Silicon−Carbon Unsaturated Compounds. 58. Reactions of Silenes Produced Thermally from Acylpolysilanes with Carbonyl Compounds

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The cothermolysis of acetyl-, pivaloyl-, adamantoyl-, benzoyl-, and mesitoyltris(trimethylsilyl)silane (**1**−**5**) with acetone and benzophenone at 140 °C was investigated. The reaction of the silene formed from **1** with acetone and benzophenone afforded no adducts but produced a dimer of the silene. The silene produced thermally from **2** reacted with acetone to give two cyclopropane derivatives (**11**) and (**12**), and a silyl enol ether (**9**). Similar reaction of the silene formed from **3** with acetone afforded a cyclopropane derivative (**14**), along with a silyl enol ether (**13**). The reaction of the silene generated from **4** with acetone gave bicyclic compound **16** as the sole product, while similar reaction of the silene formed from **5** produced 2,2-dimethylmesityl(trimethylsiloxy)ethene. The thermolysis of **2** and **3** with benzophenone yielded the respective cycloheptatrienes **20** and **22**, and silyl enol ethers **19** and **21**, respectively. Similarly, the reactions of the silenes produced from **4** and **5** afforded silyl enol ethers **26** and **28**. Compound **22** was characterized by X-ray crystallography.

Introduction

Numerous examples for the synthesis and reactions of silenes including kinetically stable silenes, which are produced photochemically from acylpolysilanes, have been reported by Brook and his co-workers.[1a,b] We have been interested in the synthesis of silenes from acylpolysilanes using methods that do not involve a photochemical reaction and have found that treatment of acylpolysilanes with organolithium reagents produces silenes via a Peterson-type reaction.[2,3] The synthesis of silenes by way of a Peterson-type reaction has also been reported by Brook et al.[4] and Apeloig and his co-workers.[5] The thermolysis of acylpolysilanes also offers a convenient method for the synthesis of silenes. Brook and his co-workers have reported that treatment of pivaloyltris(trimethylsilyl)silane in the presence of a trapping agent such as an alcohol at 160 °C gives products arising from the reaction of 2-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene with the trapping agent.[6] We have also demonstrated that the thermolysis of adamantoyltris(trimethylsilyl)silane in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in benzene at 120 °C affords 2-[adamantyl(trimethylsiloxy)methyl]hexamethyl-2-phenyltrisilane and 2-[adamantyl(trimethylsiloxy)methyl]-2-methyl-1-phenylpentamethyltrisilane derived from reactions of 2-adamantyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene with benzene.[7] In the absence of the nickel catalyst, no adducts were formed, and the starting acylpolysilane was recovered quantitatively. Interestingly, when adamantoyltris(trimethylsilyl)silane was heated in the presence of 2,3-dimethylbutadiene, styrene, and α-methylstyrene as a trapping agent, the respective adducts arising from the reaction of the silene with the trapping agents were obtained.[8] We also found that the thermolysis of various acylpolysilanes, $(Me_3Si)_3SiCOR$ with R = Me, *iso*-Pr, *tert*-Bu, Ph, and Mes, proceeds cleanly to give the respective silenes.[8]

To date, the reactions of the silenes with many types of organic compounds have been extensively investigated.[9] Many papers concerning the reaction of the silenes with carbonyl compounds have been published. In the reaction of the relatively stable silenes with nonenolizable carbonyl compounds, the [2 + 2] cycloadducts, siloxetanes, have been isolated,[10−14] and the structure of one siloxetane, 2,2-bis(trimethylsilyl)-4,4-biphenyl-3-adamantyl-3-(trimethylsiloxy)-2-siloxetane, has been confirmed by X-ray crystallographic analysis.[14] As a part of our studies on the chemistry of the silenes produced thermally from acylpolysilanes, we have examined the cothermolysis of acylpolysilanes with carbonyl compounds. In this paper, we report the

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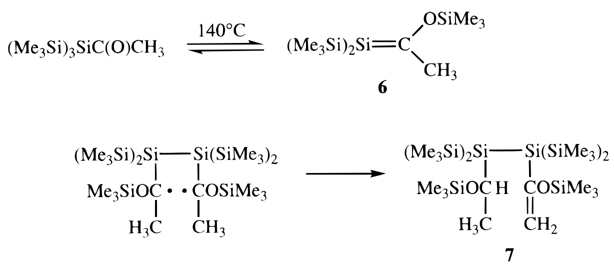
Scheme 1



reactions of the silenes with acetone and benzophenone under thermal conditions.

Results and Discussion

Five acylpolysilanes, acetyl-, pivaloyl-, adamantoyl-, benzoyl-, and mesitoyltris(trimethylsilyl)silane (**1**−**5**) were synthesized by the reaction of tris(trimethylsilyl)silyllithium with acyl chlorides, as reported in the literature.[15−17]

$$(Me_3Si)_3SiLi \quad + \quad RC(O)Cl \longrightarrow (Me_3Si)_3SiC(O)R \quad + \quad LiCl$$

1, R = CH_3
2, R = tert-Bu
3, R = Ad
4, R = Ph
5, R = Mes

When acetyltris(trimethylsilyl)silane (**1**) was treated with 2 equiv of acetone in a degassed sealed tube at 140 °C for 24 h, 92% of starting compound **1** was recovered unchanged. A compound (**7**) derived from head-to-head radical dimerization of 2-methyl-2-(trimethylsiloxy)bis(trimethylsilyl)silene (**6**) produced from **1**, followed by disproportionation of the resulting carbon diradical, was obtained in 8% yield (Scheme 1).

All spectral data obtained for **7** were identical with those reported in the literature.[17] No other products were detected by either GLC analysis or spectrometric analysis of the reaction mixture.

The reaction of pivaloyltris(trimethylsilyl)silane (**2**) with 3 equiv of acetone under the same conditions, however, afforded three isomers of acetone adducts, *(E)*-2-*tert*-butyl-1,2-dimethyl-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]ethene (**9a**), 2,2-dimethyl-1-{dimethyl[(trimethylsiloxy)bis(trimethylsilyl)siloxy]methyl}cyclopropane (**11a**), and *trans*-2-*tert*-butyl-1-methyl-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]cyclopropane (**12a**) in 11, 23, and 11% yields, respectively (Scheme 2). In this reaction, 55% of starting compound **2** was recovered unchanged.

The formation of products **9a**, **11a**, and **12a** may be best understood in terms of thermal degradation of siloxetane (**8**) formed by [2 + 2] cycloaddition of the silene generated thermally from **2** with acetone. Product **9a** would be produced by a 1,2-trimethylsiloxy shift to a central silicon atom, with a simultaneous 1,2-shift of a methyl group on the C3 position to the C4 position in the siloxetane ring, giving the ring opened product **9a**. This type of isomerization has been found by Brook et al. in the thermal reaction of the siloxetane derived from the cophotolysis of benzoyltris(trimethylsilyl)silane with di-*p*-tolyl ketone.[14] No *(Z)*-isomer was detected by spectrometric analysis. Presumably, the *(E)*-isomer is sterically more favorable than the *(Z)*-isomer.

The production of the siloxetanes has been proposed in the reactions of silenes and various ketones.[9] Indeed, stable siloxetanes have been isolated in some of these reactions,[12,18−20] and the structure of the siloxetane obtained from the reaction of 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)silene with benzophenone has been confirmed by X-ray crystallographic analysis.[14] Isomerization of the siloxetanes involving a 1,2-trimethylsiloxy shift to the silyl enol ethers, analogous to **9**, has also been reported.[12,14]

Products **11a** and **12a** are probably produced by C−H insertion of a carbene intermediate (**10**) derived from a 1,2-trimethylsiloxy shift in siloxetane **8**, as shown in Scheme 2. Intramolecular insertion of carbene **10** into a C−H bond of a methyl group in the *tert*-butyl moiety would produce product **11a**, while insertion into a methyl C−H bond of the acetone moiety would form product **12a**. In order to confirm this mechanism, we carried out the reaction using acetone-d_6. In fact, the reaction of **2** with 3 equiv of acetone-d_6 under the same conditions gave three isomers of acetone-d_6 adducts, *(E)*-2-*tert*-butyl-1,2-di(trideuteriomethyl)-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]ethene (**9b**), 1-[di(trideuteriomethyl)(trimethylsiloxy)bis(trimethysilyl)siloxy]-2,2-dimethylcyclopropane (**11b**), and *trans*-2-*tert*-butyl-2,3,3-trideuterio-1-(trideuteriomethyl)-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]cyclopropane (**12b**) in 11, 27, and 4% yields, together with 58% of the unreacted starting compound **2**. The formation of **11b** and **12b** clearly indicates that carbene **10** is produced as a reactive intermediate in the present reaction.

As expected, a similar reaction of adamantoyltris(trimethylsilyl)silane (**3**) with acetone at 140 °C for 24 h yielded two isomers of adducts, *(E)*-2-adamantyl-1,2-dimethyl-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]ethene (**13a**), and *trans*-2-adamantyl-1-methyl-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]cyclopropane (**14a**) in 15 and 77% yields, respectively (Scheme 3). No other products were detected by either GLC or spectrometric analysis.

Treatment of **3** with acetone-d_6 under the same conditions again afforded two deuterated products **13b** and **14b** in 31 and 62% yields, respectively. As in the reaction of **2** with acetone, compound **13** would be produced from isomerization of a siloxetane analogous to **8**, involving a 1,2-trimethylsiloxy shift with a simultaneous 1,2-methyl shift, while **14** may be explained by intramolecular insertion of the carbene analogous to **10** arising from a 1,2-trimethylsiloxy shift in the siloxetane into a C−X bond to form the cyclopropane ring.

The structures of **9a**,**b**, **11a**,**b**, and **12a**,**b**−**14a**,**b** were confirmed by spectrometric and elemental analysis. Configurations of **9a** and **13a** were verified by NOE-FID difference experiments at 270 MHz. Thus, saturation of the methyl protons at δ 1.86 ppm of **9a** caused a positive NOE of the trimethylsilyl protons and also of the *tert*-butyl protons, while irradiation of the methyl

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(19) The formation of a siloxetane has also been reported by Ando et al.; see ref 18.

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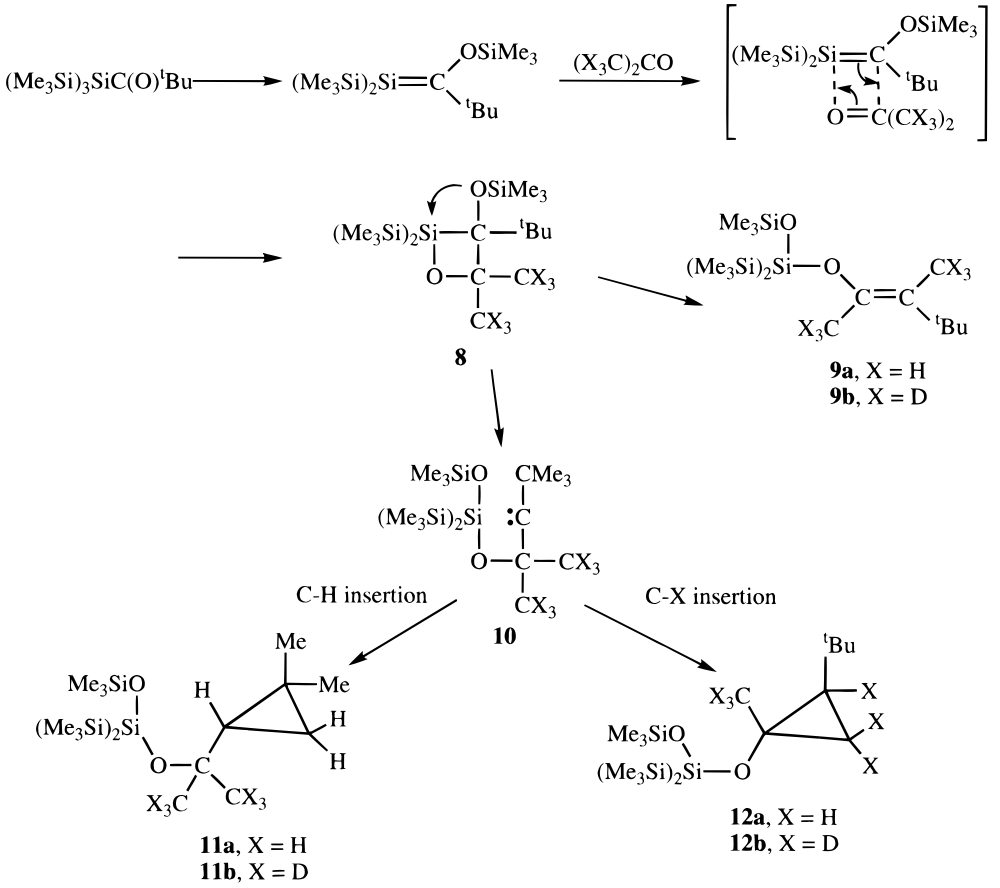
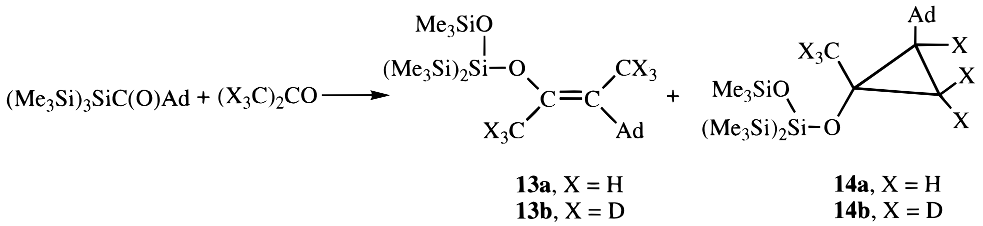
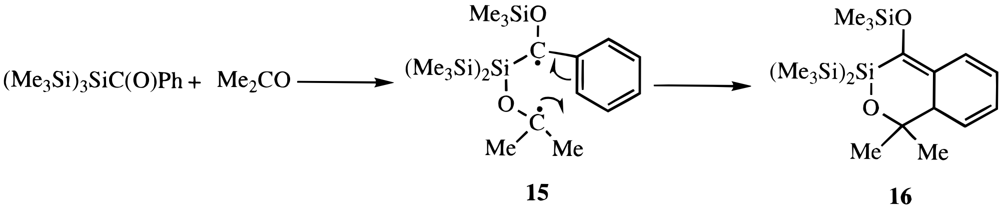
Scheme 2



Scheme 3



Scheme 4

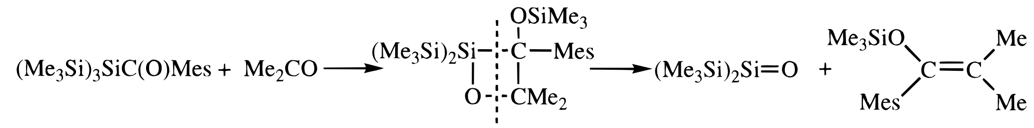


protons at 2.08 ppm led to enhancement of the *tert*-butyl protons. For **13a**, saturation of the methyl protons at 1.85 ppm produced a positive NOE of the adamantyl protons, and irradiation of the methyl protons at 2.13 ppm again led to enhancement of the adamantyl protons. These results clearly indicate that **9a** and **13a** must have the *(E)*-configuration. The configurations of cyclopropanes **12a** and **14a** were also verified by NOE-FID difference experiments at 270 MHz. Saturation of the *tert*-butyl protons on the three-membered ring in **12a** resulted in enhancement of the methyl protons, indicating that both *tert*-butyl and methyl groups are located in a *cis* fashion on the cyclopropyl ring. Similarly, irradiation of the methyl protons on the cyclopropyl ring in **14a** produced a positive NOE of the adamantyl protons, showing that these groups are *cis* to each other.

The reaction of benzoyltris(trimethylsilyl)silane (**4**) with acetone proceeded in a different fashion from those of acylpolysilanes **2** and **3**. Thus, the reaction of **4** with 2.5 equiv of acetone at 140 °C for 24 h afforded a formal [4 + 2] cycloadduct, [4.4.0] bicyclic compound (**16**), in 62% isolated yield (Scheme 4). No other isomers were detected by spectrometric analysis.

Product **16** is probably produced by homolytic scission of a carbon−carbon bond in the four-membered ring of the siloxetane, which would be formed from [2 + 2] cycloaddition of 2-phenyl-2-(trimethylsiloxy)bis(tri-

Scheme 5



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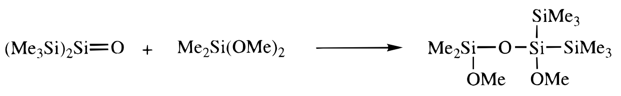
methylsilyl)silene with acetone, leading to diradical species **15**, followed by addition of the resulting siloxy(dimethyl)methyl radical to the phenyl group. At present, a possibility of direct [4 + 2] cycloaddition of a silene and acetone for the formation of **16**, where the silene provides the 4π component, cannot be excluded. However, it has been reported that the siloxetane formed from the reaction of mesityl(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene with benzophenone isomerizes at room temperature to give the [4.4.0] bicyclic compound analogous to **16**.[14] Such [4.4.0] bicyclic compounds have also been found to be produced in the cophotolysis of benzoyltris(trimethylsilyl)silane with ketones such as benzophenone, fluorenone, and di-*p*-tolyl ketone.[12,14] The structure of **16** was verified by mass, IR, and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis. The ^{13}C NMR spectrum for **16** shows the presence of six olefinic carbons, one dimethylsiloxy substituted carbon, and one methine carbon, which are consistent with the structure proposed for **16**.

Mesitoyltris(trimethylsilyl)silane (**5**) also reacted with acetone under the same conditions to give 2,2-dimethyl-1-mesityl-1-(trimethylsiloxy)ethene (**17**), but product **17** was obtained only in low yield. A large amount of starting compound **5** was recovered unchanged. Thus, treatment of **5** with 1.7 equiv of acetone at 140 °C for 24 h afforded **17** in 19% yield as the sole product, in addition to 78% recovery of the unchanged starting compound **5** (Scheme 5). It seems likely that product **17** is produced from splitting of the siloxetane derived from [2 + 2] cycloaddition of the silene generated from **5** with acetone. Brook et al. reported that the thermolysis of the siloxetane obtained from the reaction of 2-mesityl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)silene with fluorenone underwent a retro [2 + 2] cleavage reaction to give a trimer of bis(trimethylsilyl)silanone and olefin.[16] In our case, however, the trimer of bis(trimethylsilyl)silanone could not be detected by GC-mass spectrometric analysis in the resulting reaction mixture. However, the cothermolysis of **5** with acetone in the presence of dimethoxydimethylsilane produced an Si−O insertion product. Thus, treatment of **5** with acetone in the presence of a 3-fold excess of dimethoxydimethylsilane in benzene at 140 °C for 24 h afforded **17** and 2-methoxy-2-(methoxydimethylsiloxy)hexamethyltrisilane (**18**) in 9 and 3% yields, in addition to 90% of the unreacted starting compound **5**. The formation of the Si−O insertion product **18** clearly indicates the intermediacy of bis(trimethylsilyl)silanone.

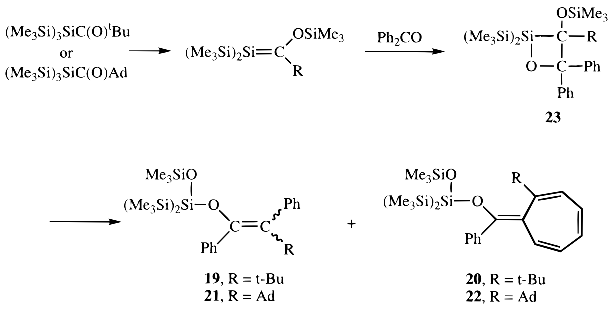


$(Me_3Si)_2Si{=}O + Me_2Si(OMe)_2 \longrightarrow Me_2Si(OMe){-}O{-}Si(OMe)(SiMe_3){-}SiMe_3$

18

Next, we investigated the reaction of acylpolysilanes **1**−**5** with benzophenone. The reaction of **1** with benzophenone in a sealed degassed tube at 140 °C for 24 h afforded no adduct. As observed in the reaction of **1** with acetone, product **7** arising from dimerization of silene **6** was obtained in 4% yield, together with 86% of the unreacted starting compound **1**.

Scheme 6

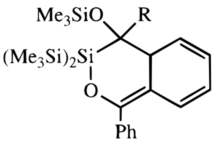


23

19, R = t-Bu
21, R = Ad

20, R = t-Bu
22, R = Ad

In marked contrast to the reaction of the silenes produced from the photolysis of **2** and **3** with benzophenone at room temperature, in which [2 + 4] cycloadducts, whose structures are shown as follows, are formed, the silenes generated thermally from acylpolysilanes **2** and **3** react with benzophenone to give two isomers of adducts. When a mixture of **2** and 1.3 equiv of benzophenone was heated at 140 °C for 24 h, 2-*tert*-butyl-1,2-diphenyl-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]ethene (**19**) and *(Z)*-2-*tert*-butyl-1-{phenyl[(trimethylsiloxy)bis(trimethylsilyl)siloxy]methylene}cyclohepta-2,4,6-triene (**20**) were obtained in 46 and 24% yields, respectively, along with a 29% recovery of the unreacted starting compound **2** (Scheme 6).

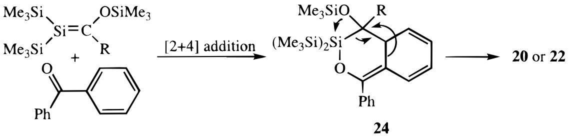


R=t-Bu, Ad

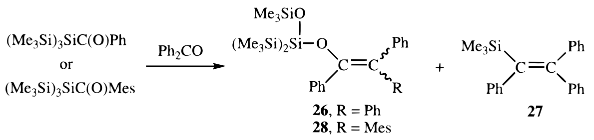
The reaction of **3** with benzophenone proceeded with a fashion similar to that of **2**. Two products, 2-adamantyl-1,2-diphenyl-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]ethene (**21**) and *(Z)*-2-adamantyl-1-{phenyl[(trimethylsiloxy)bis(trimethylsilyl)siloxy]methylene}cyclohepta-2,4,6-triene (**22**) were obtained in 46 and 35% yields, respectively, in addition to 7% of the unreacted starting compound **3**. For the production of **19** and **21**, no other isomers were detected by spectrometric analysis. In order to confirm the configuration of **19** and **21**, we carried out NOE-FID difference experiments at 270 MHz. Unfortunately, no clearcut results with respect to *(E)*- and *(Z)*-configuration of these products were obtained. The formation of **19** and **21** can be best understood in terms of two distinct 1,2-shifts, a 1,2-trimethylsiloxy shift and 1,2-phenyl shift in siloxetane (**23**). The structure of **22** was confirmed by X-ray crystallographic analysis (see below).

Scheme 7 illustrates a possible mechanistic interpretation for the formation of products **20** and **22**. The [2

Scheme 7



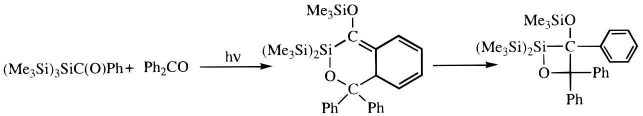
Scheme 8



+ 4] cycloaddition in which benzophenone provides the 4π component would produce the [4.4.0] bicyclic compound (**24**, R = *t*-Bu or Ad). The bicyclic compound thus formed would undergo ring enlargement to the seven-membered ring system to produce **20** or **22**. Although direct evidence for the formation of the [4.4.0] bicyclic compound has not been obtained in these reactions, the formation of the [2 + 4] cycloadducts has been observed in the reactions of the stable silenes and ketones.[13,14]

In order to learn more about the formation of **20** and **22**, we synthesized [4.4.0] bicyclic compound **24**, according to the method reported by Brook et al. Thus, the reaction of 2-adamantyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene produced photochemically from acylpolysilane **3** with benzophenone at room temperature afforded a mixture of **24** (R = Ad) and siloxetane **23** (R = Ad) in a ratio of 6/1. Brook et al. reported that **24** completely rearranges to give **23** (R = Ad) on standing in the dark at room temperature over 24 h. In our case, however, the rate of isomerization of a deuteriobenzene solution of **24** (R = Ad) to **23** (R = Ad) is very slow at room temperature. When the mixture (**24**/**23** = 6/1) was allowed to stand at room temperature for 3 days, the ratio of **24**/**23** was found to be 2/1 by ^{1}H NMR spectroscopy. After standing over 8 days, the ratio was determined to become 1/2. At 40 °C, the ratio of the mixture (**24**/**23** = 5.8/1) was changed to be 1/2.7 after 2 days. Products **21** and **22** were observed after standing over 4 days, and the product ratio at this point was found to be **24**/**23**/**21**/**22** = 1/3/0.3/0.3. On heating the solution of **24** (R = Ad) involving a trace of **23** (R = Ad) at 140 °C for 24 h, a mixture consisting of compounds **21** and **22** in a ratio of 1.25/1 was obtained. On the basis of these results, it seems likely that compound **21** is produced by thermolysis of the siloxetane formed from isomerization of **24** (R = Ad). Product **22**, however, is probably produced directly by thermolysis of **24**.

In marked contrast to the cophotolysis of **4** with benzophenone, in which the initially formed [4.4.0] bicyclic compound is transformed into a siloxetane in the dark,[14] the reaction of **4** with benzophenone at 140 °C produced a silyl enol ether, 1,2,2-triphenyl-1-[(trimethylsiloxy)bis(trimethylsilyl)siloxy]ethene (**26**), and 1,2,2-triphenyl-1-(trimethylsilyl)ethene (**27**) in 52 and 22% yields, respectively. The formation of **26** can be understood in terms of a 1,2-shift of a trimethylsiloxy group in a siloxetane (**25**), followed by a 1,2-phenyl shift, while the origin of the latter compound **27** is unknown at present (Scheme 8).



25

Unlike the thermolysis of the siloxetane produced from 2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene and benzophenone at room temperature, which gives a mixture of the [4.4.0] bicyclic compound and a siloxetane,[14] the reaction of **5** with benzophenone at 140°C gave 2-mesityl-1,2-diphenyl-1-[(trimethylsilylsiloxy)bis(trimethylsilyl)siloxy]ethene (**28**) in 46% yield as the sole product. In this reaction, 54% of the starting compound **5** was recovered unchanged. The configuration of **28**, however, could not be determined even in NOE-FID difference experiments.

Crystal Structure of 22. The structure of **22** was determined by X-ray crystallographic analysis, confirming the methylenecyclohepta-2,4,6-triene structure. Light yellow crystals of **22** were obtained by recrystallization from ethanol. Detailed crystal data are shown in Table 1. The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 2. The molecular structure with the atomic numbering system is shown in Figure 1, and selected bond distances and angles are listed in Table 3.

The bond lengths of the carbon–carbon double bonds, C_9-C_{10}, $C_{11}-C_{12}$, and $C_{13}-C_{14}$ in the methylenecycloheptatriene system are in the range of 1.329–1.344 Å. They are remarkably short compared with those of the tropone derivatives, 6,8-dibenzocycloheptene-1,4,7-triones[21] (1.353–1.357 Å). On the other hand, the bond angle of $Si_2-Si_1-Si_3$ (112.8°) in a (trimethylsiloxy)bis(trimethylsilyl)siloxy group is larger than an sp^3 angle, presumably due to the repulsive interaction of two large trimethylsilyl groups on the central silicon atom. To compensate for this large angle, the $Si_2-Si_1-O_5$ angle (103.6°) is smaller than the normal one. The other bond angles in $O_5-Si_1-O_6$ and $Si_3-Si_1-O_6$ are 109.5 and 110.3°, respectively. There are no close intermolecular contacts.

In conclusion, the thermolysis of **1** in the presence of acetone and benzophenone gave only the product derived from dimerization of the silene generated from **1**. The silenes produced thermally from acylpolysilanes **2**–**5** reacted with acetone to give the products which can be best understood in terms of isomerization of the siloxetanes formed from [2 + 2] cycloaddition of the silenes and acetone. The reactions of silenes generated from **2** and **3** with benzophenone afforded products derived from [2 + 2] and [2 + 4] adducts, while silenes from **4** and **5** reacted with benzophenone to give the product arising from the thermolysis of the respective siloxetanes.

Experimental Section

General Procedure. All reactions were carried out in a degassed sealed tube (1.0 cm × 15 cm). Yields for **7**, **13**, **14**, **17**–**22**, and **26**–**28** were determined by analytical GLC with the use of tridecane as an internal standard, on the basis of the acylpolysilanes used. Yields of products **9**, **11**, and **12** were determined by the ^{1}H NMR spectra of the reaction mixture, and that of product **16** was calculated on the basis of the

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(21) Furuich, K.; Toda, H.; Itoh, A.; Takeuchi, Y.; Mitoori, M.; Kato, M.; Matsumoto, S.; Hashimoto, M. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 1363.

Table 1. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 22

compound		diffractometer	Rigaku AFC-6C
mol formula	$C_{33}H_{52}O_2Si_4$	temp, K	298
mol wt	593.12	wavelength, Å	1.5418 (Cu Kα)
space group	$P2_1/n$	monochrometer	graphite crystal
cell dimens		scan type	$\omega-2\theta$
a, Å	9.923 (1)	scan speed, deg/min	4
b, Å	34.093 (2)	scan width, deg	$0 < 2\theta < 126$
c, Å	10.7820 (8)	diffraction geometry	symmetrical A
α, deg	90.0	ranges of *h*, *k*, *l*	
β, deg	100.72 (1)	*h*	$-11 \le h \le 11$
γ, deg	90.0	*k*	$0 \le k \le 39$
V, Å^3	3584.2 (8)	*l*	$0 \le l \le 12$
D_{calcd}, Mg/m^3	1.100	no. of unique reflns	5737
Z	4	no. of obsd reflns ($\|F_o\| \ge 3\sigma(F_o)$)	4046
cryst size, mm^3	0.5 × 0.5 × 0.4	*R*	0.066
cryst color	light yellow	R_w[a]	0.062
μ, mm^{-1}	1.61		

[a] Weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for 22 with Esd's in Parentheses

atom	*x*	*y*	z	B_{eq}[a]
Si1	0.0800(1)	0.15087(2)	0.7314(1)	4.7(1)
Si2	0.1882(1)	0.14531(2)	0.5555(1)	6.1(1)
Si3	0.1954(1)	0.11722(3)	0.9121(1)	6.4(1)
Si4	0.0966(1)	0.23861(2)	0.8353(1)	5.7(1)
O5	−0.0782(3)	0.13440(6)	0.6794(2)	4.5(1)
O6	0.0749(3)	0.19771(6)	0.7584(3)	5.8(2)
C7	−0.1784(4)	0.1233(1)	0.7454(3)	4.1(2)
C8	−0.2344(4)	0.0876(1)	0.7293(3)	4.2(2)
C9	−0.2003(4)	0.0572(1)	0.6405(4)	4.4(2)
C10	−0.1366(5)	0.0245(1)	0.6904(5)	6.1(2)
C11	−0.1170(7)	0.0125(2)	0.8215(6)	7.6(2)
C12	−0.2018(8)	0.0206(2)	0.9006(6)	8.3(3)
C13	−0.3221(6)	0.0439(2)	0.8769(5)	6.8(2)
C14	−0.3417(5)	0.0743(1)	0.7984(4)	5.6(2)
C15	−0.2281(4)	0.1546(1)	0.8223(3)	4.2(2)
C16	−0.2397(5)	0.1490(1)	0.9466(4)	5.4(2)
C17	−0.2908(5)	0.1785(1)	1.0134(5)	6.6(2)
C18	−0.3314(5)	0.2136(1)	0.9554(5)	6.4(2)
C19	−0.3216(5)	0.2195(1)	0.8323(5)	6.2(2)
C20	−0.2683(4)	0.1903(1)	0.7662(4)	5.3(2)
C21	−0.2584(4)	0.0612(1)	0.5000(4)	4.4(2)
C22	−0.1898(9)	0.0325(3)	0.4187(6)	12.1(3)
C23	−0.2596(9)	0.0370(2)	0.2695(6)	9.7(3)
C24	−0.242(1)	0.0783(4)	0.2405(9)	14.5(5)
C25	−0.318(2)	0.1064(2)	0.3014(8)	13.8(5)
C26	−0.255(2)	0.1022(2)	0.4503(7)	15.2(6)
C27	−0.396(1)	0.0258(2)	0.2722(8)	10.6(3)
C28	−0.4801(8)	0.0537(4)	0.3278(8)	11.3(4)
C29	−0.455(2)	0.0942(4)	0.307(1)	14.7(6)
C30	−0.4057(7)	0.0482(4)	0.4792(6)	12.8(4)
C31	0.0840(8)	0.1684(2)	0.4148(7)	9.2(3)
C32	0.3626(7)	0.1665(3)	0.5920(9)	10.8(4)
C33	0.2071(8)	0.0905(2)	0.5154(9)	9.4(3)
C34	0.2459(8)	0.0681(2)	0.8635(7)	9.7(3)
C35	0.094(2)	0.1094(5)	1.040(1)	11.7(4)
C36	0.3584(9)	0.1456(3)	0.9641(8)	10.6(3)
C37	−0.0259(7)	0.2750(2)	0.7512(7)	7.7(2)
C38	0.2743(7)	0.2559(2)	0.8397(7)	8.9(3)
C39	0.0647(8)	0.2311(2)	0.9974(6)	8.4(3)

[a] $B_{eq} = (4/3)(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)$.

isolated products. NMR spectra were recorded on a JEOL Model EX-270 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. Gel permeation chromatographic separation was performed with a RI Model 504 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.).

Materials. Acylpolysilanes **1**−**5** were prepared according to the method reported by Brook et al.[15−17] Acetone was dried over calcium sulfate and distilled just before use. Benzene used as a solvent was dried over lithium aluminum hydride and distilled before use.

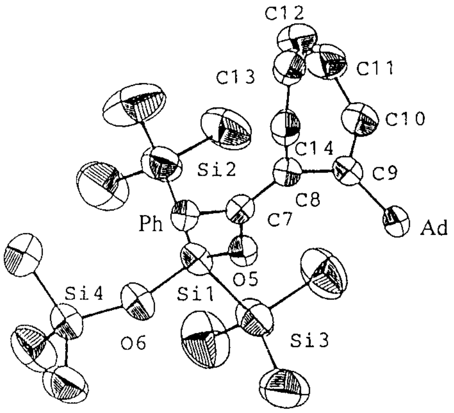

Figure 1. Molecular structure of **22** with atomic labeling scheme. (Adamantyl and phenyl carbon atoms are omitted for clarity.)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 22 with Their Esd's in Parentheses

Bond Lengths					
Si1−Si2	2.361(2)	Si1−Si3	2.365(2)	Si1−O5	1.664(3)
Si1−O6	1.626(3)	Si4−O6	1.616(3)	O5−C7	1.379(5)
C7−C8	1.337(5)	C7−C15	1.490(5)	C8−C9	1.490(5)
C8−C14	1.480(6)	C9−C10	1.344(6)	C9−C21	1.524(5)
C10−C11	1.450(8)	C11−C12	1.33(1)	C12−C13	1.42(1)
C13−C14	1.329(7)				

Bond Angles			
Si2−Si1−Si3	112.81(6)	Si2−Si1−O5	103.6(1)
Si2−Si1−O6	106.4(1)	Si3−Si1−O5	113.3(1)
Si3−Si1−O6	110.8(1)	O5−Si1−O6	109.5(1)
Si1−O5−C7	130.2(2)	Si1−O6−Si4	159.1(2)
O5−C7−C8	120.4(3)	O5−C7−C15	115.8(3)
C8−C7−C15	123.5(4)	C7−C8−C9	125.3(4)
C7−C8−C14	122.2(4)	C9−C8−C14	112.5(3)
C8−C9−C10	117.7(4)	C8−C9−C21	119.2(3)
C10−C9−C21	122.3(4)	C9−C10−C11	126.4(5)
C10−C11−C12	125.4(6)	C11−C12−C13	127.6(6)
C12−C13−C14	124.9(6)	C8−C14−C13	121.7(5)
C7−C15−C16	122.5(3)		

Thermolysis of 1 with Acetone. A mixture of 300 mg (1.0 mmol) of **1** and 80 mg (1.4 mmol) of acetone in 1.0 mL of benzene was heated at 140 °C in a sealed tube for 24 h. The mixture was analyzed by GLC as being **7** (8% yield) and 82% of the starting compound **1**. Product **7** was isolated by MPLC. All spectral data obtained for **7** were identical with those reported in the literature.[16]

Thermolysis of 2 with Acetone. Heating a mixture of 361 mg (1.1 mmol) of **2** and 205 mg (3.5 mmol) of acetone in 1.0 mL of benzene at 140 °C in a sealed tube for 24 h gave **9a**, **11a**, and **12a**. The yields of products **9a**, **11a**, and **12a** were determined to be 11, 23, and 11%, respectively, by integration in ^{1}H NMR spectrum of the reaction mixture, and 46% of the starting compound was recovered unchanged. Products **9a**, **11a**, and **12a** were isolated by MPLC. For **9a**. ^{1}H NMR (C$_6$D$_6$): δ 0.23 (s, 9H, Me$_3$Si), 0.28 (s, 18H, two Me$_3$Si), 1.18 (s, 9H, Me$_3$C), 1.86 (s, 3H, Me), 2.08 (s, 3H, Me). ^{13}C NMR (C$_6$D$_6$): δ -1.5 (two Me$_3$Si), 2.3 (Me$_3$Si), 15.1 (Me), 22.8 (Me), 31.0 (*Me*$_3$C), 33.3 (*C*Me$_3$), 121.4, 143.6 (olefinic carbons). ^{29}Si NMR: (C$_6$D$_6$) δ -22.5 (two SiMe$_3$), -5.4 (*Si*(SiMe$_3$)$_2$), 7.4 (OSiMe$_3$). IR: 2954, 2896, 1254, 1058, 993, 839 cm^{-1}. MS: *m/z* 390 (M$^+$). Anal. Calcd for C$_{17}$H$_{42}$O$_2$Si$_4$: C, 52.24; H,10.83. Found: C, 52.20; H, 10.80. For **11a**. ^{1}H NMR (C$_6$D$_6$): δ 0.21 (s, 9H, Me$_3$Si), 0.25 (s, 9H, Me$_3$Si), 0.26 (s, 9H, Me$_3$Si), 0.39 (dd, 1H, H$_a$−CH$_b$, J = 4 Hz, 9 Hz), 0.54 (dd, 1H, HC, J = 6 Hz, 9 Hz), 0.77 (dd, 1H, H$_b$−CH$_a$, J = 4 Hz, 6 Hz), 1.08 (s, 3H, Me), 1.44 (s, 3H, Me), 1.46 (s, 6H, two Me). ^{13}C NMR (CDCl$_3$): δ -1.5 (Me$_3$Si), -1.4 (Me$_3$Si), 2.3 (Me$_3$Si), 15.0 (CH$_2$), 16.2 (*C*Me$_2$), 19.5 (Me), 29.1 (Me), 30.7 (Me), 32.7 (Me), 36.6 (CH), 73.6 (O*C*Me$_2$). ^{29}Si NMR (CDCl$_3$): δ -23.7 (two SiMe$_3$), -12.1 (*Si*(SiMe$_3$)$_2$), 5.8 (OSiMe$_3$). IR 2956, 2895, 1254, 1058, 1036, 1020, 840 cm^{-1}. MS: *m/z* 390 (M$^+$). Anal. Calcd for C$_{17}$H$_{42}$O$_2$Si$_4$: C, 52.24; H, 10.83. Found: C, 52.12; H, 10.68. For **12a**. ^{1}H NMR (C$_6$D$_6$): δ 0.23 (s, 9H, Me$_3$Si), 0.27 (s, 18H, two Me$_3$Si), 0.37 (dd, 1H, H$_a$−CH$_b$, J = 5 Hz, 8 Hz), 0.96 (s, 9H, Me$_3$C), 1.00 (dd, 1H, H$_b$-CH$_a$, J = 8 Hz, 11 Hz), 1.17 (dd, 1H, HC, J = 8 Hz, 11 Hz), 1.60 (s, 3H, Me−CO). ^{13}C NMR (C$_6$D$_6$): δ -1.5 (Me$_3$Si), -1.4 (Me$_3$Si), 2.3 (Me$_3$Si), 17.6 (CH$_2$), 22.5 (*Me*-CO), 29.9 (*Me*$_3$C), 30.1 (*C*Me$_3$), 37.5 (CH), 58.6 (O*C*Me). ^{29}Si NMR (C$_6$D$_6$): δ -23.3 (SiMe$_3$), -23.2 (SiMe$_3$), -7.2 (*Si*(SiMe$_3$)$_2$), 7.1 (OSiMe$_3$). IR 2956, 2897, 1362, 1254, 1224, 1187, 1057, 1045, 840 cm^{-1}. MS: *m/z* 375 (M$^+$−Me). Anal. Calcd for C$_{17}$H$_{42}$O$_2$Si$_4$: C, 52.24; H, 10.83. Found: C, 52.14; H, 10.60.

Thermolysis of 2 with Acetone-*d*$_6$. Heating a mixture of 334 mg (1.0 mmol) of **2** and 225 mg (3.5 mmol) of acetone-*d*$_6$ in 1.0 mL of benzene at 140 °C gave **9b**, **11b**, and **12b**. The yields of products **9b**, **11b**, and **12b** were determined to be 11, 27, and 4%, respectively, by integration in ^{1}H NMR spectrum of the reaction mixture, and 48% of the starting compound was recovered unchanged. Products **9b**, **11b**, and **12b** were isolated by MPLC. For **9b**. ^{1}H NMR (C$_6$D$_6$): δ 0.23 (s, 9H, Me$_3$Si), 0.28 (s, 18H, two Me$_3$Si), 1.18 (s, 9H, Me$_3$C). ^{13}C NMR (C$_6$D$_6$): δ -1.4 (two Me$_3$Si), 2.3 (Me$_3$Si), 14.2 (sep, CD$_3$, J = 19 Hz), 22.0 (sep, CD$_3$, J = 19 Hz), 31.0 (*Me*$_3$C), 33.3 (*C*Me$_3$), 121.3, 143.5 (olefinic carbons). ^{29}Si NMR (C$_6$D$_6$): δ -22.5 (two SiMe$_3$), -5.5 (*Si*(SiMe$_3$)$_2$), 7.5 (OSiMe$_3$). IR: 2955, 2896, 1254, 1085, 1056, 842 cm^{-1}. MS: *m/z* 396 (M$^+$). For **11b**. ^{1}H NMR (C$_6$D$_6$): δ 0.21 (s, 9H, Me$_3$Si), 0.245 (s, 9H, Me$_3$Si), 0.254 (s, 9H, Me$_3$Si), 0.38 (dd, 1H, H$_a$−CH$_b$, J = 4 Hz, 9 Hz), 0.53 (dd, 1H, HC, J = 6 Hz, 9 Hz), 0.76 (dd, 1H, H$_b$−CH$_a$, J = 4 Hz, 6 Hz), 1.08 (s, 3H, Me), 1.44 (s, 3H, Me). ^{13}C NMR (C$_6$D$_6$): δ -1.16 (Me$_3$Si), -1.23 (Me$_3$Si), 2.4 (Me$_3$Si), 15.5 (CH$_2$), 16.5 (*C*Me$_2$), 19.9 (Me), 29.3 (Me), 30.0 (sep, CD$_3$, J = 20 Hz), 32.0 (sep, CD$_3$, J = 21 Hz), 36.8 (CH), 73.8 (O*C*(CD$_3$)$_2$). ^{29}Si NMR (C$_6$D$_6$): δ -23.5 (two SiMe$_3$), -11.5 (*Si*(SiMe$_3$)$_2$), 6.3 (OSiMe$_3$). IR: 2954, 2895, 1254, 1060, 841 cm^{-1}. MS: *m/z* 396 (M$^+$). For **12b**. ^{1}H NMR (C$_6$D$_6$): δ 0.24 (s, 9H, Me$_3$Si), 0.28 (s, 18H, two Me$_3$Si), 0.97 (s, 9H, Me$_3$C). ^{13}C NMR (C$_6$D$_6$): δ -1.5 (Me$_3$Si), -1.4 (Me$_3$Si), 2.3 (Me$_3$Si), 16.7 (quin, CD$_2$, J = 24 Hz), 21.6 (sep, *CD*$_3$-CO, J = 19 Hz), 29.9 (*Me*$_3$C), 31.0 (*C*Me$_3$), 36.8 (t, CD, J = 23 Hz), 58.3 (O*C*(CD$_3$)). ^{29}Si NMR (C$_6$D$_6$): δ -23.4 (SiMe$_3$), -23.2 (SiMe$_3$), -7.2 (*Si*(SiMe$_3$)$_2$), 7.1 (OSiMe$_3$). IR: 2955, 2896, 1364, 1254, 1211, 1105, 1051, 843 cm^{-1}. MS: *m/z* 396 (M$^+$).

Thermolysis of 3 with Acetone. A mixture of 410 mg (1.0 mmol) of **3** and 101 mg (1.7 mmol) of acetone in 1.0 mL of benzene was heated at 140 °C for 24 h. The mixture was analyzed by GLC as being **13a** (15% yield) and **14a** (77% yield). Products **13a** and **14a** were isolated by MPLC. For **13a**. ^{1}H NMR (C$_6$D$_6$): δ 0.24 (s, 9H, Me$_3$Si), 0.28 (s, 18H, two Me$_3$Si), 1.70−1.92 (m, 15H, Ad), 1.85 (s, 3H, Me), 2.13 (s, 3H, Me). ^{13}C NMR (C$_6$D$_6$): -1.3 (two Me$_3$Si), 2.3 (Me$_3$Si), 13.8 (Me), 23.3 (Me), 29.6, 35.8, 37.3, 42.0 (Ad), 121.9, 143.9 (olefinic carbons). ^{29}Si NMR (CDCl$_3$): δ -22.7 (two SiMe$_3$), -5.1 (*Si*(SiMe$_3$)$_2$), 7.0 (OSiMe$_3$). IR 2949, 2904, 2850, 1636, 1253, 1163, 1063, 1048, 842 cm^{-1}. MS: *m/z* 468 (M$^+$). Anal. Calcd for C$_{23}$H$_{48}$O$_2$Si$_4$: C, 58.91; H, 10.32. Found: C, 58.91; H, 10.15. For **14a**. ^{1}H NMR (C$_6$D$_6$): δ 0.25 (s, 9H, Me$_3$Si), 0.29 (s, 18H, two Me$_3$Si), 0.40 (dd, 1H, H$_a$−CH$_b$, J = 3 Hz, 4 Hz), 0.98−0.99 (m, 2H, H$_b$−CH$_a$ and HC), 1.50−1.92 (m, 15H, Ad), 1.62 (s, 3H, Me). ^{13}C NMR (C$_6$D$_6$): δ -1.5 (Me$_3$Si), -1.3 (Me$_3$Si), 2.3 (Me$_3$Si), 16.1 (CH$_2$), 23.4 (Me), 29.1, 32.1, 37.3, 42.6 (Ad), 38.4 (CH), 58.3 (O*C*Me). ^{29}Si NMR (C$_6$D$_6$): δ -23.4 (SiMe$_3$), -23.2 (SiMe$_3$), -7.3 (*Si*(SiMe$_3$)$_2$), 7.1 (OSiMe$_3$). IR 2902, 2849, 1253, 1206, 1058, 838 cm^{-1}. MS: *m/z* 453 (M$^+$ − Me). Anal. Calcd for C$_{23}$H$_{48}$O$_2$Si$_4$: C, 58.91; H, 10.32. Found: C, 58.77; H, 10.20.

Thermolysis of 3 with Acetone-*d*$_6$. A mixture of 410 mg (1.0 mmol) of **3** and 243 mg (3.8 mmol) of acetone-*d*$_6$ in 1.0 mL of benzene was heated at 140 °C for 24 h. The mixture was analyzed by GLC as being **13b** (31% yield) and **14b** (62% yield). Products **13b** and **14b** were isolated by MPLC. For **13b**. ^{1}H NMR (C$_6$D$_6$): δ 0.24 (s, 9H, Me$_3$Si), 0.29 (s, 18H, two Me$_3$Si), 1.70−1.97 (m, 15H, Ad). ^{13}C NMR (C$_6$D$_6$): δ -1.4 (two Me$_3$Si), 2.3 (Me$_3$Si), 13.0 (sep, CD$_3$, J = 20 Hz), 22.5 (sep, CD$_3$, J = 20 Hz), 29.5, 35.7, 37.3, 41.9 (Ad), 121.8, 143.9 (olefinic carbons). ^{29}Si NMR (C$_6$D$_6$): δ -22.5 (two SiMe$_3$), -5.5 (*Si*(SiMe$_3$)$_2$), 7.4 (OSiMe$_3$). IR 2956, 2903, 2851, 1628, 1254, 1171, 1053, 1014, 839 cm^{-1}. MS: *m/z* 474 (M$^+$). For **14b**. ^{1}H NMR (C$_6$D$_6$): δ 0.25 (s, 9H, Me$_3$Si), 0.29 (s, 18H, two Me$_3$Si), 1.50−1.92 (m, 15H, Ad). ^{13}C NMR (C$_6$D$_6$): δ -1.5 (Me$_3$Si), -1.3 (Me$_3$Si), 2.3 (Me$_3$Si), 15.3 (quin, CD$_2$, J = 23 Hz), 22.5 (sep, CD$_3$, J = 19 Hz), 29.2, 32.0, 37.4, 42.6 (Ad), 37.6 (t, CD, J = 23 Hz), 58.0 (O*C*(CD$_3$)). ^{29}Si NMR (C$_6$D$_6$): δ -23.4 (SiMe$_3$), -23.2 (SiMe$_3$), -7.3 (*Si*(SiMe$_3$)$_2$), 7.1 (OSiMe$_3$). IR: 2956, 2904, 2848, 1253, 1167, 1050, 841 cm^{-1}. MS: *m/z* 459 (M$^+$ − Me).

Thermolysis of 4 with Acetone. Heating a mixture of 505 mg (1.4 mmol) of **4** and 210 mg (3.6 mmol) of acetone in 1.4 mL of benzene gave 253 mg (62% yield) of **16**. Product **16** was isolated by MPLC. For **16**. ^{1}H NMR (C$_6$D$_6$): δ 0.23 (s, 9H, Me$_3$Si), 0.26 (s, 9H, Me$_3$Si), 0.32 (s, 9H, Me$_3$Si), 1.16 (s, 3H, Me), 1.30 (s, 3H, Me), 3.20 (d, 1H, HC, J = 4 Hz), 5.61−5.66 (m, 2H, olefinic protons), 5.86−5.92 (m, 1H, olefinic proton), 6.73 (dd, 1H, olefinic proton, J = 1 Hz, 10 Hz). ^{13}C NMR δ (C$_6$D$_6$): -0.8 (Me$_3$Si), -0.2 (Me$_3$Si), 1.2 (Me$_3$Si), 24.7 (Me), 29.2 (Me), 50.3 (HC), 76.6 (CMe$_2$), 119.4, 121.9, 124.7, 128.1, 133.1, 157.3 (olefinic carbons). ^{29}Si NMR (C$_6$D$_6$): δ -18.7 (SiMe$_3$), -17.6 (SiMe$_3$), -9.4 (*Si*(SiMe$_3$)$_2$), 17.8 (OSiMe$_3$). IR: 2956, 2894, 1707, 1253, 1070, 842, 756, 692 cm^{-1}. Exact MS: (M$^+$) Calcd for C$_{19}$H$_{38}$O$_2$Si$_4$, 410.1947; found, 410.1967.

Thermolysis of 5 with Acetone. A mixture of 399 mg (1.0 mmol) of **5** and 201 mg (3.5 mmol) of acetone in 1.0 mL of benzene was heated at 140 °C for 24 h. The mixture was analyzed by GLC as being **17** (19% yield) and 78% of starting compound **5**. Product **17** was isolated by MPLC. For **17**. ^{1}H NMR (CDCl$_3$): δ -0.10 (s, 9H, Me$_3$Si), 1.35 (s, 3H, Me), 1.76 (s, 3H, Me), 2.20 (s, 6H, Me−Ar), 2.25 (s, 3H, Me), 6.80 (s, 2H, H−Ar). ^{13}C NMR (CDCl$_3$): δ 0.5 (Me$_3$Si), 16.8 (Me), 18.7 (Me), 19.9 (two Me), 21.1 (Me), 112.0, 127.9, 134.7, 136.7, 136.8, 141.0 (olefinic and Ar carbons). ^{29}Si NMR (CDCl$_3$): δ 14.4 (SiMe$_3$). IR: 2958, 2918, 2855, 1675, 1612, 1279, 1251, 1169, 1146, 1037, 891, 870, 842 cm^{-1}. MS: *m/z* 262 (M$^+$). Anal. Calcd for C$_{16}$H$_{26}$OSi: C, 73.22; H, 9.98. Found: C, 73.14; H, 9.84.

Thermolysis of 5 with Acetone in the Presence of Dimethoxydimethylsilane. A mixture of 392 mg (1.0 mmol) of **5**, 172 mg (3.0 mmol) of acetone, and 356 mg (3.0 mmol) of dimethoxydimethylsilane in 1.0 mL of benzene was heated at 140 °C for 24 h. The mixture was analyzed by GLC as being **17** (9% yield), **18** (3% yield), and 91% of starting compound **5**. For **18**. ^{1}H NMR (CDCl$_3$): δ 0.13 (s, 18H, two Me$_3$Si), 0.14 (s, 6H, Me$_2$Si), 3.50 (s, 3H, MeO), 3.55 (s, 3H, MeO). ^{13}C NMR (CDCl$_3$): δ -1.7 (two Me$_3$Si), -1.5 (Me$_2$Si), 49.8 (MeO), 52.3 (MeO). MS: *m/z* 295 (M$^+$ − Me), 273 (M$^+$ − Me$_3$Si). Exact MS: (M$^+$) Calcd for C$_{10}$H$_{30}$O$_3$Si$_4$, 310.1270; found, 310.1257.

Thermolysis of 1 with Benzophenone. A solution of 428 mg (1.5 mmol) of **1** and 292 mg (1.6 mmol) of benzophenone in 1.5 mL of benzene was heated at 140 °C for 24 h. The mixture was analyzed by GLC as being **7** (4% yield) and 86% of the starting compound **1**.

Thermolysis of 2 with Benzophenone. A solution of 339 mg (1.0 mmol) of **2** and 235 mg (1.3 mmol) of benzophenone in 1.0 mL of benzene was heated at 140 °C for 24 h. GLC analysis showed the presence of **19** (46% yield), **20** (24% yield), and the starting acylpolysilane **2** (29%). Products **19** and **20** were isolated by MPLC. For **19**. ^{1}H NMR ($CDCl_3$): δ −0.16 (s, 18H, two Me_3Si), −0.03 (s, 9H, Me_3Si), 0.84 (s, 9H, Me_3C), 7.25−7.50 (m, 10H, phenyl protons). ^{13}C NMR ($CDCl_3$): δ −1.8 (two Me_3Si), 2.1 (Me_3Si), 32.4 (*Me*$_3$C), 33.8 (*C*Me$_3$), 125.5, 127.6, 127.8, 128.0, 130.19, 130.24, 130.8, 140.4, 142.4, 146.2 (olefinic and phenyl carbons). ^{29}Si NMR ($CDCl_3$): δ −22.6 (two $SiMe_3$), −7.6 (*Si*($SiMe_3$)$_2$), 6.2 ($OSiMe_3$). IR: 2954, 2897, 1595, 1443, 1393, 1360, 1253, 1101, 1054, 844 cm^{-1}. MS: *m/z* 514 (M^+). Anal. Calcd for $C_{27}H_{46}O_2Si_4$: C, 62.97; H, 9.00. Found: C, 62.73; H, 9.11. For **20**. ^{1}H NMR ($CDCl_3$): δ −0.08 (s, 9H, Me_3Si), −0.05 (s, 18H, two Me_3Si), 1.24 (s, 9H, Me_3C), 5.70 (d, 1H, olefinic proton, 10 Hz), 6.09 (dd, 1H, olefinic proton, J = 6 Hz, 10 Hz), 6.30 (d, 1H, olefinic proton, J = 6 Hz), 6.42 (dd, 1H, olefinic proton, J = 6 Hz, 11 Hz), 6.54 (dd, 1H, olefinic proton, J = 6 Hz, 11 Hz), 7.22−7.43 (m, 5H, phenyl protons). ^{13}C NMR ($CDCl_3$): δ −1.6 (Me_3Si), −1.5 (Me_3Si), 2.2 (Me_3Si), 32.4 (*Me*$_3$C), 37.4 (*C*Me$_3$), 118.4, 122.0, 125.8, 126.4, 127.4, 127.5, 127.6, 129.4, 130.8, 139.3, 143.6, 146.7 (olefinic and phenyl carbons). ^{29}Si NMR ($CDCl_3$): δ −22.2 (two $SiMe_3$), −4.2 (*Si*($SiMe_3$)$_2$), 6.4 ($OSiMe_3$). IR: 2956, 2898, 1253, 1122, 1057, 840, 806 cm^{-1}. MS: *m/z* 514 (M^+). Anal. Calcd for $C_{27}H_{46}O_2Si_4$: C, 62.97; H, 9.00. Found: C, 62.72; H, 8.85.

Thermolysis of 3 with Benzophenone. A solution of 414 mg (1.0 mmol) of **3** and 230 mg (1.3 mmol) of benzophenone in 1.0 mL of benzene was heated at 140 °C for 24 h. GLC analysis showed the presence of **21** (46% yield), **22** (35% yield), and the starting acylpolysilane **3** (7%). Products **21** and **22** were isolated by MPLC. All spectral data for **21** were identical with those reported in the literature.[14] For **22**. mp: 115−116 °C (after recrystallization from ethanol). ^{1}H NMR ($CDCl_3$): δ −0.01 (s, 9H, Me_3Si), 0.05 (s, 18H, two Me_3Si), 1.77−2.06 (m, 15H, Ad), 5.69 (d, 1H, olefinic proton, J = 9 Hz), 6.10 (dd, 1H, olefinic proton, J = 6 Hz, 9 Hz), 6.24 (d, 1H, olefinic proton, J = 6 Hz), 6.42 (dd, 1H, olefinic proton, J = 6 Hz, 11 Hz), 6.55 (dd, 1H, olefinic proton, J = 6 Hz, 11 Hz), 7.27−7.54 (m, 5H, phenyl protons). ^{13}C NMR ($CDCl_3$): δ −1.7 (Me_3Si), −1.5 (Me_3Si), 2.2 (Me_3Si), 29.2, 36.9, 39.3, 44.0 (Ad), 117.8, 121.1, 125.7, 126.0, 127.3, 127.5 (2C), 129.3, 130.9, 139.3, 143.6, 147.3 (olefinic and phenyl carbons). ^{29}Si NMR ($CDCl_3$): δ −22.4 ($SiMe_3$), −22.2 ($SiMe_3$), −4.6 (*Si*($SiMe_3$)$_2$), 6.3 ($OSiMe_3$). IR: 2902, 2848, 1636, 1490, 1443, 1252, 1055, 838 cm^{-1}. MS: *m/z* 592 (M^+). Anal. Calcd for $C_{33}H_{52}O_2Si_4$: C, 66.83; H, 8.84. Found: C, 66.79; H, 8.84.

Thermal Isomerization of 24 (R = Ad). In a NMR tube was placed 110 mg (0.27 mmol) of **3** in 0.3 mL of deuteriobenzene. Dry argon was passed through to remove air from inside of the tube. Then the tube was capped with a rubber septum. The tube was irradiated with a high-pressure mercury lamp bearing a Vycor filter at 0 °C for 24 h. At this point, all of **3** was transformed into **24** (R = Ad). To this was added 60 mg (0.33 mmol) of benzophenone under argon atmosphere. The tube was allowed to stand at room temperature, and the reaction was monitored by ^{1}H NMR spectrometry. After 1 h reaction, the formation of a mixture consisting of **24** (R = Ad) and **23** (R = Ad) in a ratio of 6/1 was observed. The ratio of **24** and **23** changed to 2/1 after 2 days and 1/2 after 8 days, respectively. Chemical shifts for **24** (R = Ad) and **23** (R = Ad) were identical with those of the authentic samples. A similar mixture consisting of **24** (R = Ad) and **23** (R = Ad) in a ratio of 5.8/1 was treated at 40 °C. The ratio of **24**/**23** was determined to be 1/2.7 after 2 days. After standing 4 days, the formation of **21** and **22** was observed, and the ratio of **24**/**23**/**21**/**22** was measured to be 1/3/0.3/0.3. Chemical shifts of all products were identical with those of the authentic samples. When the solution of **24** (R = Ad) involving a trace of **23** (R = Ad) was heated at 140 °C for 24 h, a mixture consisting of compounds **21** and **22** in a ratio of 1.25/1 was obtained. The ratio was determined by ^{1}H NMR spectrometry, and chemical shifts for **21** were identical with those of the authentic samples.

Thermolysis of 4 with Benzophenone. A solution of 350 mg (1.0 mmol) of **4** and 225 mg (1.2 mmol) of benzophenone in 1.0 mL of benzene was heated at 140 °C for 24 h. GLC analysis showed the presence of **26** (52% yield) and **27** (20% yield). Products **26** and **27** were isolated by MPLC. All spectral data for **26** were identical with those reported in the literature.[12,14] For **27**. ^{1}H NMR ($CDCl_3$): δ −0.16 (s, 9H, Me_3Si), 7.01−7.38 (m, 15H, phenyl protons). ^{13}C NMR ($CDCl_3$): δ −6.1 (Me_3Si), 124.9, 125.9, 127.1, 127.2, 127.4, 127.9, 129.2, 129.3, 129.4, 143.2, 143.9, 144.3 (2C), 153.6 (olefinic and phenyl carbons). ^{29}Si NMR ($CDCl_3$): δ −6.1 ($SiMe_3$). IR 3076, 3057, 3024, 2951, 2892, 1596, 1491, 1442, 1246, 861, 838, 757, 734, 698 cm^{-1}. MS: *m/z* 328 (M^+). Anal. Calcd for $C_{23}H_{24}Si$: C, 84.09; H, 7.36. Found: C, 83.86; H, 7.30.

Thermolysis of 5 with Benzophenone. A solution of 407 mg (1.0 mmol) of **4** and 235 mg (1.3 mmol) of benzophenone in 1.0 mL of benzene was heated at 140 °C for 24 h. GLC analysis showed the presence of **28** (46% yield) and starting acylpolysilane **5** (54% yield). Products **28** was isolated by MPLC. All spectral data for **28** were identical with those reported in the literature.[14]

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Supporting Information Available: Figure of an ORTEP view with full aromatic numbering scheme and tables of crystal data, experimental conditions and summary of structure refinement, full bond lengths and angles, atomic coordinates and equivalent isotropic thermal parameters, and anisotropic thermal parameters for **22** and NMR spectra (25 pages). Ordering information is given on any current masthead page.

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