Journal of Organometallic Chemistry, 219 (1981) 153—161
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

EVIDENCE FOR THE INTERMEDIACY OF 1,1-DIMETHYL-2-PHENYL-1-SILA-1,3-BUTADIENE IN THE PHOTOCHEMISTRY AND PYROLYSIS OF 1,1-DIMETHYL-2-PHENYL-1-SILA-2-CYCLOBUTENE

DONGJAW TZENG, RAYMOND H. FONG, H.S. DILANJAN SOYSA and WILLIAM P. WEBER

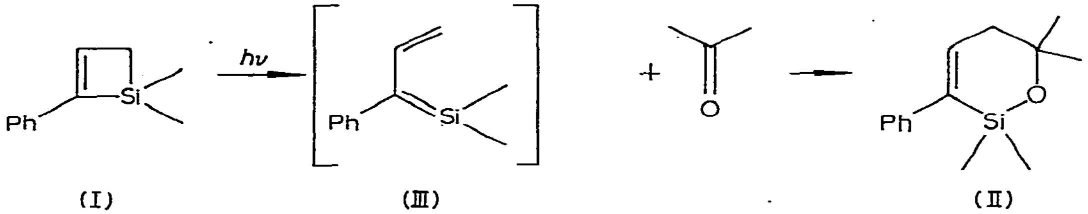
Department of Chemistry, University of Southern California, Los Angeles, California 90007 (U.S.A.)

(Received April 29th, 1981)

Summary

Photolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene (I) in methanol and methanol-O-d_1 yields dimethylmethoxy(1-phenyl-2-propenyl)silane and dimethylmethoxy(1-d_1-1-phenyl-2-propenyl)silane, respectively, as major products. These products may be formed by reaction of methanol or methanol-O-d_1 with 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene. Gas phase pyrolysis of I and acetone or formaldehyde have also been studied.

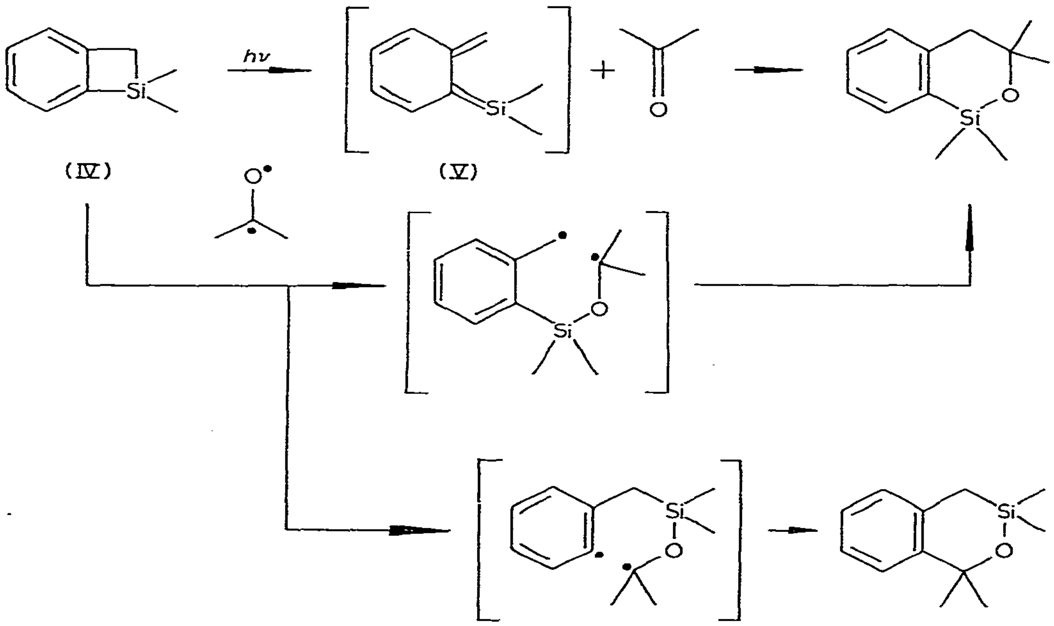
Photolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene (I) in acetone has been reported to yield 2,2,6,6-tetramethyl-1-oxa-3-phenyl-2-silacyclo-3-hexene (II). This result has been accounted for as follows: photoexcitation of I results in ring opening to yield 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene (III), a reactive intermediate which undergoes a [4+2]cycloaddition reaction with acetone to yield II [1].



A potential problem with interpretation of this experiment is that both acetone and I absorb light [UV of I λ_{max} 2570 Å (ϵ 16 100) and λ_{max} 2920 Å (ϵ 1350); UV of acetone [2] λ_{max} 2706 Å (ϵ 16)]. Recently in fact, evidence has been presented that the photoreaction of the analogous system 2,3-benzo-1,1-dimethyl-1-sila-2-cyclobutene (IV) may occur by two reaction pathways.

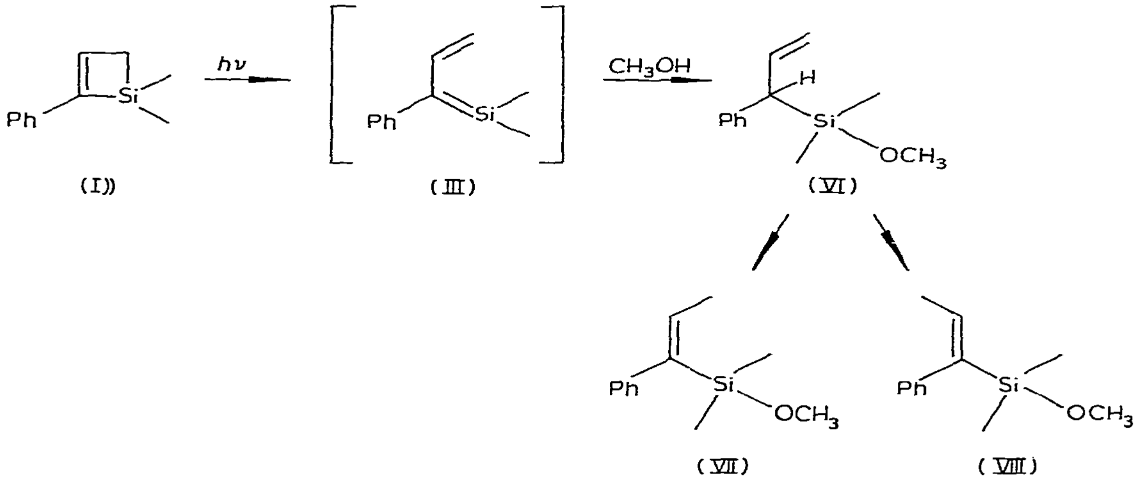
0022-328X/81/0000—0000/$02.75

The first involves ring opening of IV to yield a reactive *ortho*-silaquinone methide (V) which undergoes [4+2]cycloaddition reactions with carbonyl compounds, while the second involves an $S_{\mathrm{H}}2$ reaction of the photoexcited $n \to \pi^*$ triplet carbonyl compound on the Si—C bonds of the strained silacyclobutene ring system [3].

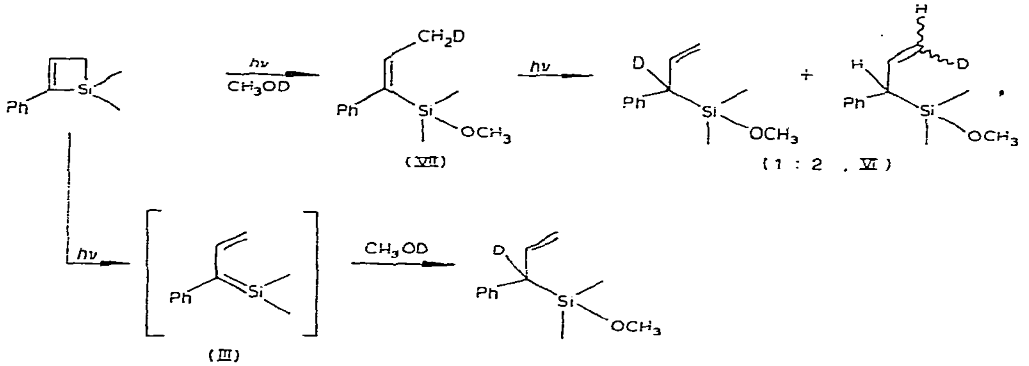


For these reasons, we should like to present additional evidence that we believe supports the formation of 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene as a reactive intermediate in our system. Recognizing the inherent problem of interpretation when two species can absorb light, we have examined the photolysis of I in methanol solution. Under these conditions, we have isolated dimethylmethoxy(1-phenyl-2-propenyl)silane (57%) (VI), *Z*-dimethylmethoxy-(1-phenyl-1-propenyl)silane (25%) (VII), and *E*-dimethylmethoxy(1-phenyl-1-propenyl)silane (17%) (VIII). Similar photolysis of I in methanol-O-d_1, yields dimethylmethoxy(1-d_1-1-phenyl-2-propenyl)silane (60%), *Z*-dimethylmethoxy-(3-d_1-1-phenyl-1-propenyl)silane (25%) and *E*-dimethylmethoxy(3-d_1-1-phenyl-1-propenyl)silane (15%). The formation of VI may result from reaction of 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene with methanol. Control experiments demonstrate that photolysis of VI in methanol yields a mixture of VI, VII, and VIII in approximately the same ratio found above. It should be noted that I and methanol do not react at all in the dark at room temperature.

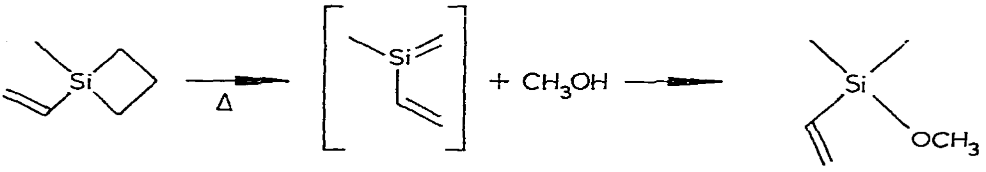
An alternative interpretation of these results is that the photo-excited state of I undergoes direct reaction with methanol to yield VII, which undergoes photo-isomerization to yield a mixture of VI, VII, and VIII. This possibility is not unreasonable since 1,1-dimethyl-2-phenyl-1-silacyclobutane has been found to undergo photochemical reaction with methanol to yield 3-phenylpropyldimethylmethoxysilane [4]. This possibility was eliminated by photolysis of I with methanol-O-d_1. The above mechanism requires that the primary photo-



product formed by reaction with methanol-O-d_1 be *Z*-dimethylmethoxy-(3-d_1-1-phenyl-1-propenyl)silane. Photo-isomerization of this compound to form VI would both dimethylmethoxy(1-d_1-1-phenyl-2-propenyl)silane as well as dimethylmethoxy(3-d_1-1-phenyl-2-propenyl)silane in a 1 : 2 ratio. Experimentally, we only observe dimethylmethoxy(1-d_1-1-phenyl-2-propenyl)silane. This is consistent with reaction of methanol-O-d_1 with intermediate III. Further, this result indicates that while VI undergoes photoisomerization to VII and VIII, the reverse process is less favorable.

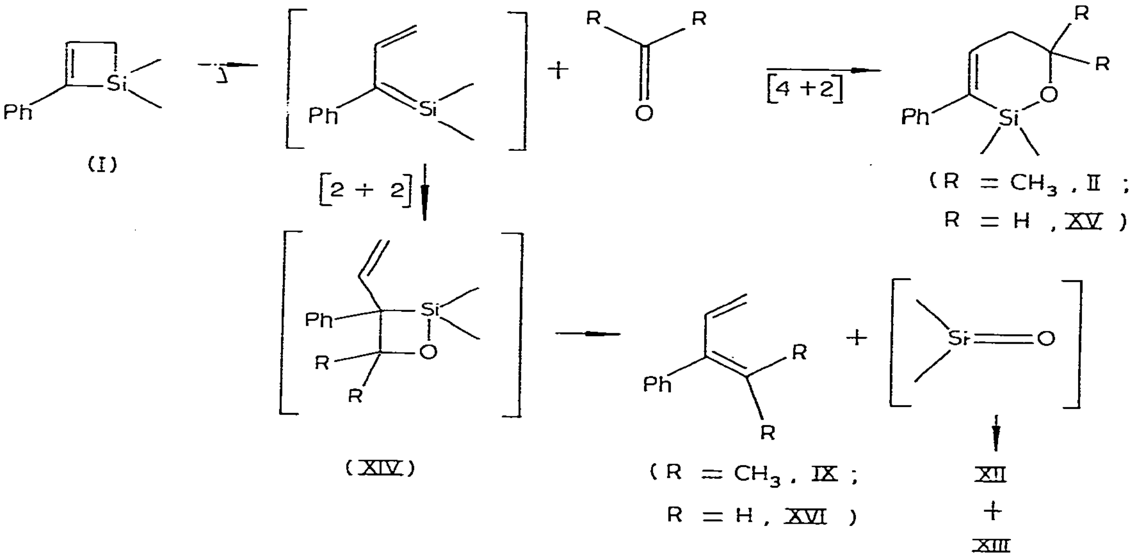


Methanol has been utilized as a trapping reagent for silicon—carbon doubly bonded intermediates generated both by pyrolysis [5] in the gas phase as well as by photolysis in solution [6—8]. In fact, methanol was utilized to trap 2-methyl-2-sila-1,3-butadiene produced by pyrolysis of 1-methyl-1-vinylsilacyclobutane in the gas phase [9].

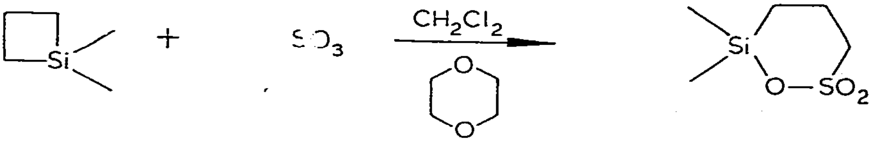


In addition, we have evidence that I undergoes gas phase pyrolysis to yield III as a reactive intermediate. There are numerous analogies between the high energy processes of pyrolysis and photolysis [10]. Specifically, we find that copyrolysis of I and acetone in the gas phase at 400°C yields a mixture of II (38%), 2-methyl-3-phenyl-2,4-pentadiene (20%) (IX), *E*-2-methyl-3-phenyl-1,3-pentadiene (18%) (X), *Z*-2-methyl-3-phenyl-1,3-pentadiene (2%) (XI), and hexamethylcyclotrisiloxane (4%) (XII), and octamethylcyclotetrasiloxane (6%) (XIII). These products would be expected from competitive [2+2] and [4+2]-cycloaddition reactions of III and acetone [11—13]. A [2+2]cycloaddition would result in an unstable 2,2-dimethyl-3-phenyl-3-vinyl-2-sila-1-oxetane (XIV) which decomposes to yield dimethylsilanone and 2-methyl-2-phenyl-2,4-butadiene (IX). Cyclooligomerization of dimethylsilanone yields XII and XIII. A thermally allowed 1,5-sigmatropic hydrogen migration may isomerize IX to a mixture of X and XI.

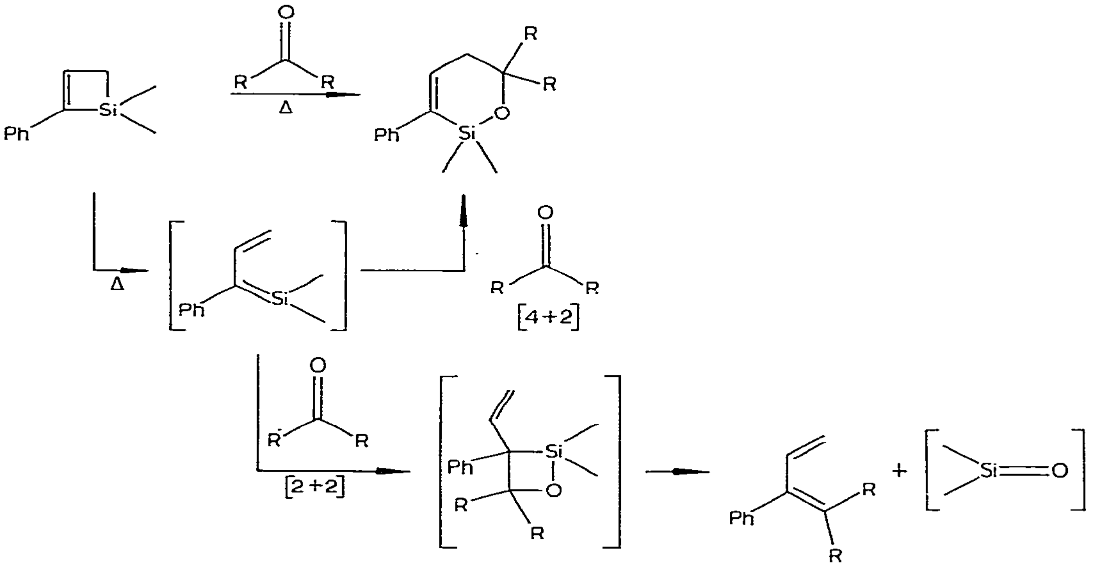
Similarly, we find that copyrolysis of I and formaldehyde yields 2,2-dimethyl-3-phenyl-1-oxa-2-silacyclohex-3-ene (35%) (XV), 2-phenyl-1,3-butadiene (30%) (XVI), XII (4%), and XIII (8%). This mixture of products is expected from competing [2+2] and [4+2]cycloaddition reactions of III and formaldehyde.



While we favor the above mechanism, there is at least one alternative interpretation of our pyrolysis data. Several direct bimolecular thermal insertion reactions of small polar molecules into silacyclobutanes are known. For example, both sulfur dioxide [14] and sulfur trioxide [15,16] are known to insert into silacyclobutanes.



Similar direct bimolecular insertion reactions of I with acetone or formaldehyde would yield II and XV, respectively. Formation of IX, XVI and dimethylsilanone oligomers might then result from [2+2]cycloaddition reaction of III with acetone and formaldehyde, respectively.



(R = CH_3, IX ;
R = H, XVI)

We have not been able to devise an experiment to distinguish between these alternatives. Nevertheless, we believe this additional data supports the formation of 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene as a reactive intermediate in both photolysis and pyrolysis reactions of I. The reasons why an S_H2 process is favored in the related 2,3-benzo-1,1-dimethyl-1-sila-2-cyclobutene remains unclear. Certainly, these differences serve to stress the necessity for care in the generalization of mechanistic pathways in such energetic reactions.

Experimental section

IR spectra were recorded as 2% CCl_4 solutions on a Perkin-Elmer 281 spectrometer. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode using 1% solutions in $CDCl_3$ with an internal standard of chloroform. UV spectra were obtained on a Beckman ACTA M VI spectrometer. Spectral grade ethanol was used as solvent. Elemental analysis were performed by Galbraith Laboratories, Inc. Mass spectra were recorded on a Hewlett Packard 5985 GC-MS at an ionizing voltage of 70 eV. Samples of all compounds for spectra and elemental analyses were purified by preparative vapor-phase chromatography on a Hewlett-Packard F&M 700 using a 26 ft × 0.25 in 20% SE-30 on Chromosorb W 60-80 mesh column. GC analysis of reactions were performed in a temperature-programming mode. The initial oven temperature (70°C) was increased at a rate of 0.5°C/min. Yields of products were determined by GC with 1,1-dimethyl-2-phenyl-1-sila-cyclobutane as an external standard. Yields are based on the quantity of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene consumed.

1,1-Dimethyl-2-phenyl-1-sila-2-cyclobutene was prepared as described previously [1].

Photolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene in methanol

A solution of 155 mg of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene (0.89 mmol) and 1.035 g of methanol was placed in a 5 mm quartz NMR tube. The solution was photolyzed with a 450 W medium pressure Hanovia Hg lamp which was housed in a water-cooled quartz well. It was photolyzed for 4.5 hours at 0—5°C. The progress of the reaction was monitored by NMR from time to time. After the photolysis, excess methanol was removed by evaporation under reduced pressure. The pale yellow residue was subjected to GC analysis.

Dimethylmethoxy(1-phenyl-2-propenyl)silane (VI) was obtained (57%) from the above reaction: NMR: δ 7.05—7.30 (m, 5 H), 6.19 (ddd, 1 H, $J = 9.5, 12, 15$ Hz), 5.01 (dd, 1 H, $J = 1, 15$ Hz), 4.99 (dd, 1 H, $J = 1, 12$ Hz), 3.36 (s, 3 H), 3.08 (br. d, 1 H, $J = 9.5$ Hz), 0.083 (s, 3 H), 0.066 ppm (s, 3 H). IR: 1650, 1623 (C=C), 1268, 845 ($Si(CH_3)_2$), 1100 cm^{-1} (SiOC). Mass spectrum: m/e (relative intensity) 206 (6.1, parent), 191 (1.7, $P - 15$), 115 (11.5), 89 (100); UV: λ_{max} 222 nm (ϵ 8300), 258 (ϵ 280). Anal. Found: C, 69.58; H, 8.95. Calcd. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

(Z)-Dimethylmethoxy(1-phenyl-1-propenyl)silane (VII) was obtained (25%) from the above reaction: NMR: δ 6.92—7.42 (m, 5 H), 6.22 (q, 1 H, $J = 6.5$ Hz), 3.40 (s, 3 H), 1.61 (d, 3 H, $J = 6.5$ Hz), 0.13 ppm (s, 6 H). IR: 1635 (C=C), 1268, 848 ($Si(CH_3)_2$), 1100 cm^{-1} (SiOC). Mass spectrum: m/e (intensity) 206 (45, parent), 191 (71, $P - 15$), 151 (75), 115 (27), 89 (100). UV: λ_{max} 216 nm (ϵ 9500). Anal. Found: C, 69.58; H, 8.95. Calcd. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

(E)-Dimethylmethoxy(1-phenyl-1-propenyl)silane (VIII) was obtained (17%) from the above reaction. NMR: δ 7.00—7.24 (m, 5 H), 6.30 (q, 1 H, $J = 7$ Hz), 3.38 (s, 3 H), 1.98 (d, 3 H, $J = 7$ Hz), 0.21 ppm (s, 6 H). IR: 1622 (C=C), 1270, 845 ($Si(CH_3)_2$), 1105 cm^{-1} (SiOC). Mass spectrum: m/e (intensity) 206 (18, parent), 191 (40, $P - 15$), 151 (62), 115 (28), 89 (100). UV: λ_{max} 220 nm (ϵ 10 000). Anal. Found: C, 69.58%; H, 8.95. Calcd. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

Photolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene in methanol-O-d_1

The reaction was carried out as above with methanol-O-d_1 (Merck) as solvent.

Dimethylmethoxy(1-d_1-1-phenyl-2-propenyl)silane was obtained (60%) from the above reactions: NMR: δ 7.05—7.30 (m, 5 H) 6.08—6.40 (m, 1 H), 4.99 (dd, 1 H, $J = 0.5, 15$ Hz), 4.97 (dd, 1 H, $J = 0.5, 11$ Hz), 3.36 (s, 3 H), 0.083 (s, 3 H), 0.066 ppm (s, 3 H). Mass spectrum: m/e (intensity) 207 (25, parent), 192 (13, $P - 15$), 116 (53), 89 (100).

(Z)-Dimethylmethoxy(3-d_1-1-phenyl-1-propenyl)silane was obtained (25%) from the above reaction: NMR: δ 6.92—7.42 (m, 5 H), 6.22 (br. t, 1 H, $J =$

6 Hz), 3.40 (s, 3 H), 1.59 (td, 2 H, $J = 2, 6$ Hz), 0.134 ppm (s, 6 H). Mass spectrum: m/e (intensity) 207 (43, parent), 192 (97, $P - 15$), 151 (100), 116 (22), 89 (96).

(E)-Dimethylmethoxy(3-d_1-1-phenyl-1-propenyl)silane was obtained (15%) from the above reaction. NMR: δ 6.98—7.38 (m, 5 H), 6.30 (br t, 1 H, $J =$ 7 Hz), 3.38 (s, 3 H), 1.95 (td, 2 H, $J = 2, 7$ Hz), 0.21 ppm (s, 3 H). Mass spectrum: m/e (intensity) 207 (12, parent), 192 (23, $P - 15$), 151 (26), 116 (15), 89 (100).

The (E) and (Z) isomers above were assigned by comparison of the NMR chemical shifts with NMR spectra of *cis* and *trans* β-methyl-styrene [17] and *cis* and *trans* 1-trimethylsilyl-propene [18].

A control reaction was run in a pyrex NMR tube covered with aluminum foil at room temperature for 24 h. No reactions occurred under these conditions. 1,1-Dimethyl-2-phenyl-1-sila-2-cyclobutene was recovered quantitatively.

Photolysis of dimethylmethoxy(1-phenyl-2-propenyl)silane in methanol

Dimethylmethoxy(1-phenyl-2-propenyl)silane (5 mg) was dissolved in 100 ml of methanol. The solution was placed in a 5 mm quartz NMR tube and photolyzed for 2 h at 0—5° C. This solution was subjected to GC analysis. Dimethylmethoxy(1-phenyl-2-propenyl)silane and (Z)- and (E)-dimethylmethoxy(1-phenyl-1-propenyl)silanes were found in a ratio of 60 : 25 : 15.

Pyrolysis apparatus

The pyrolyses were performed using a 30 cm vertical tube oven. The pyrolysis tube consisted of a 50 cm long pyrex glass tube (o.d. 12.5 mm, i.d. 9 mm). It was packed with 1 cm long pieces of 3 mm pyrex tubing. A pressure-equalizing addition funnel and a nitrogen inlet were connected to the top of pyrolysis tube. The exit of the column was connected to one neck of a two-necked flask which was immersed in a dry ice-acetone bath. The second neck of the flask was connected to rubber tubing, the other end of which was placed in an efficient fume hood. The temperature of pyrolysis oven was determined by use of a potentiometer and an Iron-Constantan thermal couple. The nitrogen flow rate was determined by a soap bubble flow meter.

Copyrolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene and acetone

A mixture of 1.8 g (10.0 mmol) of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene and 10 ml acetone was placed in the addition funnel. The nitrogen flow rate was adjusted to 30 ml/min. The oven temperature was set at 400° C. The solution was added dropwise to the pyrolysis column over 30 min. The pyrolysis tube was cooled with nitrogen still flowing. When it has reached room temperature, 10 ml of acetone was running through the pyrolysis tube. The pyrolysate and additional acetone were combined. Acetone was removed by evaporation under reduced pressure. The residue was subjected to GC analysis.

1,1-Dimethyl-2-phenyl-1-sila-2-cyclobutene was found in 48% yield. All other yields reported are corrected for recovering starting material.

Hexamethylcyclotrisiloxane was obtained in 4% yield.

Octamethylcyclotetrasiloxane was obtained in 6% yield.

2,2,6,6-Tetramethyl-1-oxa-3-phenyl-2-silacyclohex-3-ene was obtained in 38% yield [1].

2-Methyl-3-phenyl-2,4-pentadiene was obtained in 20% yield. NMR: δ 6.98—7.42 (m, 5 H), 6.96 (dd, 1 H, $J = 11, 16$ Hz), 5.00 (br. d, 1 H, $J = 11$ Hz), 4.52 (br. d, 1 H, $J = 16$ Hz), 2.01 (s, 3 H), 1.62 ppm (s, 3 H). IR: 1650 and 1620 cm^{-1} (C=C). UV λ_{max}: 234 nm (ϵ 20 800). Anal. Found: C, 90.92; H, 8.99. Calcd.: for $C_{12}H_{14}$: C, 91.08; H, 8.92%.

E-2-Methyl-3-phenyl-1,3-pentadiene was obtained in 18% yield. NMR: δ 7.15—7.51 (m, 5 H), 5.87 (q, 1 H, $J = 7$ Hz), 5.27 (br. s, 1 H), 4.91 (br. s, 1 H), 1.90 (d, 3 H, $J = 7$ Hz), 1.82 ppm (br. s, 3 H). IR: 1647 and 1618 cm^{-1} (C=C). UV: λ_{max} 242 nm (ϵ 14 800). Mass spectrum: *m/e* (intensity) 158 (23, parent), 143 (100, $P - 15$), 128 (99), 115 (95), 102 (13), 77 (27). Anal. Found: C, 90.92; H, 8.99. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92%.

A compound formed in 2% yield, had a very close GC retention time to that of (*E*)-2-methyl-3-phenyl-2,4-pentadiene. It is presumed to be (*Z*)-2-methyl-3-phenyl-1,3-pentadiene. No spectral data were obtained for this compound.

Copyrolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene and formaldehyde

Formaldehyde was generated by the pyrolysis of paraformaldehyde (MC&B). The formaldehyde vapor was introduced into the pyrolysis system by a U-shaped connection at the top of the addition funnel. The nitrogen flow rate was adjusted to 30 ml/min. The oven temperature was set at 415°C. A mixture of 2.2 g (12.6 mmol) of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene and 10 ml benzene was placed in the addition funnel. A stream of formaldehyde vapor was run through the pyrolysis system. During this time, the solution was added dropwise over 30 min to the pyrolysis tube. The oven was allowed to cool down to room temperature. Nitrogen gas continued to flow. The pyrolysis column was rinsed with 10 ml of benzene. The pyrolysate and benzene rinse solutions were combined. Benzene was removed by evaporation under reduced pressure. The residue was subjected to GC analysis.

Unreacted 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene was found in 30% yield. All other yields are corrected for recovered starting material.

Hexamethylcyclotrisiloxane was found in 4% yield.

Octamethylcyclotetrasiloxane was found in 8% yield.

2-Phenyl-1,3-butadiene was found in 30% yield. Its IR was in agreement with literature values [19]. NMR: δ 7.31 (s, 5 H), 6.56—6.78 (m, 1 H), 5.12—5.40 ppm (m, 4 H).

Styrene was found in 12% yield.

2,2-Dimethyl-3-phenyl-1-oxa-2-silacyclohex-3-ene was found in 35% yield. NMR: δ 7.10—7.36 (m, 5 H), 6.78 (t, 1 H, $J = 5$ Hz), 4.06 (t, 2 H, $J = 5$ Hz), 2.54 (q, 2 H, $J = 5$ Hz), 0.44 ppm (s, 6 H). IR: 1270, 885 ($Si(CH_3)_2$) 1100, 1035 cm^{-1} (Si—OC). UV: λ_{max} 247 nm (ϵ 10 400), 296 nm (ϵ 650). Mass spectrum: *m/e* (intensity) 204 (76, parent), 189 (100, $P - 15$), 159 (42), 130 (42), 128 (37), 115 (30), 102 (39), 74 (35). Anal. Found: C, 70.31; H, 7.92. Calcd. for $C_{12}H_{16}SiO$: C, 70.53; H, 7.89%.

Acknowledgement

This work was supported in part by the Air Force Office of Scientific Research, Grant Number 80-0006.

References

1 P.B. Valkovich and W.P. Weber, Tetrahedron Lett., (1975) 2153.
2 F.O. Rise, J. Amer. Chem. Soc., 42 (1920) 727.
3 R. Okazaki, K.T. Kang and N. Inamoto, Tetrahedron Lett., (1981) 235.
4 P.B. Valkovich, T.I. Ito and W.P. Weber, J. Org. Chem., 39 (1974) 3543.
5 T.J. Barton, G.T. Burns, E.V. Arnold and J. Clardy, Tetrahedron Lett., (1981) 7.
6 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., 118 (1976) 166.
7 M. Ishikawa, H. Sugisawa, K. Yamamoto and M. Kumada, J. Organometal. Chem., 179 (1979) 377.
8 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., 149 (1978) 37.
9 G. Bertrand, G. Manuel and P. Mazerolles, Tetrahedron Lett., (1978) 2149.
10 For a review see: R.C. Dougherty, Topics in Current Chemistry, Vol. 45, (1974) 94.
11 For a recent review of the chemistry of silicon—carbon doubly bonded intermediates see L.E. Gusel'nikov and N.S. Nametkin, Chem. Rev., 79 (1979) 529.
12 P.B. Valkovich and W.P. Weber, J. Org. Chem., 40 (1975) 229.
13 P.B. Valkovich and W.P. Weber, J. Organometal. Chem., 99 (1975) 231.
14 J. Dubac, P. Mazerolles, M. Jolly, W. Kitching, C.W. Fong and W.H. Atwell, J. Organometal. Chem., 25 (1970) C20.
15 J. Dubac and P. Mazerolles, J. Organometal. Chem., 20 (1969) P5.
16 J. Dubac, P. Mazerolles, M. Lesbre and M. Joly, J. Organometal. Chem., 23 (1970) 367.
17 F.H.A. Rummens and J.W. DeHaan, Organic Magnetic Resonance, 2 (1970) 351.
18 D. Seyferth and L.G. Vaughan, J. Organometal. Chem., 1 (1963) 138.
19 C.S. Marvel and R.G. Woolford, J. Org. Chem., 23 (1958) 1658.