ELSEVIER

Journal of Organometallic Chemistry 499 (1995) 17–26

Journal of Organometallic Chemistry

1 : 2-Adducts from Silylenes and 1,3-butadiene ☆

Kevin L. Bobbitt, Peter P. Gaspar *

Department of Chemistry, Washington University, Saint Louis, MO 63130-4899, USA

Received 15 March 1995

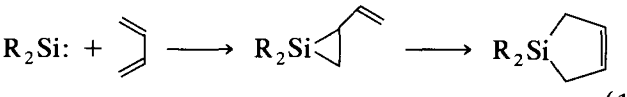
Abstract

Photochemical generation of dimethylsilylene, methyl(phenyl)silylene and diphenylsilylene in the presence of high concentrations of 1,3-butadiene leads to the formation of 1-sila-3,4-divinylcyclopentanes as major products in addition to the anticipated 1-silacyclopent-3-enes. Also obtained are the ene-reaction products from the silenes, formed by formal 1,3-silyl shifts in the bis(trimethylsilyl)arylsilanes that are employed as the photochemical precursors of MePhSi: and Ph_2Si:. Evidence is presented that both the divinylsilacyclopentanes and the silacyclopent-3-enes arise from vinylsilirane intermediates that can be trapped by acetone, yielding stable 3,3-dimethyl-4-vinyl-1-sila-2-oxolanes.

Keywords: Silicon; Silylene

1. Introduction

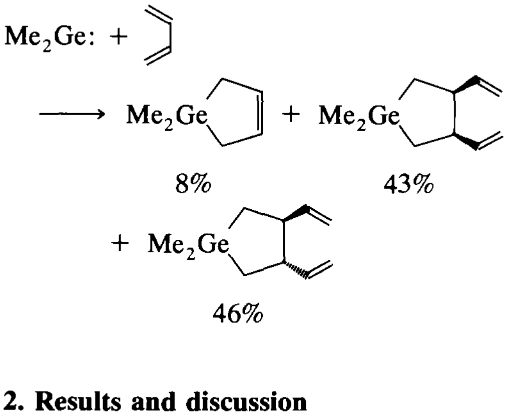
One of the earliest reported reactions of the compounds of divalent silicon, silylenes, was their addition to 1,3-dienes leading to the formation of 1-silacyclopent-3-enes [1]. This process was astutely formulated by Atwell and Weyenberg, its discoverers, as consisting of a 1,2-addition leading to a vinylsilirane intermediate that undergoes rearrangement to the observed products (Eq. (1)) [2]:



(1)

Even before the recent isolation of a vinylsilirane intermediate by Zhang and Conlin [3], considerable evidence had accumulated for their intermediacy in the silylene-diene addition reaction [1]. The evidence includes: (1) the results of trapping experiments [6] and those from the study of the stereospecificity of addition [5]; and (2) The formation of other kinds of end-products most economically rationalized by invoking vinylsilirane intermediates [6,7]. The mechanism of this reaction remains of topical interest [8].

Recently it has been found that the closely related addition of compounds containing divalent germanium atoms, germylenes, to 1,3-dienes seems to differ from the addition of silylenes in two respects, both of mechanistic interest: (1) germylene addition to stereoisomeric 1,3-dienes is stereospecific [9,10], while the silylene addition is not [11,12]; and (2) The addition of germylenes to 1,3-dienes at ambient temperatures can lead to the formation of 1 : 2-adducts as the predominant products (Eq. (2)) [13,14].



(2)

2. Results and discussion

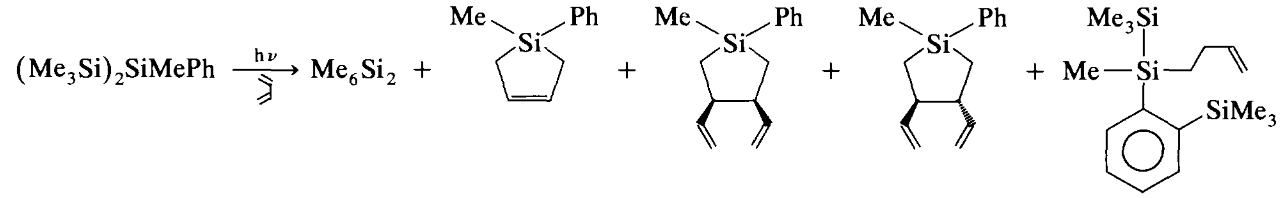
It can now be reported that the formation of 1 : 2-adducts upon reaction with butadiene is also an important process for silylenes when the butadiene serves as sol-

---

☆ This paper is dedicated to Professor Hideki Sakurai on the occasion of his embarking on a new phase in his fruitful scientific career. As a world leader in the investigation of compounds of the higher Group 14 elements, he has shaped our view of much of chemistry, and will continue to do so.

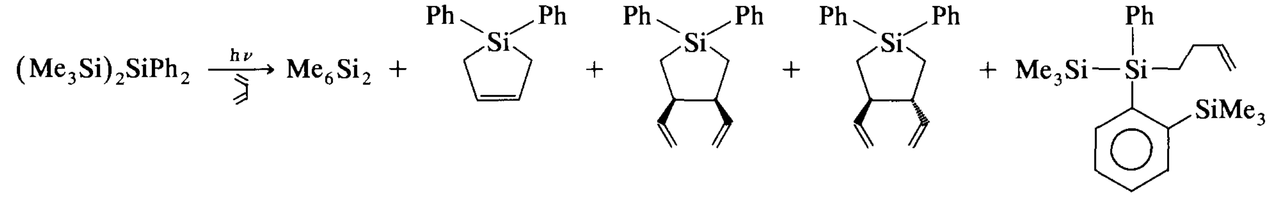
* Corresponding author.

SSDI 0022-328X(95)00321-5



(3)

70% **1** 15% **2** 17% two diastereomers **3** 35% **4** 13%



(4)

80% **5** 17% **6** 7% **7** 21% **8** 14%

vent. When a butadiene solution of 2-phenylheptamethyltrisilane is irradiated with 254 nm radiation from a bank of low-pressure mercury lamps, the products, shown above, include *cis*- and *trans*-3,4-divinylsilacyclopentanes **2** and **3** (Eq. (3)) [15].

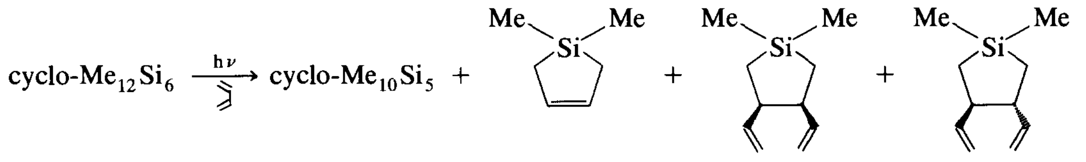
The expected 1 : 1 silylene–diene adduct, 1-methyl-1-phenyl-1-silacyclopent-3-ene **1**, is only a minor product, as is the product **4** of an ene-reaction of the silene formed by formal 1,3-migration of a trimethylsilyl group to the *ortho*-position of the phenyl ring in the starting trisilane. Both **1** and **4** had previously been found by Ishikawa et al. upon irradiation of 2-phenylheptamethyltrisilane in a 1 M hexane solution of butadiene, but, presumably due to the low concentration of trapping agent, they did not observe the 1 : 2-silylene–diene adducts **2** and **3** [16].

Similar results have been obtained from the irradiation of 2,2-diphenylhexamethyltrisilane in butadiene. Diphenylsilylene is generated and yields both 1 : 1 and 1 : 2-adducts, with the latter formed in somewhat higher aggregate yield (Eq. (4)). Again, there is a product of an ene-reaction from a silene formed by photorearrangement of the initial trisilane by migration of a trimethylsilyl group to an *ortho*-position of one of the phenyl rings.

Dimethylsilylene Me_2Si: also yields 1 : 2-adducts when a solution of dodecamethylcyclohexasilane in butadiene is irradiated. Only low yields of products were identified in complex mixtures (Eq. (5)).

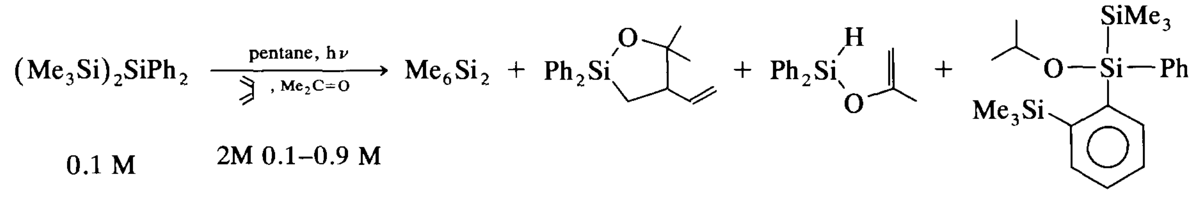
Experiments in which the silylene precursors were irradiated in the presence of acetone as well as butadiene provided clues to the mechanism for the formation of the 1 : 2-adducts. Adducts containing a unit each of silylene, acetone and butadiene, 3,3-dimethyl-4-vinyl-1-sila-2-oxolanes, were observed, but the formation of silacyclopent-3-enes and of 3,4-divinylsilacyclopentanes was suppressed (Eq. (6)).

The reactions observed in the presence of acetone can be explained by several possible mechanistic pathways, including: (1) Formation of the vinylsiloxolane



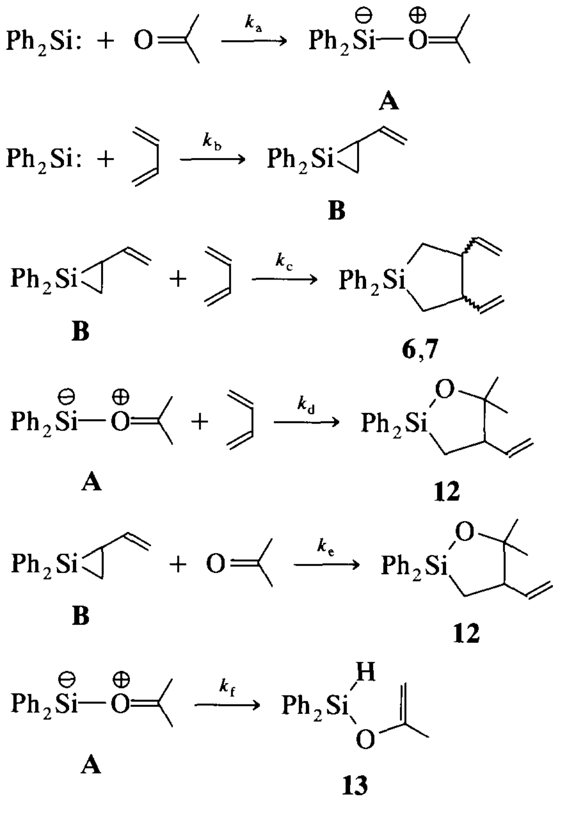
(5)

9 0.5% **10** 9% **11** 10%



(6)

57–60% **12** 33–56% **13** 4–18% **14** 33–40%



Scheme 1.

by insertion of an acetone molecule into a silicon–carbon bond of the highly strained three-membered ring of a vinylsilirane intermediate. This has precedent in the reaction of hexamethylsilirane with carbonyl compounds via a "two-atom" insertion, discovered by Seyferth et al. [17] (2). Formation of a silylene–ketone ylide as the initial adduct that undergoes 1,3-dipolar addition to butadiene. (3) Formation of the vinylsiloxolanes by a combination of processes 1 and 2. Such a mechanistic scheme for the formation of all the silylene-derived products formed in the presence of butadiene or acetone is shown in Scheme 1. It is clear from the formation of silyl-enol ether **13** that direct attack of silylene on acetone, a known process, has occurred [1,18].

By invoking the steady-state approximation for intermediates **A** and **B** in Scheme 1, and solving for the ratio of concentrations of products **12** and **13**, the following relationship is obtained, in which BD = butadiene, AC = acetone:

$$\frac{[12]}{[13]}=\frac{(k_ak_ck_d+k_bk_dk_e)[\mathrm{BD}]^2+k_ak_dk_e[\mathrm{AC}][\mathrm{BD}]+k_bk_ek_f[\mathrm{BD}]}{k_ak_ck_f[\mathrm{BD}]+k_ak_ek_f[\mathrm{AC}]} \qquad (7)$$

This expression has been tested for two mechanistic extremes: (1) product **12** is formed entirely by reaction of vinylsilirane **B** with acetone, and (2) product **12** is formed entirely by addition of carbonyl-ylide **A** to butadiene. For case (1)$k_d = 0$ and Eq. (7) simplifies to Eq. (8):

$$\frac{[13]}{[12]}=\frac{k_ak_c}{k_bk_e}+\frac{k_a[\mathrm{AC}]}{k_b[\mathrm{BD}]} \qquad (8)$$

It is thus predicted that if dipolar addition of ylid **A** to butadiene makes a negligible contribution to siloxane formation, the product ratio **13**/**12** will be a linear function of the ratio of acetone to butadiene, with a slope equal to the relative reactivity of acetone and butadiene toward the silylene. The ratio of the slope to the intercept of such a linear function would give the relative reactivity of vinylsilirane **B** toward butadiene and acetone.

For case (2) $k_e = 0$, and Eq. (7) simplifies to Eq. (9):

$$\frac{[\mathbf{13}]}{[\mathbf{12}]}=\frac{k_f}{k_d}\frac{1}{[\mathrm{BD}]} \qquad (9)$$

Hence it is predicted that if the reaction of vinylsilirane with acetone makes a negligible contribution to the formation of siloxolane **12**, the ratio of **13** to **12** will be independent of the acetone concentration and will be a linear function of 1/[BD] with zero intercept and slope k_f/k_d.

Three series of experiments were carried out to test this scheme. In the first the butadiene concentration was kept nearly constant at 2.0 and 1.9 M, and the acetone concentration was varied from 0.10 to 0.93 M. The results are given in Table 1 and the **13** : **12** product ratio

Table 1

Variation of product yields and product ratios with acetone concentration upon 254 nm irradiation of 0.1 M solutions of $(Me_3Si)_2SiPh_2$ in pentane solutions containing butadiene and acetone

Butadiene (M)	Acetone (M)	[Acetone]/[butadiene]	Yields [a] (%)				Yield ratio [b] **13** : **12**
			Me_6Si_2	**12**	**13**	**14**	
2.0	0.10	0.05	62	56	4	33	0.07
2.0	0.20	0.10	60	44	5	38	0.11
2.0	0.50	0.25	57	42	11	37	0.26
1.9	0.67	0.35	59	34	13	39	0.38
1.9	0.76	0.40	60	37	14	36	0.38
1.9	0.93	0.49	61	33	18	40	0.55

[a] Yields determined by capillary GC analysis.

[b] Yield ratios determined by integration of selected ^1H NMR signals for compounds **12** and **13** in spectra of crude reaction mixtures.

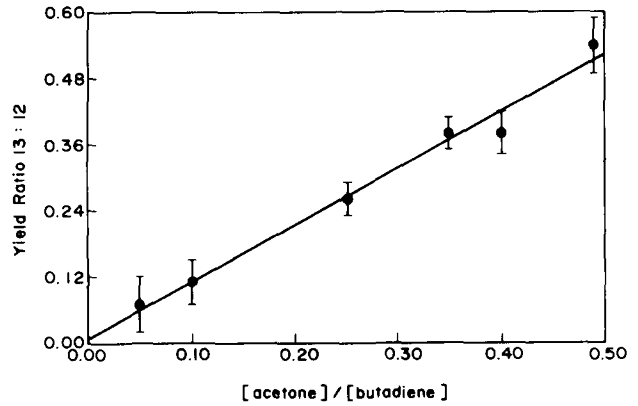


Fig. 1. Variation of the ratio of the yields of products **13** and **12** with the ratio of the concentrations of acetone and butadiene upon 254 nm irradiation of pentane solutions of $(Me_3Si)_2SiPh_2$ at nearly constant [butadiene]. See Table 1 for numerical data.

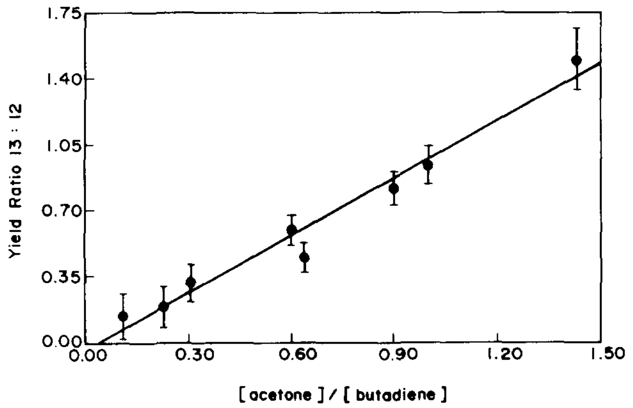


Fig. 2. Variation of the ratio of the yields of products **13** and **12** with the ratio of the concentrations of acetone and butadiene upon 254 nm irradiation of pentane solutions of $(Me_3Si)_2SiPh_2$ at varying [butadiene]. See Table 2 for numerical data.

is plotted as a function of the acetone : butadiene concentration ratio (proportional to the acetone concentration at constant butadiene concentration) in Fig. 1. It can be seen that the product ratio **13** : **12** is a linear function of the ratio of acetone to butadiene and thus clearly a function of the acetone concentration. The slope is 1.03 ± 0.07 and the intercept 0.009 ± 0.02, $r^2 = 0.9837$.

In the second series the acetone concentration was varied only slightly (0.7–1.0 M) while the butadiene concentration varied over an order of magnitude (0.7–6.5 M). Results are given in Table 2 and displayed in Fig. 2. Again, the **13** : **12** product ratio is a linear function of the acetone : butadiene concentration ratio with slope 1.01 ± 0.07 and intercept −0.04 ± 0.06, $r^2 = 0.9689$.

In a third series of experiments 1 : 1 ratios of acetone and butadiene were employed at varying absolute concentrations, [AC] = [BD] = 0.53 M and [Ac] = [BD] = 3.0 M, yielding constant product ratios **13** : **12** = 0.96 and 1.03, respectively. The data from all three sets of experiments lie on a single line with slope 0.99 ± 0.03 and intercept 0.01 ± 0.02, $r_2 = 0.9901$.

These experiments would seem to point toward a mechanism in which acetone and butadiene are equally reactive toward diphenylsilylene, and the vinylsilirane intermediate formed by 1,2-addition of Ph_2Si: to butadiene reacts at least two orders of magnitude more rapidly with acetone than with butadiene.

The problem with this interpretation is that Conlin et al. have found, in direct kinetic measurements that dimesitylsilylene Mes_2Si: reacts 3000 times more rapidly with acetone than with 2,3-dimethylbutadiene [19]! Hence the mechanism presented in Scheme 1 requires modification. The dependence of the product ratio **13** : **12** on the [AC] : [BD] substrate ratio suggests that one more molecule of acetone is contained in the transition state for the rate-determining step in the formation of **13** than in the transition state for the formation of **12**. Since only one molecule of acetone is likely to be required for the formation of **13**, one is led to the conclusion that acetone is not involved in the rate-de-

Table 2

Variation of product yields and product ratios with butadiene and acetone concentrations upon 254 nm irradiation of 0.1 M solutions of $(Me_3Si)_2SiPh_2$ in pentane solutions containing butadiene and acetone

Butadiene (M)	Acetone (M)	[Acetone]/ [butadiene]	Yields [a] (%)				Yield ratio [b] **13** : **12**
			Me_6Si_2	**12**	**13**	**14**	
6.5	0.70	0.11	61	50	5	18	0.14
3.9	0.90	0.23	65	47	7	21	0.19
2.6	0.80	0.30	65	45	13	34	0.32
1.5	0.90	0.60	60	35	18	20	0.60
1.4	0.90	0.66	59	27	21	24	0.45
1.0 [c]	0.90	0.91	–	–	–	–	0.82
0.9	0.90	1.00	55	31	24	33	0.94
0.7 [c]	1.0	1.42	–	–	–	–	1.50

[a] Yields determined by capillary GC analysis.

[b] Yield ratios determined by integration of selected ^1H NMR peaks for compounds **12** and **13** in spectra of crude reaction mixtures.

[c] Absolute yields not determined.

termining step for the formation of **12**. This would rule out reaction schemes in which vinylsilirane **B** is formed by transfer of a silylene unit from carbonyl ylide **A** to butadiene or in which siloxolane **12** is formed directly by addition of **A** to butadiene.

A reaction scheme in which a silylene reacts more rapidly with acetone than with butadiene and yet vinylsilirane **B** is formed by addition of free silylene to butadiene is identical to that of Scheme 1 above with the addition of k_{-a} the reversal of the step that forms ylide **A**. With this change, Eq. (8) becomes Eq. (10):

$$\frac{[\mathbf{13}]}{[\mathbf{12}]} = \frac{k_a k_c k_f}{k_{-a} k_b k_e + k_b k_e k_f} + \frac{k_a k_e k_f [\mathrm{AC}]}{(k_{-a} k_b k_e + k_b k_e k_f)} \tag{10}$$

If $k_{-a} \gg k_f$ Eq. (10) reduces to Eq. (11):

$$\frac{[\mathbf{13}]}{[\mathbf{12}]} = \frac{k_a k_c k_f}{k_a k_b k_e} + \frac{k_a k_f [\mathrm{AC}]}{k_{-a} k_b [\mathrm{BD}]} \tag{11}$$

Here the slope is no longer the relative reactivity of acetone and butadiene toward a silylene k_a/k_b, but is this ratio divided by the ratio of the rate of dissociation of carbonyl ylide **A** to its rate of rearrangement k_{-a}/k_f. Hence acetone could be 10^3 times as reactive toward a silylene as butadiene, and yet a slope of ca. unity could be observed, so long as carbonyl ylide **A** dissociated a thousand times faster than it rearranges to **13**. Such a slope would be accommodated by a set of reasonable absolute rate constants with values such as: $k_a = 10^{10}$ and $k_b = 10^7\ 1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, and $k_{-a} = 10^7$ and $k_f = 10^4\ \mathrm{s}^{-1}$.

In conclusion it has been found that silylenes, like germylenes form 1:2 adducts, 3,4-divinylsilacyclopentanes and 3,4-divinylgermacyclopentanes, respectively, as major products upon reaction with 1,3-butadiene. Hence the silylene–butadiene and germylene–butadiene addition mechanisms seem to be closely related, as has been suggested recently [20]. The formation of 1:2-diene adducts is not a feature that has been observed in the gas-phase chemistry of either silylenes or germylenes [1,10,21]. Whether this is because the higher temperatures and lower collision frequencies at which gas-phase reactions are carried out favor intramolecular rearrangements of vinyl siliranes and germiranes over bimolecular reactions with a second diene molecule remains to be determined. An amusing possibility that has not been tested is that divinylsila- and germa-cyclopentanes are formed in the gas-phase, but extrude butadiene to yield the observed sila- and germa-cyclopent-3-ene 1:1-adducts.

A further finding reported here is that when silylenes are generated in solution in the presence of both acetone and butadiene, the products include enol ethers whose formation can be rationalized by reaction of a silylene and acetone, as well as siloxolanes containing a unit each of silylene, acetone, and butadiene. In the case of diphenylsilylene the ratio of these products has been found to be a linear function of the acetone:butadiene concentration ratio. This observation seems to demand that the siloxolane be formed by reaction of a vinylsilirane intermediate with acetone, and that the vinylsilirane arise from addition of free silylene with butadiene.

3. Experimental details

3.1. General data

^{1}H NMR spectra were recorded on a Varian XL-300 or Gemini-300 FT spectrometer at 300 MHz. ^{13}C NMR spectra were recorded on a Varian XL-300 or Gemini-300 spectrometer at 75.4 MHz. All chemical shifts are reported as ppm downfield from TMS. Mass spectra were recorded on a Finnegan 3200 GC-MS system, with ionization energy 70 eV. High resolution mass spectra were recorded on a VG ZAB-SE double focusing instrument at the Washington University mass spectroscopy resource. All mass spectra were calibrated internally against perfluorokerosene. UV spectra were recorded on a Varian Carey 219 spectrometer. Analytical gas chromatography was performed on a Varian Aerograph Series 2700 instrument with flame ionization detection, or on a Hewlett-Packard 5890A instrument coupled to a Hewlett-Packard 3394A integrator.

All yields obtained by GC analysis were calculated by the internal standard method, as follows. A known mass of starting material (SM) and of internal standard (IS) (mass accuracy ±0.0001 g) were mixed and diluted with a low-boiling hydrocarbon (typically n-pentane), and the mixture subjected to gas chromatography to determine the response factor (rf) for the starting material from the equation: (rf)(peak area ratio SM:IS) = (molar ratio SM:IS). In a similar manner response factors were determined for all starting materials and products. With the use of response factors and internal standards, absolute quantities of starting materials remaining at the end of a reaction and of products could be determined. All yields are expressed as (moles of product × 100)/(moles of starting material consumed).

Preparative gas chromatography was carried out on a home made instrument employing 1/4″ o.d. aluminum columns and a thermal conductivity detector equipped with Gow-Mac code 13-002 dual rhenium–tungsten filaments. Frequently used columns: (A) 12 ft. 10% OV-17 on 80/100 mesh Supelcoport; (B) 10 ft. same packing; (C) 4 ft., same packing; (D) 12 ft. 7.5% SE-30 on 80/100 mesh Supelcoport.

Flash chromatography was performed on a 1 m × 7 cm Ace Glass 5902-49 column with dinitrogen as pressurizing gas. A typical procedure employed 100 g silica gel with 80 ml min^{-1} eluent flow. Fractions (100 ml) were analyzed on Fisher 05-729 UV-active TLC sheets [22].

Elemental analysis was performed by Galbraith Analytical Laboratories, Knoxville, TN.

3.2. Materials

Unless otherwise specified all chemicals, including lithium, magnesium, and magnesium sulfate (Aldrich, 99%) were of reagent quality and used as supplied. Ethyl ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane were distilled from a blue solution of benzophenone ketyl over sodium and used immediately. Pentane was distilled from CaH_2 and stored in an argon-flushed ground glass-stoppered bottle. Acetone (Aldrich, < 0.2% H_2O) was purified by distillation from K_2CO_3. 1,3-Butadiene (Matheson Gas Co., 99.9%) was purified by passage through anhydrous KOH followed by trap-to-trap distillation through a −40°C trap and collected in a cold trap at −196°C. A density of 0.6211 g ml^{-1} at 25°C was assumed. Chlorotrimethylsilane, dichloromethylphenylsilane, and dichlorodiphenylsilane (Petrarch, 97%) were distilled from CaH_2 and used immediately. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (Aldrich, 98%) was vacuum distilled (b.p. 146°C/44 Torr) and used immediately. Dodecamethycyclohexasilane (98%) was a gift from Professor Robert West, University of Wisconsin, Madison.

3.3. 2-Phenylheptamethyltrisilane

Upon synthesis by the method of Kumada, et al. in 37% isolated yield [23] a purity of 93% was found after distillation. Further purification was by preparative GC on a column B, injection temperature 290°C, head temperature 150°C. He flow 85 cm^3 min^{-1}, retention time 7 min. ^1H NMR and MS data were in accordance with a previous report [24].

3.4. 2,2-Diphenylhexamethyltrisilane

The following preparation avoids the use of HMPA employed in the previous synthesis by Tortorelli et al. [25]. In a 500 ml three-necked flask equipped with a reflux condenser, mechanical stirrer, and pressure-equalizing addition funnel capped with a nitrogen-inlet was placed 19 g (0.78 mol) of Mg turnings, 100 g freshly distilled 1,3-dimenthyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone, and 63.2 g (0.58 mol) chlorotrimethylsilane. The mixture was heated to 95°C, and from the dropping funnel 49.3 g (0.20 mol) dichlorodiphenylsilane was added dropwise over 3 h. To the yellow, viscous reaction mixture was added 125 ml THF, and stirring was continued for 3 d. After being allowed to cool, the reaction mixture was washed twice with water and extracted with 200 ml ether. The extract was dried over $MgSO_4$, filtered, and the ether removed in vacuo. The residue was distilled under vacuum to yield 25 g (38%) diphenylhexamethyltrisilane b.p. 145°C (1.3 Torr) (lit. 147–8°C, 1.5 Torr) [23]. The ^1H and ^{13}C NMR spectra were in agreement with the literature [23] MS m/e (relative intensity) 328 (M^+, 5), 255 (23), 197 (32), 179 (10), 178 (51), 177 (23), 164 (11), 163 (59), 136 (14), 135 (100), 107 (15), 105 (40), 73 (42).

3.5. Irradiation procedures

Unless otherwise specified, solutions in dry pentane were loaded into a 35 cm by 2 cm quartz reaction tube fused to a vacuum stopcock by a graded seal. Samples were degassed by at least three freeze–pump–thaw cycles on a vacuum line (typical pressure ca. 5 mTorr) and irradiated immediately employing 253.7 nm irradiation from an array of low-pressure Hg lamps in a Rayonet RS Preparative Photochemical Reactor. Samples were re-degassed every 12 h to insure complete exclusion of oxygen.

3.6. Irradiation of 2-phenylheptamethyltrilsilane in neat butadiene

To 0.25 g (0.94 mmol) 2-phenylheptamethyltrisilane and 0.25 g dodecane (internal standard) 35 ml, 1,3-butadiene was added by transfer on a vacuum line. The mixture, after degassing, was irradiated for 15 h (67% conversion of the trisilane). After careful evaporation of the butadiene, five products were detected by GC: Me_6Si_2 (70%), 1-methyl-1-phenylsilacyclopent-3-ene **1** (15%) *cis, cis-* and *cis,trans*-1-methyl-1-phenyl-3,4-divinylsilacyclopentane **2** (inseparable mixtures of two stereoisomers, 17%) *trans*-1-methyl-1-phenyl-3,4-divinylsilacyclopentane **3** (35%), and 3-butenyl(methyl)-(trimethylsilyl)(2-trimethylsilylphenyl)silane **4** (13%). These products were easily separated (except for **2** which decomposed on the column) by preparative gas chromatography on column A, injection temperature 290°C, oven temperature 210°C, flow rate 83 cm^3 min^{-1}, retention times **1** 6 min, **3** 18 min, **4** 35 min. The *trans*-configuration of **3** was established from the observation of four inequivalent protons in the methylene groups adjacent to silicon and two inequivalent vinyl groups, whose positions of attachment are clearly established from the coupling constants for the methylene hydrogens. **1**: ^1H NMR ($CDCl_3$) δ 0.44 (s, 3H, SiMe), 1.46 (d, 2H, $J_{gem} = 17$ Hz, SiCHH'), 1.59 (d, 2H, $J_{gem} = 17$ Hz, SiCHH'), 5.94 (bs, 2H, –CH=CH–), 7.33–7.56 (m,5H, phenyl) (lit. [26] (100 MHz, CCl_4) δ 0.33 (s, 3H, SiMe), 1.53 (bs, 4H, $SiCH_2$), 5.88 (bs, 2H, –CH=CH–), 7.10–7.56 (m, 5H, phenyl)); MS m/e

(relative intensity) 174 (M^+, 13), 159 (99), 146 (100), 129 (98), 121 (93), 105 (88), 96 (97), 79 (72), 69 (51), 59 (39), 53 (93). **2**: MS *m/e* (relative intensity) 228 (M^+, 6), 213 (12), 174 (95), 158 (100), 146 (93), 131 (62), 121 (48), 106 (94), 97 (54), 81 (84), 67 (80), 53 (77). **3**: ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 3H, SiMe), 0.67 (dd, 1H, J_{gem} = 14.4 Hz, J_{ab} = 12.0 Hz, SiCH*H'*), 0.82 (dd, 1H, J_{gem} = 14.4 Hz, J_{ab} = 12.0 Hz, SiC*H*H'), 1.14 (dd, 1H, J_{gem} = 14.4 Hz, J_{ab} = 6.0 Hz, SiC*H*H'), 1.25 (dd, 1H, J_{gem} = 14.4 Hz, J_{ab} = 6.3 Hz, SiCH*H'*), 2.11 (m, 2H, C*H*CH=CH$_2$), 4.94 (dd, 2H, J_{gem} = 1.0 Hz, J_{ab} = 8.7 Hz, CH=CH*H'*), 4.98 (dd, 2H, J_{gem} = 1.0 Hz, J_{ab} = 13.2 Hz, CH=C*H*H'), 5.79 (m, 2H, C*H*=CHH'), 7.24–7.37 (m, 3H, Ar–H), 7.54–7.56 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$) δ −2.7 (SiMe), 20.42, 20.53, (SiCH$_2$), 49.72, 50.41 (*C*HCH=CH$_2$), 112.97 (CH=*C*H$_2$), 127.80 (Ar–C), 129.07 (Ar–C), 133.62 (Ar–C), 138.29 (*ipso*-C), 143.80, 143.86 (*C*H=CH$_2$); MS *m/e* (relative intensity) 228 (M^+, 0.13), 209 (16), 174 (100), 158 (95), 146 (72), 131 (97), 121 (95), 106 (96), 97 (96), 81 (91), 67 (73), 53 (85); exact mass determination for $C_{15}H_{20}Si$ (M^+), Calc. 228.1334, found 228.1384; Anal. Calc. for $C_{15}H_{20}Si$ C, 78.86; H, 8.83; Found C, 78.48; H, 8.99, **4**: ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H, SiMe$_3$), 0.36 (s, 9H, SiMe$_3$), 0.52 (s, 3H, SiMe), 1.11 (m, 2H, SiCH$_2$), 2.06 (m, 2H, C*H*$_2$CH=CH$_2$), 4.92 (m, 2H, CH=C*H*$_2$), 5.88 (m, 1H, C*H*=CH$_2$), 7.28–7.32 (m, 2H, Ar–H), 7.55–7.59 (m, 2H, Ar–H), 7.63–7.65 (m, 1H, Ar–H) (lit. [24] (100 MHz, CCl_4) δ 0.09 (s, 9H, SiSiMe$_3$), 0.36 (s, 9H, ArSiMe$_3$), 0.50 (s, 3H, SiMe), 0.74–1.30 (m, 2H, SiCH$_2$), 2.01 (m, 2H, C*H*$_2$CH=CH$_2$), 4.74–5.04 (m, 2H, CH=C*H*$_2$), 5.57–5.93 (m, 1H, C*H*=CH$_2$), 7.07–7.60 (m, 4H, Ar–H); MS *m/e* (relative intensity 320 (M^+, 6), 247 (97), 231 (32), 217 (92), 204 (35), 192 (97), 176 (100), 161 (93), 146 (78), 134 (88), 121 (64).

3.7. Irradiation of 2-phenylheptamethyltrisilane in a 1 M solution of butadiene

To a solution of 0.10 g (0.4 mmol) 2-phenylheptamethyltrisilane and 0.10 g hexadecane (internal standard) in 25 ml pentane, 1.4 g (25 mmol, 2.3 ml) butadiene was added. After 2 h irradiation (32% conversion of trisilane), three products were detected by GC: Me_6Si_2 (64%). **1** (45%), and **4** (14%).

3.8. Irradiation of 2,2-diphenylhexamethyltrisilane in neat butadiene

To 0.50 g (1.5 mmol) 2,2-diphenylhexamethyltrisilane and 0.40 g hexadecane (internal standard) was added, by transfer on a vacuum line, 30 ml purified butadiene. The mixture, after three cycles of freeze–pump–thaw degassing, was irradiated 15 h (48% conversion of trisilane). After careful evaporation of the butadiene, five products were detected by GC: Me_6Si_2 (80%), 1,1-2 diphenylsilacylclopent-3-ene **5** (17%), *cis*-1,1-diphenyl-3,4-divinylsilacyclopentane **6** (7%), *trans*-1,1-diphenyl-3,4-divinylsilacyclopentane **7** (21%), and 3-butenyl(phenyl)(trimethylsilyl)(2-trimethylsilylphenyl)silane **8** (14%). **5** was separated from a mixture of **6**, **7** and **8** by preparative gas chromatography on column C, injection temperature 270°C, column temperature 160°C, flow rate 76 cm^3 He min^{-1}. The mixture of **6**, **7**, and **8** was reinjected on column D, injection temperature 290°C, column temperature 180°C, flow rate 68 cm^3 He min^{-1}. While **6** and **7** eluted as a single peak, nearly pure **7** was obtained by collecting the leading 3/4 of the peak. Spectroscopic data for **6** are reported from mixtures with **7**. The *trans*-configuration of **7** is clearly established from the observation of three resonances for sp^3 C–H, and the splitting pattern for these signals insures that the vinyl groups are attached at the 3- and 4-positions. **5**: ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 4H, SiCH$_2$), 6.00 (bs, 2H, –CH=CH–), 7.15–7.18 (m, 3H, ArH), 7.48–7.51 (m, 2H, ArH) (lit. [27] (CCl_4) δ 1.78 (SiCH$_2$), 5.95 (–CH=CH–), 7.1–7.6 (Ar–H)); MS *m/e* (relative intensity) 236 (M^+, 4), 181 (46), 158 (55), 130 (18), 105 (100), 79 (33), 53 (60). **6**: ^{1}H NMR ($CDCl_3$) δ 1.21 (dd, 2H, J_{gem} = 15.0 Hz, J_{nb} = 6.8 Hz, SiCH*H'*), 1.34 (dd, 2H, J_{gem} = 14.8 Hz, J_{ab} = 7.1 Hz, SiC*H*H'), 2.84 (m, 2H, vinyl-H) (remainder of vinyl and aromatic resonances obscured by presence of **7**); MS *m/e* (relative intensity) 290 (M^+, 0.03), 236 (3), 181 (19), 158 (30), 135 (100), 105 (59), 82 (7), 79 (13), 53 (19). **7**: ^{1}H NMR ($CDCl_3$) δ 1.02 (dd, 2H, J_{gem} = 15.0 Hz, J_{ab} = 11.9 Hz, C*H*H' *cis* to vinyl), 1.50 (dd, 2H, J_{gem} = 15.0 Hz, J_{ab} = 5.8 Hz, CH*H'*), 2.20 (m, 2H, J_{ab} = 6.2 Hz, $J_{ab'}$ = 12.0 Hz, C*H*CH=CH$_2$), 4.96 (dd, 4H, J_{gem} = 2.0 Hz, J_{ab} = 10.4 Hz, *cis* CH=C*H*H'), 5.00 (dd, 2H, J_{gem} = 2.2 Hz, $J_{ab'}$ = 16.0 Hz, *trans*-CH=CH*H'*), 5.81 (ddd, 2H, J_{ab} = 16.0 Hz, $J_{ab'}$ = 10.4 Hz, $J_{ab''}$ = 6.0 Hz, C*H*=CHH'), 7.35–7.40 (m, 6H, Ar–H), 7.52–7.59 (m, 4H, Ar–H); ^{13}C NMR ($CDCl_3$) δ 19.45 (SiCH$_2$), 50.00 *C*HCH=CH$_2$), 113.48 (CH=*C*H$_2$), 128.16 (A–CH), 129.65 (Ar–CH), 134.94 (Ar–CH), 143.90 (*C*H=CH$_2$) (*ipso*-Ar–C not observed); MS *m/e* (relative intensity) 290 (M^+, 0.1), 236 (7), 181 (46), 158 (78), 130 (18), 105 (100), 82 (13), 79 (24), 53 (33); exact mass determination for $C_{20}H_{22}Si$ (M^+), Calc. 290.1440, found 290.1461; Anal. Calc. for $C_{20}H_{22}Si$ C, 82.70; H, 7.63; Found C, 80.24; H, 7.74. **8**: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9H, SiMe$_3$), 0.14 (s, 9H, SiMe$_3$), 1.40 (dt, 2H, J_{gem} = 12.0 Hz, J_{ab} = 5.6 Hz, SiCHH'), 2.10 (m, 2H C*H*$_2$CH=CH$_2$), 4.88–5.06 (m, 2H, CH=C*H*$_2$), 5.82–5.94 (m, 1H, C*H*=CH$_2$), 7.27–7.41 (m, 8H, Ar–H), 7.72–7.81 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$) δ −1.28 (Si–Me), 1.49 (Si–Me), 13.01 (SiCH$_2$), 29.00 (*C*H$_2$CH=CH$_2$), 113.10 (CH=*C*H$_2$), 127.52, 127.80, 128.09, 128.26, 128.58, 134.96, 136.63, 139.03, 141.48, 141.54 (all Ar–C), 148.45 (*C*H=CH$_2$)

3.9. Irradiation of 2,2-diphenylhexamethyltrisilane in a 1 M solution of butadiene

To 0.15 g (0.46 mmol) 2,2-diphenylhexamethyltrisilane and 0.14 g dodecane (internal standard) in 25 ml pentane was added, by transfer on a vacuum line, 1.4 g (25 mmol, 2.2 ml) butadiene. After three cycles of freeze–pump–thaw degassing, the mixture was irradiated 2h (46% conversion of trisilane), and three products were detected by GC: Me_6Si_2 (77%), **5** (45%) and **8** (17%). The yields of **6** and **7** were each less than 1%.

3.10. Irradiation of dodecamethylcyclohexasilane in neat butadiene

To 0.7 g (2.0 mmol) cyclo-$(SiMe_2)_6$ and 0.5 g hexadecane (internal standard) was added, by transfer on a vacuum line, 16 g (296 mmol, 25 ml) butadiene. After three cycles of degassing and irradiation for 20 h (47% conversion of cyclo-$(SiMe_2)_6$), GC analysis revealed that the complex reaction mixture (at least 25 products!) contained cyclo-$(SiMe_2)_5$ (69%) and three silylene products, 1,1-dimethylsilacyclopent-3-ene **9** (0.5%), *cis*-1,1-dimethyl-3,4-divinylsilacyclopentane **10** (9%), and *trans*-1,1-dimethyl-3,4-divinylsilacyclopentane **11** (10%). Their mass spectra suggested that most of the unidentified products contain silicon. **10** and **11** were purified by preparative GC, collection as a single peak from column A, injection temperature 280°C, column temperature 210°C, flow rate 92 cm^3 He min^{-1}, retention time of mixture 7 min, and reinjection on column D, column temperature 150°C, retention time **11** 10 min, **10** 14 min. **9** was identified by MS, and **10** and **11** from their ^{1}H and ^{13}C NMR and mass spectra. **9**: MS *m/e* (relative intensity) 112 (M^+, 27), 97 (100), 95 (31), 71 (11), 59 (10), 58 (24) (lit. [28] *m/e* (relative intensity) 112 (M^+, 12), 97 (100), 95 (33), 58 (16), 43 (13). **10**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 3H, Si*Me*Me′), 0.17 (s, 3H, SiMe*Me′*), 0.65 (dd, 2H, J_{gem} = 14.7 Hz, J_{ab} = 6.8 Hz, C*H*H′), 0.74 (dd, 2H, J_{gem} = 14.7 Hz, J_{ab} = 6.8 Hz, CH*H′*), 1.42 (m, 2H, C*H*CH=CH$_2$), 4.96 (m, 4H, CH=C*H*$_2$), 5.78 (m, 2H, CHC*H*=CH$_2$); MS *m/e* (relative intensity) 166 (M^+, 0.6), 151 (3), 112 (42), 97 (100), 59 (10), 58 (7). **11**: ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 6H, SiMe$_2$), 0.45 (dd, 2H, J_{gem} = 14.6 Hz, J_{ab} = 11.4 Hz, CH*H′* *cis* to vinyl), 0.92 (dd, 2H, J_{gem} = 14.6 Hz, J_{ab} = 1.7 Hz, CH*H′* *trans* to vinyl), 4.90 (dd, 2H, J_{gem} = 2.1 Hz, J_{ab} = 10.1 Hz, *cis* CH=C*H*H′), 4.93 (dd, 2H, J_{gem} = 2.1 Hz, J_{ab} = 17.0 Hz, *trans* (CH=CH*H′*), 5.73 (m, 2H, C*H*=CH$_2$); ^{13}C NMR ($CDCl_3$) δ – 1.20 (SiMe$_2$), 20.83 (SiCH$_2$), 49.75 (*C*HCH=CH$_2$), 112.60 (CH=*C*H$_2$), 144.38 (*C*H=CH$_2$); MS *m/e* (relative intensity) 166 (M^+, 0.2), 151 (2), 112 (36), 97 (100), 59 (13), 58 (10).

3.11. Irradiation of 2-phenylheptamethyltrisilane in butadiene containing an acetone impurity

To 0.25 g (0.94 mmol) 2-phenylheptamethyldisilane and 0.25 g dodecane (internal standard) was added, by transfer on a vacuum line, 35 ml butadiene. The mixture was degassed and then irradiated 15 h 62% conversion of trisilane). Three products were detected by GC: Me_6Si_2 (65%), and *E*- and *Z*-2,5,5-trimethyl-2-phenyl-4-vinyl-2-silaoxacyclopentanes (28% and 26%). The latter products were easily separated and purified by preparative GC on column A. Structure was assigned on the basis of ^{1}H NMR coupling constants and the ^{13}C NMR spectrum and mass spectrum. The ^{1}H NMR spectra of the *E*- and *Z*-isomers differ only in the chemical shift of the vinyl protons. The isomer with the higher chemical shift is assumed to be the *Z*-isomer in which the phenyl group *cis*- to the vinyl group shields it. *E*-2,5,5-trimethyl-2-phenyl-4-vinyl-2-silaoxacyclopentane: ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 3H, SiMe), 1.27 (s, 3H, C*Me*Me′), 1.41 (s, 3H, CMe*Me′*), 1.87 (dd, 1H, J_{gem} = 12.8 Hz, J_{ab} = 12.9 Hz, SiC*H*H′ *trans* to Ph), 2.07 (dd, 1H, J_{gem} = 12.8 Hz, J_{ab} = 7.5 Hz, SiCH*H′* *cis* to Ph), 2.50 (dt, 1H, $J_{ab'} = J_{ab''}$ = 7.5 Hz, J_{ab} = 12.5 Hz, CHH′C*H*CH=CH$_2$), 4.88 (dd, 2H, J_{ab} (*trans*) = 17.1 Hz, $J_{ab'}$ (*cis*) = 9.6 Hz, CH=C*H*$_2$), 5.87 (m, 1H, J_{ab} = 12.5 Hz, $J_{ab'}$ = 17.1 Hz, $J_{ab''}$ = 7.5 Hz, CHC*H*=CH$_2$), 7.24–7.43 (m, 3H, Ar–H), 7.58 –7.60 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$) δ –3.81 (SiMe), 29.10 (C*Me*Me′), 31.28 (CMe*Me′*), 31.88 (SiCH$_2$), 44.00 (CH$_3$*C*HCH=CH$_2$), 79.35 (O*C*Me$_2$), 111.38 (CH=*C*H$_2$), 130.13 (Ar–C), 133.68 (Ar–C), 135.53 (Ar–C), 136.83 (Ar–*ipso*-C), 138.60 (*C*H=CH$_2$); MS *m/e* (relative intensity 232 (M^+, 3.8), 190 (10), 177 (52), 174 (12), 163 (13), 159 (54), 150 (30), 146 (16), 138 (35), 137 (72), 120 (34), 105 (70), 96 (100), 91 (34), 81 (21). *Z*-2,5,5-trimethyl-2-phenyl-4-vinyl-2-silaoxacyclopentane: ^{1}H NMR ($CDCl_3$) δ 0.50 (s, 3H, SiMe), 1.29 (s, 3H, C*Me*Me′), 1.47 (s, 3H, CMe*Me′*), 1.76 (dd, 1H, J_{gem} = 13.4 Hz, J_{ab} = 14.0 Hz, SiC*H*H′, *trans* to Ph), 2.04 (dd, 1H, J_{gem} = 13.4 Hz, J_{ab} = 8.4 Hz, SiCH*H′* *cis* to Ph), 2.39 (m, 1H, CHH′C*H*CH=CH$_2$), 4.70 (d, 1H, J_{ab} = 8.7 Hz, CH=C*H*H′ *cis*), 4.90 (d, 1H, J_{ab} = 16.5 Hz, CH=CH*H′* *trans*), 5.46 (m, 1H, C*H*=CH$_2$), 7.32–7.38 (m, 3H, Ar–H), 7.47–7.50 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$) δ –1.51 (SiMe) 29.31 (C*Me*Me′), 31.15 (CMe*Me′*), 33.54 (SiCH$_2$), 44.72 (CH$_2$*C*HCH=CH$_2$), 79.44 (O*C*Me$_2$), 110.90 (CH=*C*H$_2$), 127.60 (Ar–C), 129.68 (Ar–C), 133.91 (Ar–C), 135.14 (Ar–*ipso*-C), 138.63 (*C*H=CH$_2$); MS *m/e* (relative intensity) 232 (M^+, 13), 190 (18), 177 (84), 174 (19), 163 (18), 159

(72), 150 (37), 146 (18), 137 (100), 118 (38), 105 (50), 96 (95), 91 (20), 81 (11).

3.12. Irradiation of 2,2-diphenylhexamethyltrisilane in pentane solutions containing butadiene and acetone

A 25 ml stock solution consisting of 0.95 g (2.9 mmol) 2,2-diphenylhexamethyltrisilane and 0.95 g dodecane (internal standard) in pentane was prepared in a volumetric flask. To aliquots of this solution in a photolysis cell were added volumetrically acetone (d = 0.79 g ml^{-1}) and butadiene (d = 0.62 g ml^{-1}). The solutions were each degassed by three freeze–pump–thaw cycles and irradiated 2 h. Four products were detected by GC: Me$_6$Si$_2$, 3,3-dimethyl-1,1-diphenyl-4-vinyl-2-oxasilacyclopentane **12**, diphenylsilyl(isopropenyl)ether **13**, and isopropyloxy(phenyl)(trimethylsilyl)(2-trimethylsilylphenyl)silane **14**. The products were separated on column A, but **13** underwent partial decomposition and could not be purified. Yields are reported in Tables 1 and 2. The product ratio **13** : **12** was determined by integration of the ^{1}H NMR spectrum (4.78 ppm doublet for **12** and 4.17 ppm singlet for **13**) of reaction mixtures after evaporation of pentane. **12**: ^{1}H NMR 1.31 (s, 3H, C*Me*Me'), 1.52 (s, 3H, CMe*Me'*), 1.89 (dd, 1H, J_{gem} = 13.1 Hz, J_{ab} = 13.1 Hz, SiC*H*H' *cis* to vinyl), 2.13 (dd, 1H, J_{gem} = 13.1 Hz, J_{ab} = 7.5 Hz, SiCH*H'* *trans* to vinyl), 2.77 (dt, J_{ab} = 12.8 Hz, $J_{a(b'b'')}$ = 7.7 Hz, CH$_2$C*H*CH=CH$_2$), 4.78 (dd, 1H, J_{gem} = 1.4 Hz, J_{ab} = 10.3 Hz, CH=C*H*H' *cis*), 4.95 (dd, 1H, J_{gem} = 1.3 Hz, J_{ab} = 17.0 Hz, CH=CH*H'* *trans*), 5.67 (approx. dt, 1H, J_{ab} = 15.8 Hz, $J_{ab'}$ = $J_{ab''}$ = 10.1 Hz, C*H*=CHH'), 7.31–7.49 (m, 6H, Ar–H), 7.54–7.57 (m, 2H, Ar–H), 7.63–7.67 (m, 2H, Ar–H); ^{13}C NMR (CDCl$_3$) δ 29.10 (Me), 30.97 (SiCH$_2$), 32.20 (Me), 44.72 (*C*HCH=CH$_2$), 79.80 (*C*Me$_2$), 111.78 (CH=*C*H$_2$), 127.86, 128.00 (*o*- or *p*-Ar-C), 130.12, 130.19 (*p*-Ar–C), 133.41 (*ipso*-Ar–C), 134.65, 134.95 (*o*- or *p*-Ar-C), 138.72 (*C*H=CH$_2$); MS *m/e* (relative intensity) 294 (M$^+$, 1.7), 239 (18), 208 (14), 199 (89), 181 (72), 158 (100), 129 (21), 123 (69), 121 (61), 105 (80), 91 (20), 77 (91), 53 (65); exact mass determination for C$_{19}$H$_{22}$SiO (M$^+$), calc. 294.143994, found 294.143997. **13**: ^{1}H NMR (CDCl$_3$) δ 1.85 (s, 3H, Me), 4.08 (s, 1H, C=C*H*H'), 4.17 (s, 1H, CH=CH*H'*), 5.58 (s, 1H, SiH), 7.32–7.55 (m, 6H, Ar–H), 7.63–7.66 (m, 4H, Ar–H); ^{13}C NMR (CDCl$_3$) δ 22.11 (Me), 91.78 (CH=*C*H$_2$), 129.54 (*o*- or *m*-Ar-C), 130.72 (*p*-Ar–C), 134.36 *ipso*-Ar–C), 134.82 (*o*- or *m*-Ar–C); MS *m/e* (relative intensity) 240 (M$^+$, 7.9), 239 (32), 212 (12), 208 (24), 199 (100), 181 (99), 158 (94), 129 (29), 121 (93), 105 (67), 91 (20), 79 (80), 53 (79). **14**: ^{1}H NMR (CDCl$_3$), 0.18 (s, 9H, SiMe), 0.24 (s, 9H, SiMe), 1.03 (d, 3H, J_{ab} = 6.1 Hz, CH*Me*Me'), 1.18 (d, 3H, J_{ab} = 6.1 Hz, CHMe*Me'*), 4.09 (septet, 1H, J_{ab} = 6.0 Hz, C*H*MeMe'), 7.23–7.69 (m, 9H, Ar–H); MS *m/e* (relative intensity) 386 (M$^+$, 2.7), 385 (7), 211 (25), 195 (38), 135 (91), 133 (100), 119 (49), 103 (22), 91 (49), 73 (79), 59 (39).

Acknowledgments

Discussions with Professor Robert T. Conlin have been most helpful. The late Professor Wilhelm Neumann lent assistance by kindly sending us reprints and preprints of his work. This work received financial support from the United States National Science Foundation under Grant No. CHE-8802677. Mass spectra were recorded by Ms. Janet Braddock Wilking, Mr. Dallas New, Dr. Fong Hsu, and Dr. Andrew Tyler at the Washington University Mass Spectrometry Resource supported by National Institutes of Health Grant RR00954.

References and notes

[1] P.P. Gaspar, in M. Jones, Jr. and R.A. Moss (eds), *Reactive Intermediates*, Wiley, New York, Vol. 1, 1978, p. 229; Vol. 2, 1981, p. 335; Vol. 3, 1985, p. 333.

[2] W.H. Atwell and D.R. Weyenberg, *J. Am. Chem. Soc., 90* (1968) 3438.

[3] S. Zhang and R.T. Conlin, *J. Am. Chem. Soc., 113* (1991) 4272.

[4] M. Ishikawa, K.-I. Nakagawa and M. Kumada, *J. Organomet. Chem., 178* (1979) 105.

[5] P.P. Gaspar and R.-J. Hwang, *J. Am. Chem. Soc., 96* (1974) 6198.

[6] R.-J. Hwang, R.T. Conlin and P.P. Gaspar, *J. Organomet. Chem., 94* (1975) C38.

[7] D. Lei and P.P. Gaspar, *J. Chem. Soc., Chem. Commun.*, (1985) 1149.

[8] M.P. Clarke and I.M.T. Davidson, *J. Chem. Soc., Chem. Commun.*, (1988) 241.

[9] M. Schriewer and W. Neumann, *J. Am. Chem. Soc., 105* (1983) 897.

[10] E.C.-L. Ma, K. Kobayashi, M. Barzilai and P.P. Gaspar, *J. Organomet. Chem., 224* (1982) C13.

[11] D. Lei, R.-J. Hwang and P.P. Gaspar, *J. Organomet. Chem., 271* (1984) 1.

[12] D. Lei, Ph.D. Dissertation, Washington University, St. Louis, MO, December 1988.

[13] W.P. Neumann, E. Michels and E. Köcher, *Tetrahedron Lett., 28* (1987) 3783.

[14] K.L. Bobbitt, V.M. Maloney and P.P. Gaspar, *Organometallics, 10* (1991) 2772.

[15] Compound **2** decomposed during preparative gas chromatography and was identified on the basis of the similarity of its mass spectrum and that of **3**.

[16] M. Ishikawa, K.-I. Nakagawa, R. Enokida and M. Kumada, *J. Organomet. Chem., 201* (1980) 151.

[17] D. Seyferth, D.P. Duncan and M.L. Shannon, *Organometallics, 3* (1984) 579.

[18] W. Ando and M. Ikeno, *Chem. Lett.*, (1978) 609.

[19] R.T. Conlin, J.C. Netto-Ferreira, S. Zhang and J.C. Scaiano, *Organometallics, 9* (1990) 1332.

[20] K.L. Bobbitt, D. Lei, V.M. Maloney, B.S. Parker, J.M. Raible and P.P. Gaspar, in E. Lukevics and L. Ignatovich (eds),

Frontiers of Organogermanium, -Tin and -Lead Chemistry, Latvian Institute of Organic Synthesis, Riga, 1993, p. 41.

[21] D. Lei and P.P. Gaspar, *Polyhedron, 10* (1991) 1221.

[22] W.C. Still, M. Kahn and A. Mitra, *J. Org. Chem., 43* (1974) 2923.

[23] M. Kumada, M. Ishikawa and S. Maeda, *J. Organometal. Chem., 2* (1964) 478.

[24] W. Ando, K. Hagiwara and A. Sekiguchi, *Organometallics, 5* (1987) 2270.

[25] V.J. Tortorelli, M. Jones, Jr., S.-h. Wu and Z.-h. Li, *Organometallics, 2* (1983) 759.

[26] M. Ishikawa, K.-L. Nakagawa, R. Enokida and M. Kumada, *J. Organometal. Chem., 201* (1980) 151.

[27] G. Manual, P. Mazerolles, M. Lesbre and J.-P. Pradel, *J. Organometal. Chem., 61* (1973) 147.

[28] R.T. Conlin and Y.-W. Kwak, *Organometallics, 3* (1984) 918.