not considered, nor could the data provide a distinction. Our data strongly suggests that initial ylide formation is correct, since we find that cyclo-octene does not significantly compete with cyclooctene oxide for dimethyl-silylene.
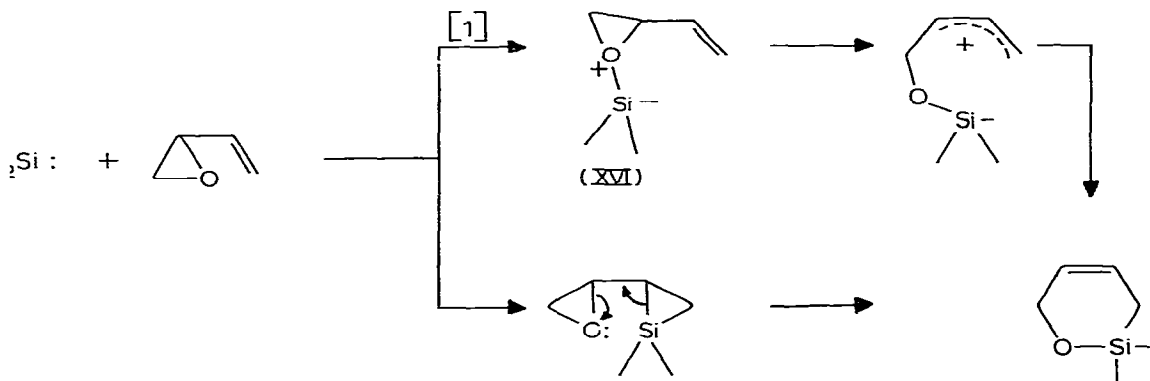
Experimental

Routine proton NMR spectra were recorded on either a Varian model EM-360 or a Hitachi R20-B spectrometer. All chemical shifts are reported as ppm

(δ scale) downfield from internal tetramethylsilane. Routine mass spectra were recorded on a Finnegan Model 4023 gas chromatograph/mass spectrometer (GCIMS), and exact mass measurements were obtained on a MS-902 mass spectrometer. Gas chromatographic (GC) data were obtained on a Tracor model gas chromatograph. All yields were obtained by GC using undecane as an internal standard.

Aldrich cyclooctene oxide was used after purification by sublimation. For the synthesis of dodecamethylcyclohexasilane (VI) the procedure of Carberry and West [9] was employed. For both the photochemical and thermal reactions control experiments were conducted to establish the stability of the reagents under reaction conditions.

Hexamethylsilacyclopropane (III)

A modification of the procedure for the synthesis of III reported by Seyferth was utilized [4a].

Diisopropylmethylsilane

A solution of 115 g (1.0 mol) of methyldichlorosilane and 369 g (3.0 mol) of isopropyl bromide in an equal volume of dry THF was added dropwise over ca. 1 h to a stirred suspension of 72 g (3.0 mol) of magnesium chips in ca. 300 ml of dry THF. After the addition was complete the solution was refluxed for 24 h. The reaction mixture was hydrolysed with dilute aqueous acid and extracted thrice with Et_2O. The organic fractions were combined, dried over $MgSO_4$, and distilled to yield 74 g (0.57 mol, 57% yield) of diisopropylmethyl-silane (b.p. 120—122°C/760 Torr): NMR (CCl_4) (ppm); δ —0.05 (d, 3 H, J 4 Hz), 0.95 (broad s, 14 H), 3.5 (broad m, 1 H), irradiation at δ 0.95 collapses the multiplet at δ 3.5 to a quartet, J 4 Hz, irradiation at δ —0.05 collapses multiplet at δ 3.5 to a broad singlet; exact mass calculated for $C_7H_{18}Si$, m/e 130.11778, measured 130.1177.

Diisopropyldimethylsilane

A solution of methyllithium (110 ml, 1.6 M, 0.176 mol) in Et_2O was added rapidly to a stirred solution of 14.69 g (0.113 mol) of diisopropylmethylsilane in ca. 200 ml of dry THF. The reaction mixture was then refluxed for 48 h. After hydrolysis with dilute aqueous acid, the reaction mixture was extracted three times with Et_2O, dried over $MgSO_4$, and distilled to yield 9.22 g (0.064 mol, 56%) of diisopropyldimethylsilane (b.p. 140—144°C/760 Torr): NMR (CCl_4) (ppm): δ —0.1 (s, 6 H), δ 0.95 (s, 14 H); exact mass calculated for $C_8H_{20}Si$, m/e 144.13343, found: m/e 144.13220.

The synthesis of III from diisopropyldimethylsilane was performed as previously reported by Seyferth [4a].

Cothermolysis of hexamethylsilacyclopropane (III) and cyclooctene oxide

A solution of 0.1773 g of cyclooctene oxide and 0.1098 g of undecane (as an internal standard) in ca. 3 ml of benzene was degassed via the freeze-thaw

method. Hexamethylsilacyclopropane (III) was then bulb-to-bulb distilled (25°C, 0.05 Torr) into the reaction vessel (cooled to —196°C). The sealed reaction vessel was heated at 84°C for 12 h. GC/MS product identification was confirmed by comparison with spectra of authentic samples. All yields were based on the amount of tetramethylethylene formed, since no accurate determination of the amount of starting silirane was performed.

Cothermolysis of hexamethylsilacyclopropane (III), cyclooctene oxide, and hexamethylcyclotrisiloxane (D_3)

A solurion od 0.1158 g of cyclooctene oxide, 0.2351 g of hexamethylcylotrisiloxane (D_3), and 0.0986 g of undecane (as an internal standard) in ca. 3 ml of benzene was degassed via the freeze-thaw method. The methods of addition of hexamethylsilacyclopropane (III), thermolysis, and product analysis were identical to that described for the copyrolysis of III and cyclooctene oxide.

Photolysis of dodecamethylcyclohexasilane (VI) and cyclooctene oxide

A typical experiment for the photolyses of dodecamethylcyclohexasilane (VI) in the presence of cyclooctene oxide is as follows: A solution of 0.1115 g of cyclooctene oxides, 0.3058 g of VI, and 0.1182 g of undecane (as an internal standard) in ca. 2 ml of dry cyclohexane was placed in a quartz NMR tube. The tube was sealed with a rubber septum and degassed by bubbling argon through the solution for ca. 15 min. The sample was irradiated for 12 h with a 450 W Hanovia lamp at ca. 40°C. Analysis of the reaction mixture and product identification (see Table 1) for the 2, 12 and 18 h reactions was conducted by GC and GC/MS. Additionally, for the 12 and 18 h photolyses preparative scale reactions were performed which allowed for product isolation via preparative gas chromotography. Compounds IV, VII, VIII, and IX were isolated and characterized spectroscopically. The low yields of X precluded any attempts of isolation.

Disiloxane VII: NMR (CCl_4) (ppm): δ 0.05 (broad s, 14 H), 1.5 (broad s, 12 H). Mass spectrum, *m/e* (% rel. inten.): 242 (parent ion, 4), 227 (2), 133 (100), 119 (12), 117, (33), 73 (23), and 59 (10).

Trisiloxane VIII: NMR (CCl_4) (ppm): δ 0.05 (broad hump, 20 H), 1.55 (broad s, 12 H). IR (CCl_4): 2960s, 2920s, 2850m, 1470w, 1447w, 1410w, 1257s, 1058s, 1015s cm^{-1}. Mass spectrum, *m/e* (% rel. inten.): 316 (molecular ion, 3), 301 (4), 207 (100), 193 (20), 192 (11), 191 (54), 147 (11), 133 (12), 103 (11), 73 (49) 59 (11). Exact mass for $C_{14}H_{32}O_2Si_3$: measured *m/e* 316.17118; calcd. 316.17102.

Tetrasiloxane IX: NMR (CCl_4) (ppm): δ 0.06 (broad hump, 26 H), δ 1.56 (broad s, 12 H). IR (CCl_4): 2960s, 2920s, 2850m, 1470w, 1445w, 1410w, 1258s, 1070s, 1015s cm^{-1}. Mass spectrum, *m/e* (% rel. inten.): 375 ($M^+ - CH_3$, 8), 281 (13), 280 (12), 265 (32), 208 (15), 207 (75), 168 (44), 153 (21), 73 (100), 59 (24). Exact mass for $C_{15}H_{35}O_3Si_4$: ($M^+ - CH_3$): measured *m/e* 375.166717; calcd. 375.166334. Exact mass for $C_{16}H_{38}O_3Si_4$: measured *m/e* 390.189011; calcd. 390.189814.

Pentasiloxane X: Mass spectrum, *m/e* (% rel. inten.): 449 (molecular ion —

CH$_3$, 7), 282 (20), 281 (76), 267 (12), 265 (11), 207 (9), 168 (26), 147 (26) 133 (34), 117 (11), 73 (100), 59 (21).

Photolysis of VI, cyclooctene oxide, and D$_3$

A typical experiment for the photolysis of dodecamethylcyclohexasilane (VI) in the presence of cyclooctene oxide and D$_3$ is as follows. A solution of 0.1334 g of VI, 0.1135 g of cyclooctene oxide, 0.2543 g of D$_3$ and ca. 2 ml of dry cyclohexane was placed in a quartz NMR tube. The tube was sealed with a rubber septum and degassed by bubbling argon through the tube for ca. 15 min. The sample was irradiated with a 450 W Hanovia lamp at ca. 40°C. Analysis of the reaction mixture and product identification was conducted via GC and GC/MS. Additionally, one reaction was performed on a preparative scale to allow for the isolation of all products by preparative gas chromatography. The GC-retention times, GC/MS, and NMR spectrum of each product was found to be identical with that of an authentic sample.

Acknowledgment

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