of ref 3) with the additional assumptions that the azimuthal angles between the two lone pairs are 60 and 180° for the gauche and trans forms, respectively, and that all other geometrical data do not vary as a function of the azimuthal angle. The values of $Q_{\mathrm{gauche}}/Q_{\mathrm{trans}}$ obtained are 1.14 (20 °C), 1.17 (65 °C), 1.18 (94 °C), 1.18 (132 °C), 1.20 (175 °C), and 1.22 (252 °C). From a plot of ln $(I_4Q_{\mathrm{gauche}}/I_3Q_{\mathrm{trans}})$ vs. $1/T$ (Figure 6) we estimate $\Delta E = -0.5 \pm 0.1$ kcal/mol and $\sigma_{\mathrm{n}_{+},\mathrm{trans}}/\sigma_{\mathrm{n}_{+},\mathrm{gauche}} = 2.5 \pm 0.4$. Accordingly, the trans form is more stable than the gauche form by 0.5 kcal/mol.

However, the ratio of cross sections found in this way is unrealistically high showing that the linear extrapolation to infinitely high temperature is not quite appropriate. The correct value of $\sigma_{\mathrm{n}_{+},\mathrm{trans}}/\sigma_{\mathrm{n}_{+},\mathrm{gauche}}$ can be easily obtained to be 1.2 ± 0.2 from a plot of I_3 vs. I_4 (Figure 7) according to

$$I_3 = \mathrm{const} - \frac{\mathrm{n}_{+,\mathrm{gauche}}}{\mathrm{n}_{+,\mathrm{trans}}} \frac{1 + \dfrac{\beta_{\mathrm{n}_{+},\mathrm{gauche}}}{4}}{1 + \dfrac{\beta_{\mathrm{n}_{+},\mathrm{trans}}}{4}} I_4 \tag{6}$$

Equation 6 follows from the fact that the total particle density equals the sum of $\mathrm{n}_{\mathrm{gauche}}$ and $\mathrm{n}_{\mathrm{trans}}$ for the various temperatures used. The particle density is kept constant during the measurements as well as the incident light intensity.

After $\Delta E = -0.5$ kcal/mol, $g_{\mathrm{trans}}/g_{\mathrm{gauche}} = 1/2$, and the respective values of $Q_{\mathrm{trans}}/Q_{\mathrm{gauche}}$ were inserted into eq 3 the populations mentioned in the Introduction were obtained.

Conclusion

The present investigation demonstrates that advanced photoelectron spectral techniques (VTPES, ADPES, and GSPES) are of considerable help in solving the rather complicated problem of rotational isomerism in tetramethyldiphosphine. In this way, it is established that the prevailing trans conformer (at room temperature) is more stable than the gauche isomer by 0.5 kcal/mol. Accordingly, at 170 °C there is 50% of the trans form as well as the gauche form. This result disagrees with the result of electron diffraction showing again[7d] that this technique might lead to considerable misinterpretation. From a photoelectron spectral standpoint it is gratifying to note that the lone pair band pattern of a mixture of gauche and trans isomers turns out to be just the same as in similar hydrazine cases.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were carried out using the TR 440 computer at the Rechenzentrum der Universität Marburg.

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Relatively Stable Silaethylenes. Photolysis of Acylpolysilanes

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Abstract: The syntheses of a variety of acyldi- and acylpolysilanes are described. All of these when photolyzed at about λ 360 nm give rise to silaethylenes, as evidenced by trapping experiments with methanol, a diene or an alkyne. In the absence of trapping agents the silaethylenes undergo head to head dimerization to 1,2-disilacyclobutanes. Of the various silaethylenes, the one produced from pivaloyltris(trimethylsilyl)silane is found to have a moderate lifetime at room temperature, and to be in a mobile equilibrium with its dimer. The silaethylene and its dimer have been characterized by UV, ^{1}H NMR, and ^{13}C NMR spectra. Thermolysis of the pivaloylsilane in the presence of alcohols, or phenylpropyne, also gave the products resulting from trapping of the silaethylene.

The pioneering work of Gusel'nikov and Flowers unambiguously demonstrated for the first time the intermediacy of reactive species containing silicon-carbon double bonds (silaethylenes) during the thermolysis of silacyclobutanes.[1] During the succeeding years a multitude of systems have been described which under thermolysis or photolysis conditions appear to give rise to short-lived silaethylenes, as demonstrated by various trapping experiments.[2]

Our entry into this field came as a logical consequence of our studies on acylsilanes[3,4] and β-ketosilanes,[5] both of which we had shown readily underwent either photochemical or thermal rearrangements. Acylsilanes, using radiation in the

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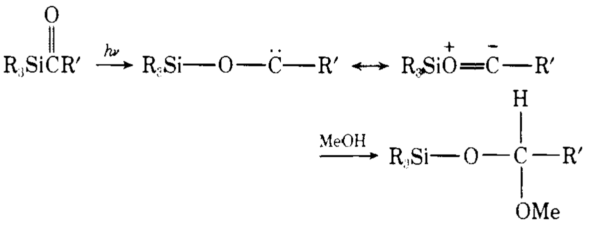
Table I. Photolysis of Acyldisilanes and Related Reactions

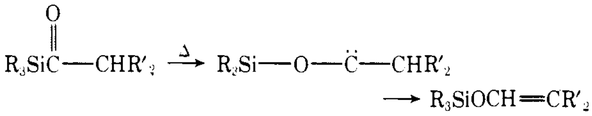
starting material (mmol)	reagents and conditions	products, compd no. (% yield), mp, °C	NMR, δ (CCl_4), ppm; IR (CCl_4), μ; *m/e*
$Ph_3SiSiPh_2COPh$, **4** (0.92)	*hν*, 10 °C, 3 h, MeOH-THF (1.3% v/v), 30.4 mL[a]	$Ph_2Si(OMe)CHPhOSiPh_3$, **13** (67), 112-113	6.80-7.60 (30 H, m, Ph), 5.06 (1 H, s, PhC*H*), 3.40 (3 H, s, OMe), *m/e* 501 $[M - Ph]^+$
$Ph_3SiSiPh_2COPh$, **4** (0.92)	*hν*, 10 °C, 30 min, MeOH-THF 1:1 (v/v), 20 mL[a]	$Ph_3SiSiPh_2OCHPhOMe$, **12** (40)[b,c]	7.00-7.70 (30 H, m, Ph), 5.67 (1 H, s, PhC*H*), 2.80 (3 H, s, MeO)
13 (1.3)	$LiAlH_4$, Et_2O, 3 h	$Ph_2SiHCHPhOSiPh_3$, **1** (73)[d]	6.80-7.60 (30 H, m, Ph), 5.17 (1 H, d, *J* = 2 Hz, PhC*H*) 4.80 (1 H, d, *J* = 2 Hz, SiH); IR, 4.69 (SiH); *m/e* 548 $[M]^+$
12 (0.35)	$LiAlH_4$, Et_2O, 24 h	$Ph_3SiSiPh_2H$, **14a** (65) + $PhCH_2OH$	
$Ph_3SiSiMe_2COPh$, **5** (0.95)	*hν*, 10 °C, 11 h, MeOH-THF (0.5%), 40.2 mL[a]	$Me_2Si(OMe)CHPhOSiPh_3$, **17** (57)[b,e]	7.00-7.80 (20 H, m, Ph), 4.70 (1 H, s, PhC*H*), 3.20 (3 H, s, OMe), 0.05, −0.03, each (3 H, s, MeSi)
$Ph_3SiSiMe_2COPh$, **5** (1.2)	*hν*, 10 °C, 1 h, MeOH[a] (20 mL)	$Ph_3SiSiMe_2OCHPhOMe$, **16**[c]	7.00-7.70 (20 H, m, Ph), 5.60 (1 H, s, PhC*H*), 2.97 (3 H, s, MeO), 0.40 (6, H, s, Me_2Si)
16	$LiAlH_4$, Et_2O, 24 h	$Ph_3SiSiMe_2H$, **14b** (61) + $PhCH_2OH$	
$Ph_3SiSiMe_2COMe$, **6** (1.4)	*hν*, 10 °C, 1.5 H, MeOH, 20 mL[a]	$Ph_3SiSiMe_2OCHMeOMe$, **18** (80)[c]	7.00-7.80 (15 H, m, Ph), 4.70 (1 H, q, *J* = 5 Hz, *H*CMe), 2.97 (3 H, s, MeO), 1.08 (3 H, d, *J* = 5 Hz, MeC), 0.38 (6 H, s, Me_2Si)
18	$LiAlH_4$, Et_2O, 24 h	$Ph_3SiSiMe_2H$, **14b** (61)	

[a] Photolysis solution contained 3-5 drops of pyridine. [b] Isolated by chromatography on silica gel. [c] Too unstable to purify for analysis. [d] n_D^{23} 1.6220. [e] n_D^{23} 1.5785.

region of [illegible] nm, isomerize to species described as siloxycarbenes which can be trapped by various protic reagents, such as methanol[3] (eq 1). Acylsilanes possessing α hydrogen, when heated, undergo self-insertion in high yields into the α-CH bond yielding siloxyalkenes[4] (eq 2).

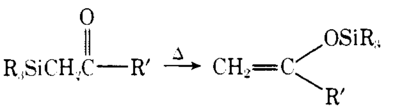


$$R_3Si\overset{\overset{O}{\|}}{C}R' \xrightarrow{h\nu} R_3Si—O—\ddot{C}—R' \longleftrightarrow R_3Si\overset{+}{O}=\overset{-}{C}—R' \xrightarrow{MeOH} R_3Si—O—\underset{\underset{OMe}{|}}{\overset{\overset{H}{|}}{C}}—R' \quad (1)$$



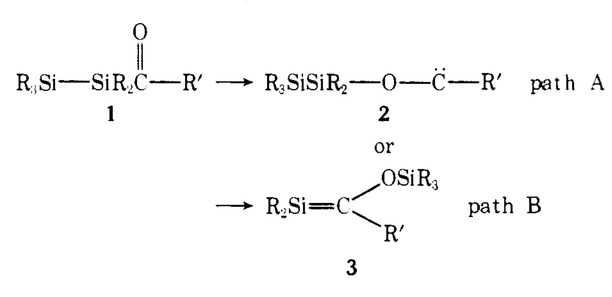
$$R_3Si\overset{\overset{O}{\|}}{C}—CHR'_2 \xrightarrow{\Delta} R_3Si—O—\ddot{C}—CHR'_2 \longrightarrow R_3SiOCH=CR'_2 \quad (2)$$

β-Ketosilanes also thermally isomerize at relatively low temperatures (80-180 °C) to yield isomeric siloxyalkenes[5] (eq 3). The question then arises as to the behavior to be expected



$$R_3SiCH_2\overset{\overset{O}{\|}}{C}—R' \xrightarrow{\Delta} CH_2=C\begin{smallmatrix}OSiR_3\\ R'\end{smallmatrix} \quad (3)$$

of an acyldisilane **1** which might conceivably give rise to a disiloxycarbene, **2**, paralleling acylsilane behavior (path A), or to a silaethylene **3**, if β-ketosilane behavior was followed (path B). Such a silaethylene could have markedly different properties from those previously described, because of the many and large substituents on the double bond. In order to learn more about this situation a variety of acyldi- and acylpolysilanes were synthesized, and their photolyses were investigated.



$$\underset{\mathbf{1}}{R_3Si—SiR_2\overset{\overset{O}{\|}}{C}—R'} \longrightarrow \underset{\mathbf{2}}{R_3SiSiR_2—O—\ddot{C}—R'} \quad \text{path A}$$

or

$$\longrightarrow \underset{\mathbf{3}}{R_2Si=C\begin{smallmatrix}OSiR_3\\ R'\end{smallmatrix}} \quad \text{path B}$$

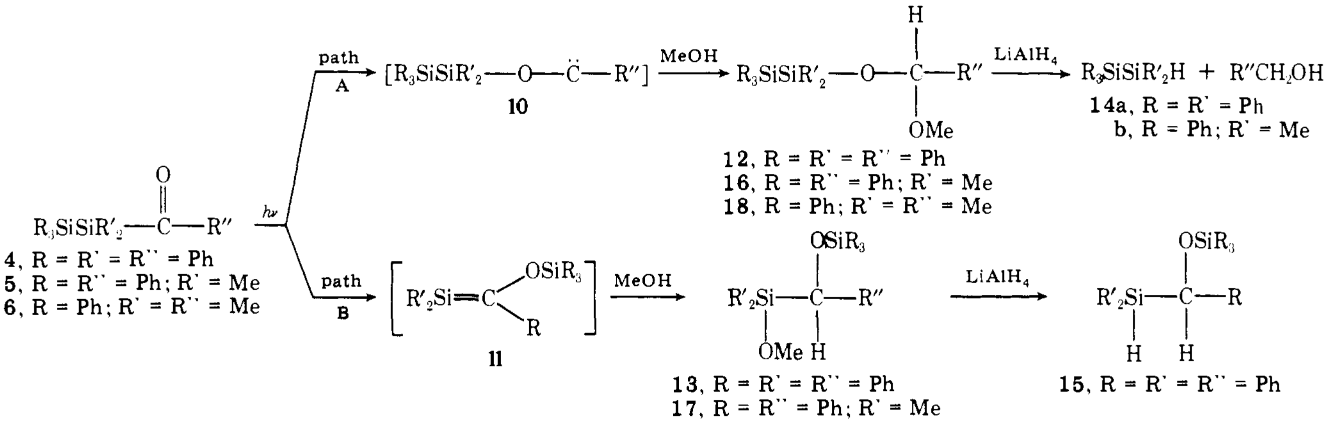
Photolysis of Acylpolysilanes. As a probe of the extent to which the reactions of the acyldi- or acylpolysilanes followed pathways A and/or B during their photolysis or thermolysis, methanol was used as a trapping agent, since it had been shown to be an efficient trapping agent for both siloxycarbenes[3] and silaethylenes.[6] Preliminary investigation showed that thermolysis reactions of the acyldisilanes gave several products but somewhat surprisingly, since β-ketosilanes do not normally undergo facile photochemical reactions,[7,8] the photochemical reactions of the compounds, using a 100-W mercury flood lamp with $\lambda_{max} \simeq 360$ nm, were rapid and clean. These reactions, and the subsequent structure-proving steps, are summarized in Scheme I, and the experimental data are summarized in Tables I and III.

Thus irradiation of benzoylpentaphenyldisilane **4** in 1:1 methanol-THF gave both the siloxycarbene-methanol insertion product **12** and the silaethylene-methanol addition product **13** in yields of 47 and 41%, respectively.

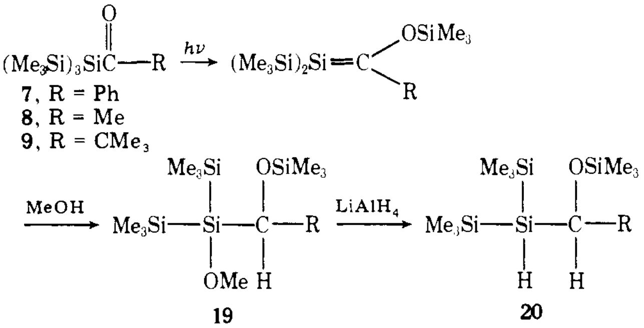
The identity of **12** was established through its reduction by lithium aluminum hydride to benzyl alcohol and pentaphenyldisilane **14a**, and by the one- and three-proton singlets found at δ 5.67 and 2.80 ppm in the NMR spectrum (the triphenylsilyl analogue had related signals at δ 5.85 and 3.01 ppm[3]). The isomer **13** by contrast had the benzylic proton at higher field (δ 5.06) and the methoxyl signal at lower field (δ 3.40 ppm), relative to the species **12**, a situation found also in model compounds. Partial reduction of **13** gave the silane **15**, which had two doublets at δ 5.17 and 4.80 ppm, *J* = 2 Hz, assigned to the benzylic and SiH protons.

The yield of **13** was increased to 90% by photolyzing the acyldisilane in a 0.3 M solution of methanol in THF, in which case **12** was obtained in only 3% yield. This result can be interpreted in terms of the known tendency of siloxycarbenes like **10** to revert to the parent acylsilane if not immediately trapped.[3] Thus when the concentration of methanol was de-

Scheme I



Scheme II



creased, trapping of **10** became less efficient and reversion back to acylsilane became more important. Evidently the silaethylene **11** does not rapidly revert to acyldisilane and hence the formation of **13** is less sensitive to the concentration of methanol.

Similar results were observed with other disilanes and are summarized in Table I. In the case of **5**, photolysis in methanol gave mainly the disiloxycarbene adduct **16** with a trace of **17**, the silaethylene adduct, but photolysis in 0.13 M methanol in THF gave **16** in only 9% yield and **17** in 57% yield.

Photolysis of the acetylsilane **6** in methanol gave 80% of **18**, the disiloxycarbene adduct, and no evidence of a silaethylene-methanol adduct. Photolysis in dilute methanol in THF gave a reduced yield of **18** and evidence of a complex mixture of other products. These probably arose at least in part from competing Norrish type I cleavage of the acylsilane, as observed previously in the photolysis of acetyltriphenylsilane in cyclohexane.[9]

In contrast to the behavior described above for acyldisilanes, the photolysis of the acyltris(trimethylsilyl)silanes **7**, **8**, and **9** in methanol, or in a dilute methanol solution in THF, gave rise to nearly quantitative yields of the silaethylene-methanol adducts with no evidence for the formation of products derived from siloxycarbenes (Scheme II and Table II).

For example, the benzoyl compound **7** gave rise, in 92% yield, to **19**, characterized by a one-proton singlet at δ 4.85 ppm and a three-proton singlet at δ 3.31 ppm and 9- and 18-proton singlets at δ 0.08 and 0.02 ppm, consistent with the proposed structure if the two trimethylsilyl groups on silicon accidentally have the same chemical shift. The mass spectrum did not contain a signal corresponding to the molecular ion at *m/e* 384, but did contain a signal corresponding to $[M - Me]^+$ at *m/e* 369. Such fragmentation is expected, and it has been reported that methoxy substituents on methyldisilanes promote Si-Me bond fragmentation.[10] Photolysis of **7** in MeOD gave a near-quantitative yield of a monodeuterio compound whose NMR spectrum lacked the benzylic absorption at δ 4.85 ppm, but which was otherwise identical.

Reduction of **19** gave the expected silane **20** (R = Ph) which contained one-proton doublets at δ 4.98 (CH) and 3.31 (SiH) ppm with a coupling constant of 3 Hz. In addition the spectrum contained three nine-proton singlets at δ 0.10, 0.07, and 0.00 ppm due to the three nonequivalent trimethylsilyl groups.

Similar results were obtained from the photolysis of the acetylsilane **8** and the pivaloylsilane **9**.

The yields of the photolysis products of all the acylsilanes under standard reaction conditions in methanol are summarized in Table III. With the disilanes it is clear that the product distributions and times required for photolysis depend on the solvent system. In neat methanol, where they are effectively trapped, siloxycarbene formation is the favored reaction process, whereas in dilute methanol not only are the yields of siloxycarbene-trapped products lower, but the required irradiation times are longer. The reversible equilibrium acylsilane + $h\nu \rightleftarrows$ siloxycarbene unquestionably plays a role here. By contrast, silaethylene formation is strongly favored with the acylpolysilanes, and siloxycarbene formation is completely suppressed regardless of whether the methanol reagent is neat or dilute. Presumably the greater number of β-silyl groups available for migration to the carbonyl oxygen contributes to the greater efficiency of silaethylene formation. In addition silyl groups attached to the silicon end of the silicon-carbon double bond may have an important stabilizing influence.

Photolysis of Acylpolysilanes in Aprotic Trapping Reagents. Since the tris(trimethylsilyl)acylsilanes had clearly revealed a strong propensity for isomerizing to silaethylenes, these compounds were used in further trapping experiments aimed at demonstrating the existence of silaethylenes (Scheme III). Thus **7**, when photolyzed in THF containing excess 2,3-dimethylbutadiene, gave the silacyclohexene **22** expected from trapping of silaethylene **21**, and **9** gave the silacyclobutene **24** expected from trapping of silaethylene **23** with phenylpropyne. The structure of **24**, which probably represents the less sterically hindered of the two possible regioisomers, was supported by the presence of intense signals in the mass spectrum at *m/e* 185 (base peak) and 263 (45% base peak) which are probably due to the ions $[Me_3C{-}C({=}CMe){-}OSiMe_3]^+$ and $[PhC{=}Si(SiMe_3)_2]^+$ arising from cleavage of **24**.

Having established that silaethylenes formed by photolysis of the acylpolysilanes could be efficiently trapped by alcohols or unsaturated compounds, it was of interest to observe the behavior of the silaethylenes in the absence of trapping reagents, where dimer formation could be anticipated. The reactions are summarized in Scheme IV.

Photolysis of **7** in ether gave rise to a solid assigned the dimeric structure **26**, which had the correct molecular weight. The mass spectrum did not contain the molecular ion at *m/e* 704, and only a few low-intensity signals were detected above the strong signal at *m/e* 352, the molecular weight of the

Table II. Photolysis of Acyltris(trimethylsilyl)silanes and Related Experiments

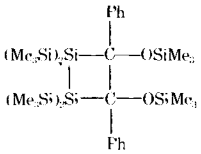
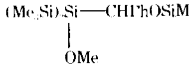
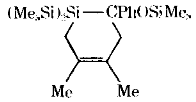
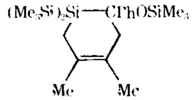
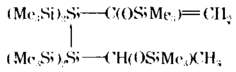
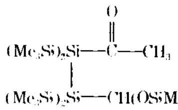
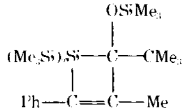
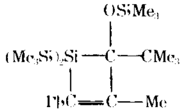
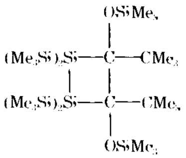
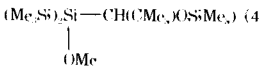
starting material	reagent	conditions	product, no. (% yield), mp, °C	n^{23}_{D}	NMR, δ (CCl_4) ppm; IR (CCl_4), μ; *m/e*
$(Me_3Si)_3SiCOPh$, **7**	MeOH	*hν*, 10 °C, 0.3 h[a]	$(Me_3Si)_2Si(OMe)CHPhOSiMe_3$, **19** (92)[b]	*c*	7.01-7.25 (5 H, m, Ph), 4.85 (1 H, s, PhC*H*), 3.31 (3 H, s, MeO), 0.08 (9 H, s, Me_3Si), 0.02 (18 H, s, Me_3Si); IR 3.53 (OMe) 9.30-9.60 (SiOC); *m/e* 369 [M − Me]$^+$
$(Me_3Si)_2Si(OMe)CHPhOSiMe_3$, **19**	$LiAlH_4$, Et_2O	20 °C, 6 h	$(Me_3Si)_2Si(H)CHPhOSiMe_3$, **20** (48)[b]	*d*	7.07-7.27 (5 H, m, Ph), 4.98 (1 H, d, *J* = 3 Hz, PhC*H*), 3.31 (1 H, d, *J* = 3 Hz, SiH), 0.10, 0.07, 0.00, each (9 H, s, $SiMe_3$); IR 4.84 (SiH); *m/e* 354 [M]$^+$, 339 [M − Me]$^+$
$(Me_3Si)_3SiCOMe$, **8**	MeOH	*hν*, 10 °C, 0.3 h[a]	$(Me_3Si)_2Si(OMe)CHMeOSiMe_3$ (90)[b]	*e*	4.03 (1 H, q, *J* = 7 Hz, MeC*H*), 3.44 (3 H, s, MeO), 1.33 (3 H, d, *J* = 2 Hz, MeC), 0.17 (18 H, s, Me_3Si), 0.07 (9 H, s, Me_3Si); IR 3.52 (OMe); *m/e* 307 [M − Me]$^+$
$(Me_3Si)_2Si(OMe)CHMeOSiMe_3$, **19**	$LiAlH_4$, Et_2O	20 °C, 6 h	$(Me_3Si)_2Si(H)CHMeOSiMe_3$ (51)[b]	*f*	4.05 (1 H, q of d, J_1 = 7.5, J_2 = 2 Hz, CHSi), 3.13 (1 H, d, *J* = 2 Hz, SiH), 1.34 (3 H, d, *J* = 7.5 Hz, MeC), 0.22 (18 H, s, Me_3Si), 0.08 (9 H, s, Me_3Si); IR 4.84 (SiH); *m/e* 277 [M − Me]$^+$
$(Me_3Si)_3SiCOCMe_3$, **9**	MeOH	*hν*, 10 °C, 0.3 h[a]	$(Me_3Si)_2Si(OMe)CH(CMe_3)OSiMe_3$ (92)[b]	*g*	3.67 (1 H, s, SiC*H*) 3.42 (3 H, s, OMe), 0.95 (9 H, s, Me_3C), 0.22 (18 H, s, Me_3Si), 0.13 (9 H, s, Me_3Si); *m/e* 349 [M − Me]$^+$
$(Me_3Si)_3SiCOPh$, **7**		*hν*, Et_2O, 10 °C, 2 h	 **26** (70)[b] 149–150		7.13-7.73 (10 H, m, Ph), 0.40, 0.07, −0.27 each (18 H, s, Me_3Si); *m/e* 352 [M/2]$^+$, 337 [(M/2) − Me]$^+$
26	MeOH-THF	65 °C, 24 h	 $(Me_3Si)_2Si(OMe)-CHPhOSiMe_3$ **19** (76)[b]		
26	THF	65 °C, 24 h	**26** (~100)		
26	2,3-dimethyl-1,3-butadiene-THF	65 °C, 24 h	 **22** (71)[b] 105–106		7.00-7.35 (5 H, m, Ph), 2.70 (2 H, m, CCH_2C), 1.73 (6 H, m, MeC=CMe), 1.40 (2 H, m, $SiCH_2C$), 0.10, −0.03, −0.20 each (9 H, s, Me_3Si); *m/e* 434 [M]$^+$
$(Me_3Si)_3SiCOPh$	2,3-dimethyl butadiene-THF	*hν*, 10 °C, 0.5 h	 **22** (30)[b]		

Table II (*Continued*)

starting material	reagent	conditions	product, no. (% yield), mp, °C	$n^{23}{}_D$	NMR, δ (CCl_4) ppm; IR (CCl_4), μ; *m/e*
$(Me_3Si)_3SiCOMe$, **8**	Et_2O	$h\nu$, 10 °C, 1.5 h	 $\begin{array}{l}(Me_3Si)_2Si{-}C(OSiMe_3){=}CH_2\\ \quad\vert\\ (Me_3Si)_2Si{-}CH(OSiMe_3)CH_3\end{array}$ **29** (74)^{b,c}		4.82 (1 H, d, *J* = 2 Hz, HC=C), 4.62 (1 H, d, *J* = 2 Hz, HC=C), 4.42 (q, *J* = 7 Hz, *H*CMe), 1.57 (3 H, d, *J* = 7 Hz, *Me*CH), 0.38 (27 H, s, Me_3Si) 0.40, 0.22, 0.09, each (9 H, s, Me_3Si); *m/e* 565 [M − Me]$^+$, 507 [M − $SiMe_3$]$^{+\,k}$
29 (0.64)	NH_4Cl (1.9), C_5H_5N, (1.9), H_2O (5.6)	MeOH (10 mL), acetone (20 mL), reflux 18 h	 $\begin{array}{l}\qquad O\\ \qquad\Vert\\ (Me_3Si)_2Si{-}C{-}CH_3\\ \quad\vert\\ (Me_3Si)_2Si{-}CH(OSiMe_3)CH_3\end{array}$ **30** (52)^b 107–109		4.37 (1 H, q, *J* = 7 Hz, MeC*H*), 2.27 (3 H, s, MeCO), 1.50 (3 H, d, *J* = 7 Hz, MeC*H*), 0.38, 0.15 each (9 H, s, $SiMe_3$), 0.37 (27 H, s, $SiMe_3$); IR 6.13 (C=O); *m/e* 493 [M − Me]$^+$, 435 [M − $SiMe_3$]$^{+k}$
$(Me_3Si)_3SiCOCMe_3$, **9** (1.5)	PhC≡CMe (20)	THF (25 mL), 10 °C, 1.5 h, $h\nu$	 **24** (50)^b 66–67		7.20 5 H, s, Ph), 1.83 (3 H, s, MeC=C), 0.88 (9 H, s, Me_3C), 0.28, 0.26, 0.23 each (9 H, s, $SiMe_3$); *m/e* 448 [M]$^+$, 263 [PhC=Si($SiMe_3$)$_2$]$^+$, 185 [MeC=C($OSiMe_3$)CMe_3]$^+$
$(Me_3Si)_3SiCOCMe_3$		Et_2O, 10 °C, 14 h, $h\nu$, then PhC≡CMe	 **24** (25)^b		
$(Me_3Si)_3SiCOCMe_3$		pentane, −80 °C, 24 h, $h\nu$	 **27** (46)^b 85–86		
$(Me_3Si)_3SiCOCMe_3$		Et_2O, 10 °C, 14 h, $h\nu$, then MeOH	 $\begin{array}{l}(Me_3Si)_2Si{-}CH(CMe_3)OSiMe_3)\\ \quad\vert\\ \quad OMe\end{array}$ (40)^b		

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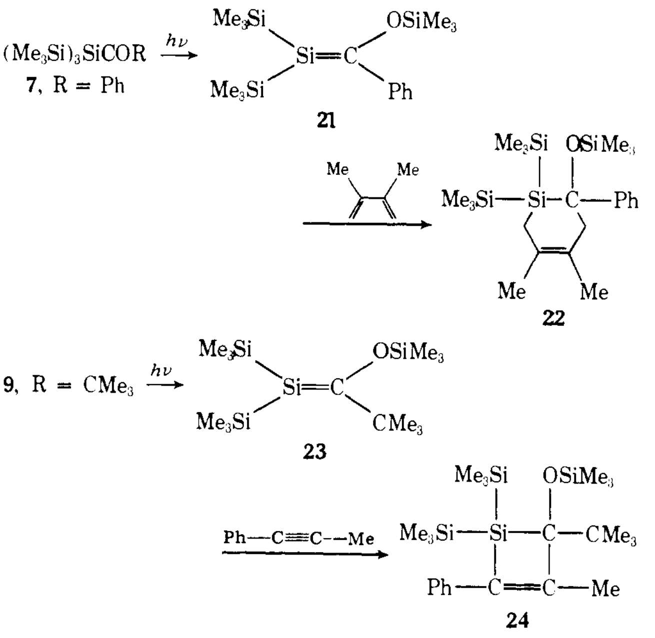
[a] System contained 0.25 acylpolysilane. [b] Isolated by column chromatography on silica gel, using pentane usually. [c] $n^{23}{}_D$ 1.5032. [d] $n_D{}^{23}$ 1.5620. [e] $n_D{}^{23}$ 1.4642. [f] $n_D{}^{23}$ 1.4637. [g] $n_D{}^{23}$ 1.4818. [h] Recrystallized from pentane acetone. [i] Dimer **26** (27%) also present. [j] $n_D{}^{23}$ 1.5284. [k] NMR in benzene. [l] See Experimental Section.

Table III. Product Yields and Irradiation Times for the Photolyses of Acylpolysilanes in Methanol Solutions[a]

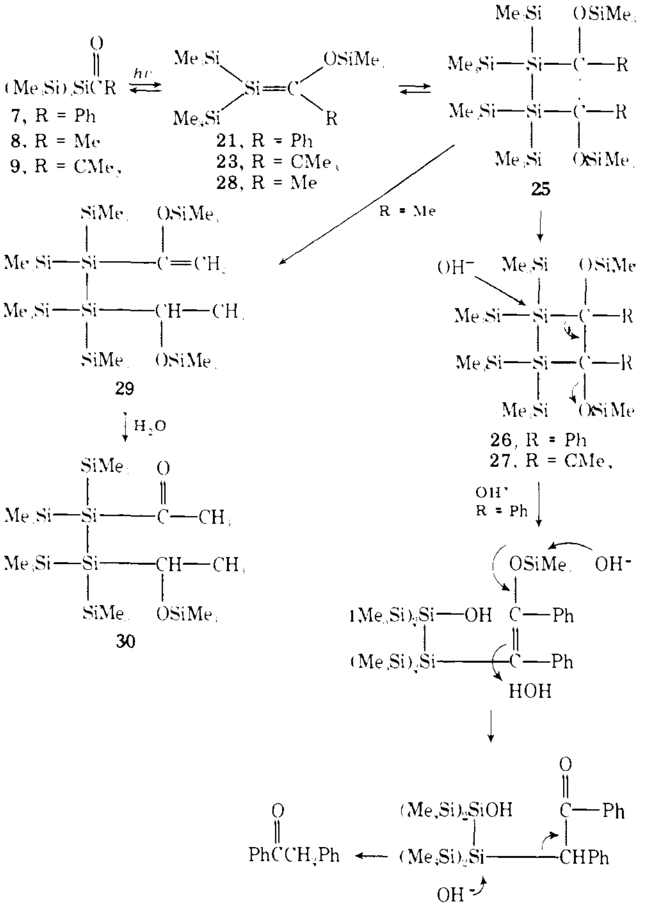
acylpolysilane	in methanol: % yields: siloxycarbene-MeOH insertion product	in methanol: % yields: silaethylene-MeOH addition product	in methanol: irradiation time, min	in 0.3 *m* methanol in tetrahydrofuran: % yields: siloxycarbene-MeOH insertion product	in 0.3 *m* methanol in tetrahydrofuran: % yields: silaethylene-MeOH addition product	in 0.3 *m* methanol in tetrahydrofuran: irradiation time, min
$PhCOSiPh_2SiPh_3$ **4**	50	38	32[b]	trace	74	59
$PhCOSiMe_2SiPh_3$ **5**	74	trace	64[b]	44	30	240[c]
$MeCOSiMe_2SiPh_3$ **6**	80	0	95[b]	35	0	390
$PhCOSi(SiMe_3)_3$ **7**	0	>95	16	0	>95	17
$MeCOSi(SiMe_3)_3$ **8**	0	>95	17	0	>95	17
$Me_3CCOSi(SiMe_3)_3$ **9**	0	>95	16	0	>95	18

[a] Photolysis of 4.6 × 10^{-4} mol of acylsilane in 20 mL of methanol or in 20 mL of 0.3 M methanol in THF. Yields were determined from NMR spectra of the photolysis solutions. [b] For solubility reasons 20 mL of 1:1 (v/v) methanol-THF was used in lieu of methanol. [c] In a preparative experiment with different proportions of solvent yields were 9 and 57%, respectively.

Scheme III



Scheme IV. Photolysis of Acyltris(trimethylsilyl)silanes in Inert Solvents



monomer **21**. The NMR spectrum in the trimethylsilyl region contained three singlets of equal intensity, consistent with the structures of either of the two possible head to head dimers **26** (or of one of the possible head to tail dimers).

Mild hydrolysis of **26** with dilute base gave an 86% yield of benzyl phenyl ketone. While a rational route to benzyl phenyl ketone from a 1,3-disilacyclobutane (head to tail dimer) is not obvious, a reasonable route from a 1,2-disilacyclobutane (head to head dimer) is easily devised, and one possibility is shown in Scheme IV.

A similar solid dimer **27** was isolated with difficulty from the photolysis solutions of **9** in pentane, by precipitation with acetone in the cold. This solid, whose NMR spectrum will be described later, gave no mass spectral signal corresponding to the dimer, but did give signals at *m/e* 332 and 317, accounted for as [monomer]$^+$, **23**, and [monomer − Me]$^+$. In the case of the acetylsilane **8**, head to head coupling of the silicon ends of the monomer **28** (R = Me) again occurred, but instead of a 1,2-disilacyclobutane being formed, the reaction took another course, disproportionation, yielding the disilane **29** which was isolated and characterized. On mild hydrolysis **29** gave the acetyldisilane **30**, also isolated and characterized. Thus the silaethylenes from each of the acyltris(trimethylsilyl)silanes couple in the same head to head manner, unlike the head to tail coupling reported for much simpler silaethylenes in the vapor phase.[2] This unusual regiospecificity may be the result of silyl radical head to head coupling of the silaethylenes (triplet character) to produce 1,4 diradicals (see below), an interpretation recently also proposed by Seyferth[11] and by Barton[12] for other related systems where silicon-silicon bonds were generated.

Dimer-Monomer Equilibria. The lack of a molecular ion in the mass spectrum of the dimer **26** suggested that the dimer might readily dissociate thermally to monomer. When dimer **26** was refluxed in THF with methanol, the methanol adduct of the silaethylene was obtained in good yield, although no reaction occurred at room temperature. Similarly, the silacyclohexene **22** isolated previously was obtained in 71% yield when dimer **26** was refluxed in THF containing dimethylbutadiene (but not at room temperature). Evidently the dimer is a ready source of silaethylene, requiring relatively low temperatures (60-65 °C) for complete dissociation.

With dimer **27**, mere dissolution at room temperature in THF-methanol gave the expected silaethylene adduct, suggesting a very mobile dimer-monomer equilibrium in this case, as further studies confirmed.

If solutions of the benzoylpolysilane **7** were photolyzed in inert solvent and then the trapping reagents methanol or dimethylbutadiene were added immediately after the light was turned off, none of the derivatives of the silaethylene (except the dimer) was detected, suggesting no accumulation of silaethylene in the photolysis solution. In contrast, photolyzed solutions of the pivaloylpolysilane **9**, when treated with methanol or phenylpropyne *after* the light was turned off, gave substantial yields of the previously isolated methanol or silacyclobutene adducts. Evidently these solutions contain significant amounts of a relatively long-lived silaethylene, or else dimer is present in a rapid equilibrium with the silaethylene, which then reacts with the added reagents. This situation was clarified by observing the NMR spectrum of a degassed photolyzed solution of the pivaloylsilane **9** in several inert solvents.

At room temperature two sets of NMR signals were observed. One, consisting of four singlets (three Me_3Si, one Me_3C) of equal intensity, was assigned to the silaethylene **23**. The second, weaker set, consisting of three *C*-methyl singlets each of relative intensity one and three $SiMe_3$ singlets each of relative intensity three, was assigned to dimer **27** in which lack of free rotation of the *tert*-butyl groups, presumably due to steric crowding, resulted in the methyl groups being magnetically nonequivalent, a phenomena previously observed in other sterically hindered situations.[13] After nearly complete photolysis of the pivaloylsilane the relative intensities of the two sets of signals was 4.3:1. On cooling to −17 °C over 24 h, the ratio of intensities of the two sets of signals changed to 1:3. Thus the minor product at room temperature, the dimer, became the major product at low temperature which is consistent with the observed thermal decomposition of dimer **27** to monomer **23** on warming. When the photolysis solutions were restored to room temperature, the ratio of intensities returned to about 4.3:1 over a few minutes.

Identical NMR spectra were also obtained when solid dimer **27** was dissolved in the same solvent, indicating that the dimer readily dissociated to monomer. Other more quantitative experiments with 0.28 M solutions of pivaloylsilane **9** in benzene at room temperature indicated that after photolysis the solutions contained about 68% silaethylene and about 20% dimer, as indicated by the intensities of the NMR signals. The remainder of the product mixture presumably consisted of silaethylene polymer and other minor products (see later).

When the photolysis solutions of the pivaloylsilane **9** were kept at room temperature for some time, the intensities of the NMR signals assigned to the monomer and dimer slowly decreased and the signals due to the *tert*-butyl and trimethylsilyl groups of the parent acylpolysilane **9** increased in intensity until after about 2 weeks the NMR spectrum was essentially that of the original pivaloylsilane. These results indicate that a slow dark rearrangement of silaethylene **23** back to acylsilane occurred and that the acylsilane is apparently thermodynamically stable relative to the photolysis products.

Partially and fully decoupled ^{13}C spectra of the photolysis solutions of the pivaloylsilane in C_6D_6 were obtained, whose signals were analyzed, except for the Me_3Si region where severe overlapping occurred, in terms of a mixture of pivaloylsilane **9**, the silaethylene **23**, and the disilacyclobutane dimer **27**. Of particular interest was the observation of a singlet at 112.7 ppm below Me_4Si, in the normal range of an sp^2-hybridized carbon, assigned to the unsaturated carbon of the silaethylene. The carbonyl carbon of the pivaloylsilane was observed as a singlet at 246.3 ppm below Me_4Si, the same region (230–247 ppm) where other acylsilanes ($RCOSiR_3$) absorb,[14] but which is much further downfield than the absorption (190–204 ppm) of the related aldehyde (RCHO). There were three distinct C–Me signals attributable to nonequivalent methyl carbon atoms in the *tert*-butyl group of the dimer, as had been observed in the proton resonance spectrum.

Preliminary ^{29}Si studies on the pivaloylsilane photolysis system show absorptions attributable to each of the silicon atoms of the pivaloylsilane **9**, the silaethylene **23**, and the dimer **27**. In particular a signal observed at 41.2 ppm downfield from $(CH_3)_4Si$, a position remarkably far downfield for a bissilyl-substituted silicon atom, seems reasonably attributed to the sp^2-hybridized silicon of the silicon–carbon double bond of **23**.[34]

In order to characterize the silaethylene **23** further, both UV and IR spectra were studied. Solutions of the pivaloylsilane are essentially colorless, with λ_{max} occurring at about 366 nm (ϵ 127) in hexane. On photolysis, the solutions acquired a yellow color as a new intense band at 339 nm developed which had significant end absorption in the visible region. When the seal of the quartz cell was broken and the contents were exposed to air, the yellow color rapidly disappeared, as the band at 339 nm disappeared. The spectrum of the resultant system was identical with that of the initial pivaloylsilane, but the intensity of the longest wavelength absorption was slightly less than before photolysis. On the assumption that the absorption at 339 nm was due to the silaethylene, and that its concentration was equal to the change in pivaloylsilane concentrations before and after the photolysis, the extinction coefficient of the silaethylene absorption was ~5200, suggesting considerable π character for the silicon–carbon double bond.

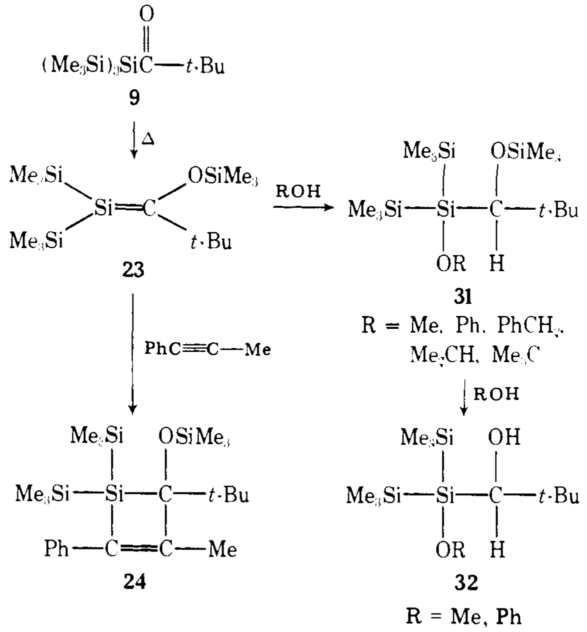
Attempts were also made to observe infrared absorption characteristic of the silaethylene. The spectra of pivaloylsilane **9** as a thin film and of dimer **27** as a solid in KBr were readily obtained. After irradiation of the pivaloylsilane film, the infrared spectrum was immediately run again. The most noticeable changes were marked decreases in the intensity of bands at 6.17 (C=O), 7.65, and 10.75 μ of the pivaloylsilane, and the development of strong new absorptions at 8.8 and 9.6 μ (broad, Si-O-C). After standing for 24 h under nitrogen in the dark, the infrared spectra was little changed, except that the band at 8.8 μ had almost disappeared. Similar behavior was observed in benzene solution.

A thin film of dimer, deposited between sodium chloride disks, gave strong absorption at 9.60 μ (Si–O–C) but no band at 8.8 μ. After the disks were warmed to about 90 °C over 30 min the infrared spectra possessed new strong bands at 6.17 (Si–C=O) and 6.80 μ (due to pivaloylsilane) as well as a medium-intensity band at 8.8 μ which gradually disappeared over 7 h at room temperature. No distinctive new absorption was observed in the 6–7.5 μ region, where Si=C stretching absorption might have been expected,[15,16] and while the new intense band at 8.8 μ appears to be attributable to the silaethylene, the identity of this infrared absorption mode is not obvious.

ESR Spectra from Photolysis Solutions of Acylpolysilanes. In an attempt to learn further about the silaethylenes and the photolysis of the acylpolysilanes, a solution of the benzoyl compound **7** in pentane was irradiated in the probe of an ESR spectrometer. Even at room temperature, there was no difficulty in observing a moderately intense ESR signal which consisted primarily of a quartet (a_1 = 4 G) of triplets (a_2 = 1.5 G) with a *g* value of 2.0027, each component of which was moderately broad (1.5 G). This splitting can be ascribed to a siloxybenzyl radical of the general structure $-\dot{C}Ph(OSiMe_3)$, the quartet arising from splitting due to the ortho plus para protons, further split to triplets by the meta protons; similar systems have been described by Jackson et al.[17]

At −20 °C, the ESR signal obtained from a 0.26 M solution of **7** in pentane photolyzed for 10 min had a half-life of about

Scheme V. Thermolysis of Pivaloyltris(trimethylsilyl)silane



112 min after the light had been turned off. Obviously the radical species is a relatively stable one.

An identical ESR signal was obtained when dimer **26** was heated in pentane in a sealed tube at 90 °C for 10 min, which was then placed in the ESR spectrometer, although no ESR spectrum was obtained from a solution of the dimer which had not been heated, or from the solid dimer.

Similar irradiation of acetylpolysilane **8** gave rise to short-lived ESR signals (half-life $\simeq$ 20 s at −20 °C), observed as quartets (a_{I} = 20.8 G, g = 2.0032), each band of which was relatively broad ($\simeq$2.5 G) with no fine structure. These signals can be ascribed to a radical species $Si\text{-}\dot{C}(OSiMe_3)\text{-}CH_3$ where the observed coupling constant is similar to that reported (20 G) for the related methyl-substituted radical $Me_2\dot{C}OSi(SiMe_3)_3$.[17]

Finally, the ESR spectra of photolysis solutions of the pivaloylsilane **9** were examined in benzene, toluene, or pentane. Intense long-lived spectra were observed consisting of a broad singlet ($\simeq$4.5 G), g = 2.0035, with two low-intensity doublets ($\simeq$3%) nearly symmetrically situated about the singlet with coupling constants of 15.0 and 9.5 G. Some fine structure, as shoulders, could be detected on the sides of the singlet, presumably due to coupling with the protons of the *tert*-butyl group, but all efforts to resolve further the broad signal failed. The intensities and couplings of the doublets suggest that they may be ^{29}Si satellites (relative abundance 4.7%), α-^{29}Si coupling constants of 15.2 and 13.5 G having been reported for the species $Et_3Si\dot{C}HMe$ and $(Me_3Si)_3\dot{C}$, respectively.[18,19] This interpretation infers that the second doublet (9.5 G) may be due to coupling with β-^{29}Si atoms.

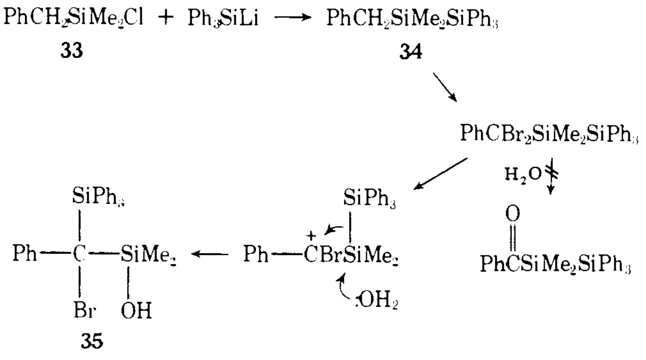
The ESR spectrum of the irradiated pivaloylsilane solution in 1:1 ether–THF at room temperature was identical with that in pentane, but when the temperature was lowered to 77 K, the ESR spectra of the material in the glass was about three times broader (max-min separation of main peak 6 G) and the intensity was about 25% of its value at room temperature. When the dimer **27** was merely dissolved in pentane at room temperature, an ESR spectrum identical with that derived from the photolysis solutions was obtained.

The above ESR observations may be explained in terms of the appropriate diradicals **25**, arising from dissociation of the carbon–carbon bond of the disilacyclobutane ring or from the radical coupling of silyl ends of two molecules of silaethylene. However, at this time we cannot unambiguously demonstrate that such diradicals are the source of the ESR signals and further discussion will be deferred until further evidence is obtained.

Thermolysis of Pivaloyltris(trimethylsilyl)silane 9 in the Presence of Trapping Agents. As mentioned earlier, the neat thermolysis of various acylpolysilanes appeared to give mixtures of compounds. However, thermolysis in the presence of alcohols was much cleaner (Scheme V), although the reactions were surprisingly slow. Thermolysis of **9** in methanol in a sealed tube and at 160–170 °C over 24 h gave as the major fraction (92%) the alcohol **32** (R = Me), which appears to be the methanolysis product of the expected product **31**, together with trimethylmethoxysilane (identified by NMR). Shorter reaction times did not yield compound **31**. When phenol was used as the trapping agent a 2:1 mixture of the two species **31** and **32** (R = Ph) was obtained consistent with the proposed solvolysis. With benzyl alcohol, isopropyl alcohol, or *tert*-butyl alcohol under similar conditions, no solvolysis was detected and only the products **31** corresponding to addition of the alcohol across the silicon–carbon double bond of **23** were obtained. When the acylpolysilane was thermolyzed in the presence of 1-phenylpropyne, the previously described silacyclobutene **24** was obtained in 72% yield.

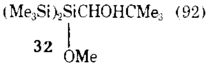
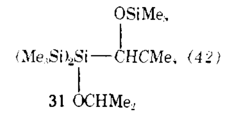
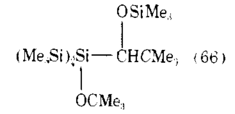
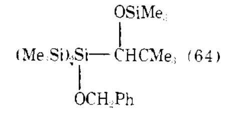
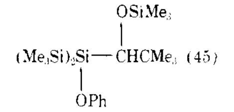
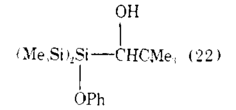
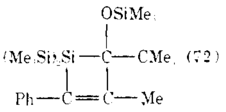
The experimental details are summarized in Table IV. These results clearly indicate that thermal rearrangements of acylpolysilanes to species containing silicon–carbon double bonds also can occur.

Syntheses. Synthetic routes to several acyldisilanes have been described previously[20] which involved either hydrolysis of an α,α-dibromobenzyldisilane or hydrolysis of disilyl-substituted dithianes, but in each case only low yields of product were obtained, so a further study of some of these reactions was desirable. Coupling of benzyldimethylchlorosilane **33** with triphenylsilyllithium gave the benzyldisilane **34** which was subsequently dibrominated with *N*-bromosuccinimide. Hydrolysis of this compound under the usual conditions gave none of the expected acyldisilane and instead a 73% yield of (α-bromo-α-triphenylsilylbenzyl)dimethylsilanol (**35**) was isolated. This product evidently arose by migration of the triphenylsilyl group to the neighboring electron-deficient center created by removal of the benzylic bromine. Thus it appeared that routes to acyldisilanes which involved hydrolysis of α-substituted disilanes were likely to lead to alternative products.

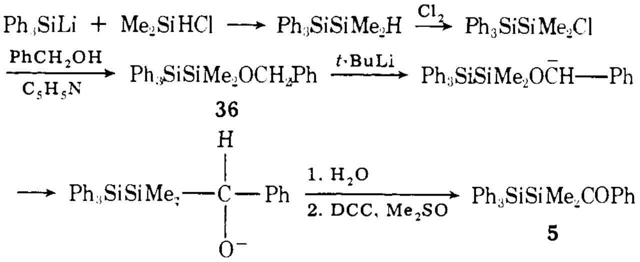


Several diverse routes were eventually developed for the synthesis of the acyldisilanes employed above. These are summarized in Table V. Thus triphenylsilyldimethylchlorosilane, from coupling of triphenylsilyllithium with dimethylchlorosilane, followed by chlorination, was converted to its benzyl ether **36**. Treatment of this at −20 °C in THF with *tert*-butyllithium following the procedures of Wright and West[21] resulted in rearrangement of the carbanion to the oxy anion, which after hydrolysis to the silylcarbinol was oxidized, using the dicyclohexylcarbodiimide–Me_2SO reagent,[22] to the acyldisilane **5**.

Table IV. Thermolyses of Pivaloyltris(trimethylsilyl)silane in Alcohols or Phenylpropyne

starting material	reagent	conditions	product no. (% yield)	mp, °C	NMR, δ (CCl_4), ppm; IR (CCl_4), μ; *m/e*
$(Me_3Si)_3SiCOCMe_3$	MeOH	24 h, 160-170 °C	 $(\mathrm{Me_3Si})_2\underset{\mathrm{OMe}}{\mathrm{Si}}\mathrm{CHOHCMe_3}$ (92) **32**	97-98	0.2 (18 H, s, $SiMe_3$), 1.0 (9 H, s, CMe_3), 3.45 (3 H, s, MeO), 3.55 (1 H, s, CH); IR 2.8 (OH), 3.5 (OMe)
$(Me_3Si)_3SiCOCMe_3$	Me_2CHOH	20 h, 180 °C	 $(\mathrm{Me_3Si})_2\underset{\mathrm{OCHMe_2}}{\mathrm{Si}}\text{—}\overset{\mathrm{OSiMe_3}}{\mathrm{C}}\mathrm{HCMe_3}$ (42) **31**	97-98	0.22, 0.27, 0.32 (each 9 H, s, $SiMe_3$), 1.05 (9 H, s, CMe_3), 1.20 (6 H, d, J = 6 Hz, Me_2CH), 3.63 (1 H, s, CH), 3.97 (1 H, septet, Me_2CH); *m/e* 377 $[M - 15]^+$
$(Me_3Si)_3SiCOCMe_3$	Me_3COH	18 h, 180 °C	 $(\mathrm{Me_3Si})_2\underset{\mathrm{OCMe_3}}{\mathrm{Si}}\text{—}\overset{\mathrm{OSiMe_3}}{\mathrm{C}}\mathrm{HCMe_3}$ (66)	92-93	0.22, 0.24, 0.29 (each 9 H, s, $SiMe_3$), 1.00 (9 H, s, *t*-Bu), 1.30 (9 H, s, O-*t*-Bu), 3.73 (1 H, s, CH)
$(Me_3Si)_3SiCOCMe_3$	$PhCH_2OH$	4 h, 190 °C	 $(\mathrm{Me_3Si})_2\underset{\mathrm{OCH_2Ph}}{\mathrm{Si}}\text{—}\overset{\mathrm{OSiMe_3}}{\mathrm{C}}\mathrm{HCMe_3}$ (64)	*a*	0.20, 0.28, 0.32 (each 9 H, s, $SiMe_3$), 1.09 (9 H, s, CMe_3), 3.90 (1 H, s, CH), 4.80 (2 H, s, OCH_2), 7.3 (5 H, s, Ph)
$(Me_3Si)_3SiCOCMe_3$	PhOH[b]	5 h, 180 °C	 $(\mathrm{Me_3Si})_2\underset{\mathrm{OPh}}{\mathrm{Si}}\text{—}\overset{\mathrm{OSiMe_3}}{\mathrm{C}}\mathrm{HCMe_3}$ (45) + **31**	*a*	0.20, 0.30, 0.40 (each 9 H, s, $SiMe_3$), 1.10 (9 H, s, CMe_3), 4.22 (1 H, s, CH), 6.9-7.3 (5 H, m, Ph)
$(Me_3Si)_3SiCOCMe_3$			 $(\mathrm{Me_3Si})_2\underset{\mathrm{OPh}}{\mathrm{Si}}\text{—}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCMe_3}$ (22) **32**	*a*	0.20, 0.28 (each 9 H, s, $SiMe_3$), 1.14 (9 H, s, CMe_3), 3.82 (1 H, s, CH), 6.8-7.4 (5 H, m, Ph); IR 2.73 (OH)
$(Me_3Si)_3SiCOCMe_3$	PhC≡CMe	10 h, 170 °C	 (72) **24**[c]		

[a] Isolated by preparative GLC on SE-30 on Chromosorb W. [b] Phenoxytrimethylsilane also isolated, identified by comparison with authentic material (IR, NMR) (12%). [c] Only detected material, identified by comparison with authentic material.



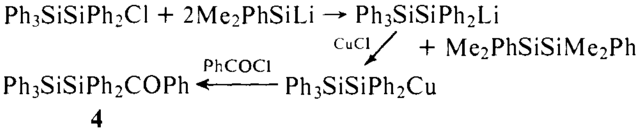
$$\mathrm{Ph_3SiLi + Me_2SiHCl \longrightarrow Ph_3SiSiMe_2H \xrightarrow{Cl_2} Ph_3SiSiMe_2Cl \xrightarrow[C_5H_5N]{PhCH_2OH} Ph_3SiSiMe_2OCH_2Ph \xrightarrow{\mathit{t}\text{-}BuLi} Ph_3SiSiMe_2O\bar{C}H\text{—}Ph}$$

36

$$\longrightarrow \mathrm{Ph_3SiSiMe_2\text{—}\overset{H}{\underset{O^-}{C}}\text{—}Ph \xrightarrow[2.\ DCC,\ Me_2SO]{1.\ H_2O} Ph_3SiSiMe_2COPh}$$

5

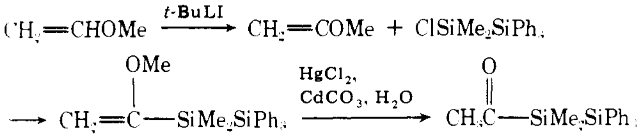
Benzoylpentaphenyldisilane **4** was prepared by halogen-metal exchange of pentaphenylchlorodisilane with 2 mol of dimethylphenylsilyllithium, taking advantage of the observation of Wittenberg and Gilman that the more arylated silicon in such a mixture preferentially existed as the anion.[23] To this mixture was added 1 equiv of cuprous chloride, and the resulting organosilylcopper reagent[24] was treated with benzoyl chloride giving the desired pentaphenylbenzoyldisilane in 50% yield. Acetyl-1,1-dimethyl-2,2,2-triphenyldisilane (**6**) was prepared by coupling methoxyvinyl anion, as previously employed by Baldwin,[25] with chlorodisilane, followed by mild hydrolysis using a suspension of mercuric chloride and cadmium carbonate in acetone-benzene-water. A similar route to acetylsilanes has recently been described by Dexheimer and Spialter.[26]



$$\mathrm{Ph_3SiSiPh_2Cl + 2Me_2PhSiLi \rightarrow Ph_3SiSiPh_2Li \xrightarrow{CuCl} Ph_3SiSiPh_2Cu + Me_2PhSiSiMe_2Ph}$$

$$\mathrm{Ph_3SiSiPh_2COPh \xleftarrow{PhCOCl} Ph_3SiSiPh_2Cu}$$

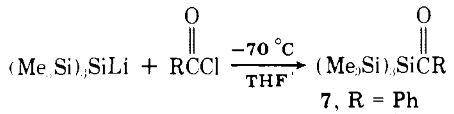
4



$$\mathrm{CH_2{=}CHOMe \xrightarrow{\mathit{t}\text{-}BuLI} CH_2{=}\bar{C}OMe + ClSiMe_2SiPh_3 \longrightarrow CH_2{=}\overset{OMe}{C}\text{—}SiMe_2SiPh_3 \xrightarrow{HgCl_2,\ CdCO_3,\ H_2O} CH_3\overset{O}{\overset{\|}{C}}\text{—}SiMe_2SiPh_3}$$

38 **6**

Finally the acyltris(trimethylsilyl)silanes were prepared in yields of 60-70% by the coupling of tris(trimethylsilyl)silyllithium with a large excess of the appropriate acid chloride at −70 °C.



$$\mathrm{(Me_3Si)_3SiLi + R\overset{O}{\overset{\|}{C}}Cl \xrightarrow[THF]{-70\ ^\circ C} (Me_3Si)_3Si\overset{O}{\overset{\|}{C}}R}$$

7, R = Ph
8, R = Me
9, R = Me_3C

Table V. Synthesis of Acylsilanes and Other Related Compounds

starting material(s) (mol)	conditions	products, compd no. (% yields), mp, °C	NMR, δ (CCl_4), ppm; IR (CCl_4) μ; *m/e*
Ph_3SiLi (0.10) + Me_2SiHCl (0.11)	THF, −80 °C, then 20 °C, 12 h	$Ph_3SiSiMe_2H$, **14a** (69), 92–93[a]	7.13–7.60 (15 H, m, Ph_3Si), 4.17 (1 H, quintet, $J = 4$ Hz, SiH), 0.25 (6 H, d, $J = 4$ Hz, Me_2Si); IR, 4.75 (SiH), 7.00, 9.05 (SiPh), 8.00 (MeSi)
$Ph_3SiSiMe_2H + Cl_2$	CCl_4, −80 °C	$Ph_3SiSiMe_2Cl$, **33** (72), 98–99[b]	7.17–7.67 (15 H, m, Ph_3Si), 0.57 (6 H, s, Me_2Si)
Ph_3SiLi (0.068) + $PhCH_2SiMe_2Cl$ (0.068)	THF, −80 °C, 5 h	$Ph_3SiSiMe_2CH_2Ph$, **34** (73), 79–80[c]	6.6–7.5 (20 H, m, Ph), 2.20 (2 H, s, CH_2), 0.14 (6 H, s, Me_2Si)
$Ph_3SiSiMe_2CH_2Ph$ (0.015) + NBS (0.032)	CCl_4, Δ, 4 h	$Ph_3SiSiMe_2CBr_2Ph$ (58), 117–118[a]	7.00–7.40 (20 H, m, Ph), 0.50 (6 H, s, Me_2Si)
$Ph_3SiSiMe_2CBr_2Ph$ (0.0088) + AgOAc (0.019)	H_2O, PhH, acetone, 20 °C, 8 h	$Ph_3SiCBrPhSiMe_2OH$, **35** (70), 131–132[d]	6.93–7.70 (20 H, m, Ph), −0.03 (3 H, s, MeSi), −0.10 (3 H, s, MeSi); IR 2.70 (SiOH), 7.00, 9.05 (SiPh), 8.00 (SiMe); *m/e* 426 [M − C_6H_6]
$Ph_3SiSiMe_2Cl$ (0.046) + $PhCH_2OH$ (0.043) + C_5H_5N (0.043)	Et_2O, 3 h, Δ	$Ph_3SiSiMe_2OCH_2Ph$, **36** (72), 42–43[e]	7.0–7.6 (20 H, m, Ph), 4.53 (2 H, s, CH_2), 0.37 (6 H, s, Me_2Si); IR 9.30 (SiOC)
$Ph_3SiSiMe_2OCH_2Ph$ (0.023) + *t*-BuLi (1.5 equiv)	THF, −80 °C, −40 °C for 3 h	$Ph_3SiSiMe_2CHOHPh$, **37** (53), 104–105[b]	6.70–7.40 (20 H, m, Ph), 4.53 (1 H, s, CHOH), 1.33 (1 H, s, OH), 0.13 (3 H, s, MeSi), 0.07 (3 H, s, MeSi); IR 2.80 (OH)
$Ph_3SiSiMe_2CHOHPh$ (0.012) + DCC (0.013) + $C_5H_6N^+CF_3COO^-$ (0.012) + Me_2SO (5 mL)	20 °C, 4 h	$Ph_3SiSiMe_2COPh$, **5** (80), 104–105[a]	7.00–7.60 (20 H, m, Ph), 0.53 (6 H, s, Me_2Si); IR 6.19 (C=O), 6.91 (C–Ph), 7.00, 9.04 (SiPh), 8.01 (SiMe)
$PhMe_2SiLi$ (0.029) + $Ph_3SiSiPh_2Cl$ (0.0084), then CuCl (0.01) then PhCOCl (0.010)	THF,[f]	$Ph_3SiSiPh_2COPh$, **4** (50) 198–200[c]	[g]
$MeOCH{=}CH_2$ (0.029) + *t*-BuLi (0.016); $Ph_3SiSiMe_2Cl$ (0.014)	THF, −80 °C; 20 °C, 2 h	$Ph_3SiSiMe_2C({=}CH_2)OMe$, **38** (49)[h]	7.14–7.57 (15 H, m, Ph), 4.50 (1 H, d, $J = 2$ Hz, HC=C), 4.17 (1 H, d, $J = 2$ Hz, HC=C), 3.33 (3 H, s, MeO), 0.24 (6 H, s, Me_2Si)
$Ph_3SiSiMe_2C({=}CH_2)OMe$ (0.016) + $HgCl_2$ (0.016) + $CdCO_3$ (0.048)	H_2O (0.017), C_5H_{12}, acetone, 20 °C, 0.6 h	$Ph_3SiSiMe_2COCH_3$, **6** (36) 65–66[c]	7.13–7.50 (15 H, m, Ph), 1.93 (3 H, s, MeCO), 0.37 (6 H, m, Me_3Si)
$(Me_3Si)_3SiLi$ + PhCOCl	THF,[f]	$(Me_3Si)_3SiCOPh$, **7** (60)[i]	7.30–7.80 (5 H, m, Ph), 0.27 (27 H, s, Me_3Si): IR, 6.22 (C=O), 6.91 (C–Ph), 8.02 (SiMe)
$(Me_3Si)_3SiLi + CH_3COCl$	[f]	$(Me_3Si)_3SiCOCH_3$, **8** (65) 105–107	2.20 (3 H, s, MeCO), 0.27 (27 H, s, Me_3Si): IR 6.13 (C=O), 7.49 (CH_3CO?), 8.01 (SiMe)
$(Me_3Si)_3SiLi + Me_3CCOCl$	[f]	$(Me_3Si)_3SiCOCMe_3$, 9 (66–70) 182–184	1.00 (9 H, Me_3C), 0.23 (27 H, s, Me_3Si): IR, 6.17 (C=O), 8.08 (MeSi)

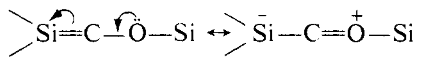
[a] Recrystallized from benzene–ethanol. [b] Recrystallized from hexane. [c] Recrystallized from absolute ethanol. [d] Recrystallized from benzene–hexane. [e] Recrystallized from pentane. [f] See Experimental Section for details. [g] See ref 20. [h] Separated by column chromatography on silica gel, eluted with hexane, n_D^{23} 1.6023. [i] Isolated by column chromatography on silica gel, eluted with pentane, n_D^{23} 1.5547.

As previously observed,[27] the carbonyl infrared stretches of the acetyldisilanes all occurred at 6.09 μ (see Table VI), while the acetylpolysilane **8** absorbed at 6.13 μ. The benzoyldisilanes absorbed at about 6.19 μ but the polysilane **7** absorbed at 6.22 μ. The pivaloylpolysilane **9** absorbed at 6.17 μ, a somewhat longer wavelength than reported for pivaloyltrimethylsilane (6.11 μ). The longer wavelength absorption of each of the polysilanes presumably is a reflection of increased steric interactions between the groups surrounding the carbonyl group.

The ultraviolet absorption spectral data for the compounds are reported in Table VI: the banded long-wavelength absorption which is characteristic of acetyl (λ_{max} 370–380 nm) and benzoylsilanes (λ_{max} 420–425 nm) was also observed with the acyldisilanes and acylpolysilanes.

Conclusion

The preceding data strongly support the conclusion that acylpolysilanes are readily photoisomerized to silaethylenes which are remarkably stable relative to the behavior previously observed for other examples of these species. It seems clear that the enhanced stability can be attributed in part to steric factors, which probably also play some role in dictating the mode of dimerization and affect the stability of the 1,2-disilacyclobutane dimers. Electronic factors probably are also important in the present cases in stabilizing the silaethylene. It is anticipated (and calculated) that a simple silicon–carbon double bond would be significantly electropositive at silicon and electronegative at carbon.[28] The presence of two weakly electron-donating trimethylsilyl groups on silicon should reduce the electron deficiency on silicon. Additionally, an electron-withdrawing trimethylsiloxy group may reduce the electron excess on the carbon atom, and resonance contributions of the sort



$$\mathrm{Si{=}C{-}\ddot{O}{-}Si} \leftrightarrow \mathrm{\overset{-}{Si}{-}C{=}\overset{+}{O}{-}Si}$$

Table VI. Infrared Carbonyl Stretching and Longest Wavelength Ultraviolet Absorption of Some Acylsilanes and Acylpolysilanes

compd	C=O stretch,[a] μ	longest wavelength UV absorption,[b] nm (ϵ)
MeCOSiMe$_2$SiMe$_3$[c]	6.09	370, 384[d]
MeCOSiMe$_2$SiPh$_3$	6.09	328 (96), 345 (188), 360 (344), 374 (454), 389 (372)
MeCOSi(SiMe$_3$)$_3$	6.13	329 (33), 342 (61), 356 (100), 368 (126), 382 (104)
MeCOSiMe$_3$[c]	6.08	333 (34), 346 (62), 358 (100), 372 (126), 388 (93)
MeCOSiPh$_2$SiPh$_3$[c]	6.09	338 (116), 351 (228), 363 (380), 378 (490), 393 (396)
MeCOSiPh$_3$[c]	6.08	337 (103), 348 (194), 362 (360), 377 (441), 392 (337)
Me$_3$CCOSi(SiMe$_3$)$_3$	6.17	348 (100), 366 (127), 380 (97)
Me$_3$CCOSiMe$_3$[e]	6.11	367 (200)
PhCOSiMe$_2$SiPh$_3$	6.19	386 (181), 404 (349), 423 (453), 444 (279)
PhCOSi(SiMe$_3$)$_3$	6.22	386 (76), 404 (133), 424 (154), 446 (92)
PhCOSiMe$_3$	6.18	386 (46), 404 (83), 424 (101), 444 (57)
PhCOSiPh$_2$SiPh$_3$	6.19	389 (131), 407 (262), 423 (342), 445 (234)
PhCOSiPh$_3$	6.18	388 (118), 405 (222), 424 (293), 440 (177)

[a] In CCl$_4$. [b] In C$_6$H$_{12}$. [c] Reference 20. [d] ϵ not available. [e] Reference 33.

may also play an important role such that the resulting silicon-carbon double bond has rather less polar character than found in simpler systems. The present data also demonstrate the facile interconversion of silaethylene both with its 1,2-disilacyclobutane dimer and with the parent acylsilane.

It is no longer beyond the realm of possibility that with other substituents, a silaethylene may be prepared which is stable and isolable at room temperature.

Experimental Section

General. A 100-W PAR 38 clear mercury spot lamp (Blak-Ray, ANSI code H44GS) was used for all photolysis experiments. Irradiations were carried out under dry nitrogen in flasks cooled in baths of running water positioned in the intense central beam about 6 in. from the lamp.

Tetrahydrofuran and diethyl ether were distilled from metallic sodium immediately prior to use. Spectra were run in carbon tetrachloride. Instruments used were Perkin-Elmer Model 337 and Model 237 infrared spectrometers, Varian T60 NMR spectrometer, Unicam SP 800 spectrophotometer, and a Varian E-4 EPR spectrometer.

Satisfactory (0.3%) analyses (C, H) were obtained for all new compounds, and were performed by A. B. Gygli, Toronto.

"Workup", as applied to all reactions involving organometallic reagents, etc., means hydrolysis of the reaction mixtures with cold dilute acid, extraction with ether, drying of the combined ether layers over sodium sulfate, and finally removal of the ether on a rotary evaporator.

Many of the reactions involving the synthesis of new compounds are summarized in Table V, which also lists important spectroscopic data for new compounds. Other UV and IR data are given in Table VI. Only typical experiments, or key reactions, are described in detail.

Benzoylpentaphenyldisilane (4). Phenyldimethylchlorosilane (4.8 mL, 29.0 mmol) in 10 mL of THF was added dropwise to 0.80 g (0.115 g-atom) of cut lithium wire in 30 mL of tetrahydrofuran and the resulting mixture was then filtered into a flask at −80 °C. Chloropentaphenyldisilane (4.0 g, 8.4 mmol) in 15 mL of THF was added over 0.5 h and the resulting brownish-red solution was stirred overnight at room temperature. The solution was then cooled to −80 °C and 1.0 g (10.1 mmol) of cuprous chloride was added to the solution which was then removed from the cold bath and stirred for 3 h. After the solution was cooled to −80 °C 1.2 mL (10.3 mmol) of freshly distilled benzoyl chloride was added, and the mixture was stirred in the dark for 3 h at 20 °C becoming greenish yellow. Workup and recrystallization from ethanol gave 2.3 g of benzoyldisilane **4** (50% yield, based on chloropentaphenyldisilane), mp 198–200 °C, identical with authentic material.[20]

1-(α-Methoxyvinyl)-1,1-dimethyl-2,2,2-triphenyldisilane (38). To methyl vinyl ether (2.3 mL, 0.029 mol) in 40 mL of THF at −80 °C was added 8.6 mL of a 1.8 M solution of *tert*-butyllithium in pentane. The solution was removed from the cold bath and stirred until the yellow color of the *tert*-butyllithium-tetrahydrofuran complex disappeared (about 15 min), and then was recooled to −80 °C; 5.0 g (0.014 mol) of 1,1-dimethyl-2,2,2-triphenylchlorodisilane in 20 mL of tetrahydrofuran was added, and the solution was stirred for 2 h at 20 °C. Workup with pentane and chromatography on silica gel using hexane gave 2.6 g (49%) of the methoxyvinyl compound **38**, n_D^{23} 1.6023.

Benzoyltris(trimethylsilyl)silane (7). A typical acyltris(trimethylsilyl)silane synthesis follows. Tris(trimethylsilyl)silyllithium was prepared according to the method of Gilman.[29] The reaction was monitored by observing the NMR spectra of the reaction mixture, the chemical shift of tetrakis(trimethylsilyl)silane being δ 0.24 ppm and that of tris(trimethylsilyl)silyllithium being δ 0.07 ppm. The tris(trimethylsilyl)silyllithium from 0.031 mol of starting tetrakissilane was added dropwise to 10.8 mL (0.093 mol) of benzoyl chloride in 100 mL of THF at −80 °C, followed by stirring in the dark for 4 h. Workup, followed by column chromatography with CCl$_4$-pentane on silica gel, gave the benzoyltris(trimethylsilyl)silane **7**, n_D^{23} 1.5547, in 60% yield.

Photolysis of Acyldisilanes in Methanol. The following is a typical procedure for the photolysis of the acyldisilanes in methanol. A solution of 0.50 g (0.92 mmol) of benzoyldisilane **4**, 0.40 mL (9.9 mmol) of methanol, and 3 drops of pyridine in 30 mL of THF at 10 °C was irradiated under nitrogen until the yellow color disappeared (3 h). The NMR spectrum of the residue in CCl$_4$ showed (α-triphenylsiloxybenzyl)diphenylmethoxysilane (**13**, 90%) and benzaldehyde methyl pentaphenyldisilyl acetal (**12**, 3%), based on the intensities of the methoxy and aryl proton signals. The former product was isolated in 67% yield by column chromatography with CCl$_4$ on silica gel, mp 112–113 °C from pentane, *m/e* 501 [M − Ph]$^+$.

Photolysis of Benzoyltris(trimethylsilyl)silane (7) in Methanol. Benzoylpolysilane **7** (0.25 g, 0.71 mmol) in 20 mL of methanol containing 6 drops of pyridine at 10 °C was irradiated until the yellow color of the benzoylpolysilane disappeared (20 min). The NMR spectrum of the residue consisted almost entirely of the resonances of (α-trimethylsiloxybenzyl)bis(trimethylsilyl)methoxysilane (**19**, R = Ph). Chromatography with benzene on silica gel gave 0.25 g (92%) of **19**.

Similar photolysis of **7** in MeOD gave a product with identical NMR spectrum except that the benzylic proton signal was absent confirming the structure as (α-trimethylsiloxy-α-deuteriobenzyl)bis(trimethylsilyl)methoxysilane.

Details of similar studies with other polysilanes are summarized in Table III, as are the spectroscopic data for new compounds.

Photolysis of Benzoyltris(trimethylsilyl)silane (7) in Ether. Benzoylpolysilane **7** (0.50 g, 1.72 mmol) in 40 mL of ether at 10 °C was irradiated for 2 h. Although the solution was still pale yellow, no infrared C=O stretch absorption of **7** was present. The ether was removed under vacuum and recrystallization of the residue from pentane-acetone gave 0.35 g (70%) of 3,4-diphenyl-3,4-bis(trimethylsiloxy)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**26**), mp 149–150 °C, mol wt (osmometry) 701 ± 1.5% (calcd, 704).

Hydrolysis of Dimer 26. A solution of 0.5 g (0.71 mmol) of dimer **26** and 0.25 g (6.3 mmol) of sodium hydroxide in 75 mL of ether, 50 mL of methanol, and 12.5 mL of water was stirred at room temperature for 12 h. The NMR spectrum of the residue, on workup, contained broad absorption in the region δ 0.0–0.17, a singlet at 4.03 ppm, and a multiplet in the aromatic proton region: IR 5.94 (C=O), 9.0–9.6 (SiOC) μ. Recrystallization of the residue from ethanol gave 0.12 g (86%) of benzyl phenyl ketone identified by its NMR and infrared spectra and mixture melting point.

Thermal Decomposition of Dimer 26 in Methanol. A solution of 0.38 g (0.54 mmol) of dimer **26** and 4 mL of methanol in 20 mL of THF was refluxed for 24 h under nitrogen. The NMR spectrum of the residue indicated that **19** (R = Ph) was formed in 76% yield, based on the relative intensities of absorptions. The major product, isolated by column chromatography with benzene on silica gel, had spectra identical with those of **19** obtained by photolysis.

Similarly, the major product of the thermal decomposition of dimer **26** in THF containing MeOD was found to be identical with the product of the photolysis of benzoyltris(trimethylsilyl)silane in MeOD.

In a control experiment, 0.4 g (0.57 mmol) of dimer **26** in 20 mL of THF was refluxed for 24 h. Removal of the solvent gave recovered starting material.

Photolysis of Benzoyltris(trimethylsilyl)silane (7) with 2,3-Dimethyl-1,3-butadiene. A solution of 0.5 g (1.4 mmol) of benzoylpolysilane **7** and 0.50 mL (4.4 mmol) of 2,3-dimethyl-1,3-butadiene in 25 mL of ether at 10 °C was irradiated until the yellow color disappeared (30 min). The NMR spectrum of the residue indicated 27% of dimer **26** and 30% of the 1-silacyclohex-3-ene **22**, as well as broad absorptions in the regions δ −0.17 to 0.33 and 1.00–2.20 ppm due to undetermined products. Chromatography with pentane on silica gel gave 0.09 g (15%) of the 1-silacyclohex-3-ene, with identical spectra with those of **22** isolated from the thermal decomposition of dimer **26**.

Photolysis of Acetyltris(trimethylsilyl)silane (8) in Ether. Acetylpolysilane **8** (0.5 g, 1.72 mmol) in 80 mL of ether at 10 °C was irradiated for 1.5 h. After removal of the solvent chromatography with pentane on Florisil gave 0.37 g (74%) of 2,5-bis(trimethylsiloxy)-3,3,4,4-tetrakis(trimethylsilyl)-3,4-disilahex-1-ene (**29**). Owing to signal overlap, the NMR spectrum of **29** in benzene contained only four trimethylsilyl proton signals with relative intensities of 1:3:1:1; in cyclohexane, five signals, 1:2:1:1:1, were observed.

A mixture of 0.37 g (0.64 mmol) of dimer **29**, 0.10 g (1.9 mmol) of ammonium chloride, 0.15 mL (1.9 mmol) of pyridine, and 0.1 mL (5.6 mmol) of water in 20 mL of acetone and 10 mL of methanol was refluxed in the dark for 18 h. After aqueous workup chromatography with pentane on silica gel gave 0.17 g (52%) of 1-acetyl-2-(1-trimethylsiloxyethyl)-1,1,2,2-tetrakis(trimethylsilyl)disilane (**30**), mp 107–109 °C; the NMR spectrum (benzene) contained only three trimethylsilyl proton signals with relative intensities of 1:3:1. In acetone, four signals were obtained with relative intensities of 2:1:1:1.

Addition of Methanol to a Pivaloyltris(trimethylsilyl)silane (9)–Ether Photolysis Solution. A solution of 0.5 g (1.5 mmol) of **9** in 5 mL of ether was irradiated at about 10 °C over 14 h, by which time infrared spectra indicated the near absence of starting material. After the light source was turned off, 1 mL of methanol was added to the solution which was stirred in the dark at 20 °C for 2 h. The workup and chromatography on silica gel (pentane) gave 0.22 g (40%) of silaethylene-methanol addition product **19** identical with the **19** derived by direct photolysis in methanol.

NMR Spectra of Pivaloyltris(trimethylsilyl)silane Photolysis Solutions. Sealed NMR tubes containing degassed 0.15 M solutions of **9** in toluene, benzene, and tetramethylsilane were cooled to about 10 °C and irradiated until most of the starting material had been consumed (about 8 h), and the NMR spectra of the resulting pale yellow solutions were recorded at ambient temperature (see Discussion). After the solutions were cooled at −17 °C for 24 h, during which time the pale yellow color disappeared, the NMR spectra of the solutions were recorded immediately, and at 5-min intervals, for a period of 40 min, as the solutions warmed to room temperature, during which time the yellow color returned. Spectra were run periodically over 2 weeks (see Discussion). Pure **9** was obtained from the NMR tubes, after removal of the solvents, by chromatography with pentane on silica gel.

Three sealed NMR tubes which contained 0.036, 0.18, and 0.90 M solutions of **9** in benzene were cooled to about 10 °C and irradiated until most of the starting material was consumed. From the intensities of the signals in the NMR spectra of the photolysis solutions, it was determined that the ratios of silaethylene to dimer **27** were 10:1, 4:1, and 1.3:1, respectively.

NMR spectra of silaethylene **23** (R = CMe_3): δ (C_6H_6) 1.25 (9 H, s, Me_3C), 0.39 (9 H, s, Me_3Si), 0.34 (9 H, s, Me_3Si), 0.28 (9 H, s, Me_3Si) ppm; δ ($C_6H_4CH_3$) 1.23 (9 H, s, Me_3C), 0.36 (9 H, s, Me_3Si), 0.33 (9 H, s, Me_3Si), 0.28 (9 H, s, Me_3Si) ppm; δ (Me_4Si) 1.12 (9 H, s, Me_3C), 0.27 (9 H, s, Me_3Si), 0.26 (9 H, s, Me_3Si), 0.22 (9 H, s, Me_3Si) ppm.

NMR spectra of dimer **27**: δ (C_6H_6) 1.60 (6 H, s, 2MeC), 1.30 (6 H, s, 2MeC), 1.22 (6 H, s, 2MeC), 0.49 (18 H, s, $2Me_3Si$), 0.46 (18 H, s, $2Me_3Si$), 0.36 (18 H, s, $2Me_3Si$) ppm; δ ($C_6H_6CH_3$) 1.53 (6 H, s, 2MeC), 1.24 (6 H, s, 2MeC), 1.17 (6 H, s, 2MeC), 0.45 (18 H, s, $2Me_3Si$), 0.43 (18 H, s, $2Me_3Si$), 0.34 (18 H, s, $2Me_3Si$) ppm; δ (Me_4Si) 1.59 (6 H, s, 2MeC), 1.22 (12 H, s, 4MeC), 0.42 (18 H, s, $2Me_3Si$), 0.38 (18 H, s, $2Me_3Si$), 0.31 (18 H, s, $2Me_3Si$) ppm.

Isolation of Dimer 27. A solution of 0.50 g (1.5 mmol) of **9** in 5 mL of pentane, cooled in a dry ice–carbon tetrachloride bath, was irradiated under nitrogen for 24 h, during which the solution became pale yellow. The solution was placed in a freezer at −17 °C for 14 h, during which time the pale yellow color had disappeared. Part of the pentane was removed from the solution by evaporation under vacuum and the residue was cooled to −80 °C under nitrogen. Dry acetone (5 mL) was added to the residue and a white precipitate formed during 14 h in a freezer. Recrystallization from cold pentane–acetone gave 0.23 g (46%) of dimer **27**, mp 85–86 °C dec. This experiment was difficult to reproduce. The mass spectrum of the dimer did not contain a signal corresponding to its molecular ion at *m/e* 664 and only a few signals of very low intensity were obtained above *m/e* 332: *m/e* 332 $[M/2]^+$, 1%; 317 $[M/2\text{-}Me]^+$, 11%; 259 $[M/2\text{-}Me_3Si]^+$, 17%; 73 $[Me_3Si]^+$, base peak.

Decomposition of Dimer 27 in Methanol. A 0.25-g (0.38 mmol) sample of dimer **27** in 16 mL of THF and 4 mL of methanol was stirred for 2 h. The solvent was removed and chromatography with pentane on silica gel gave 0.13 g (47%) of the silaethylene–methanol addition product **19** (R = CMe_3), identical with the product derived by photolysis.

Ultraviolet Spectra of the Products of the Photolysis of Pivaloyltris(trimethylsilyl)silane (9) in Hexane. A. Intensity of the Absorption. A sealed quartz cell containing a degassed 8.22×10^{-4} M solution of **9** in hexane had λ_{max} 366 nm (ϵ 127). After irradiation for 1 min its ultraviolet spectrum showed intense absorption at λ_{max} 339 nm which obscured the longest wavelength absorption of **9**. After the contents of the cell were exposed to air, the absorption at 339 nm rapidly disappeared over 5 min, and the intensity of the absorption at 366 nm was slightly lower than before the irradiation: estimated from several runs ϵ 5200 ± 100.

B. Temperature Dependence of the Ultraviolet Absorption Spectrum of the Photolysis Product. The UV spectrum of a degassed 8.22×10^{-4} M solution of **9** in hexane after irradiation for 1 min was recorded as above: absorbance 1.29 at λ 339 nm. After 24 h at −17 °C, its absorbance immediately was 1.16 at λ 339 nm. Several repetitions of this experiment afforded similar results.

Similarly, a degassed 0.15 M solution of **9** in hexane, sealed in a Pyrex cell, was irradiated at 15 °C for 7 h, and then its ultraviolet spectrum was recorded. After 24 h at −17 °C the ultraviolet spectrum was recorded immediately after it was removed from the cold and then at 5-min intervals over a 30-min period. The long-wavelength tail of the intense absorption at 339 nm had shifted to shorter wavelength during cooling, and it gradually moved to longer wavelengths as the solution warmed to room temperature until it almost reached its original position.

Infrared Spectra of the Pivaloyltris(trimethylsilyl)silane (9) Photolysis Products. A. Under N_2, a solution of **9** in pentane was applied to a sodium chloride disk and the pentane was allowed to evaporate under nitrogen leaving a thin deposit of **9** which was covered with another sodium chloride disk. The edges of the disks were sealed with Parafilm and the infrared spectrum of the material was recorded. The material was irradiated at ambient temperature for 90 min and the infrared spectrum of the material between the disks was then recorded (see Discussion).

The above experiment repeated with a small amount of diphenylmethane present as a standard for intensity measurement gave similar observations.

B. A sodium chloride cavity cell containing 0.5 mL of a 0.1 M solution of **9** in benzene was fitted to a Pyrex tube, which was sealed after being flushed with nitrogen. After the infrared spectrum was recorded, the tube and cavity cell were inverted and the solution contained in the Pyrex tube was irradiated for 4 h in a cold water bath. The infrared spectrum of the resulting pale yellow solution showed the absorptions of the starting material at 6.17, 7.65, and 10.75 μ to be considerably reduced whereas the $\text{-}SiMe_3$ absorptions at 8.00 and 12.00 μ underwent little change in intensity. The absorption of the solutions at 9.80 μ increased after irradiation and a new strong absorption appeared at 8.90 μ.

^{13}C NMR Spectrum of Pivaloylsilane 9 Photolysis Products. The fully and partially decoupled ^{13}C spectra of the products of the photolysis of pivaloyltris(trimethylsilyl)silane (**9**) and of **9** itself were

Table VII. Chemical Shifts and Coupling Constants for the Signals of the Products of the Photolysis of 9 in C_6D_6

compd	signal	M^a	$\delta(Me_4Si)$,[b] ppm	$J_{C,H}$, Hz
pivaloylsilane 9	a^1 *C*=O	s^c	246.3	
	a^2 CMe$_3$	s	49.2	
	a^3 C-*C*H$_3$	q	24.9	131
silaethylene **23**	b^1 C=Si	s^c	112.7	
(R = Me$_3$C)	b^2 CMe$_3$	s	41.8	
	b^3 C-*C*H$_3$	q	31.2	133
dimer **27**	c^1 C(ring)	s^c	43.1	
	c^2 *C*-Me$_3$	s^d	41.8	
	c^3 C-Me^1	q.	35.9	131
	c^4 C-Me^2	q	33.1	136
	c^5 C-Me^3	q	28.8	133

[a] Multiplicity in partially decoupled spectra. [b] $\delta(Me_4Si) = 128.0 + \delta(C_6D_6)$. [c] Low intensity, due to nuclear Overhauser effect[30] or long relaxation time. [d] Presumed to overlap b^2 signals: alkene and alkyl substituents have similar effects on ^{13}C chemical shifts.[31]

recorded on a Varian XL-100 instrument in the FT mode, using degassed 1.0 M solutions in C_6D_6 in order to try to detect the resonance of the unsaturated carbon of the silaethylene photolysis product **23** (R = Me$_3$C). The chemical shifts and ^{13}C-H coupling constants for the signals in the spectra are listed in Table VII.

The high-field trimethylsilyl carbon signals in the spectra could not be unambiguously assigned. A maximum of seven signals could have been produced in this region by the components of the photolysis solution, one signal from the starting material, three signals from the silaethylene, and three signals from dimer **27**, and six signals were actually observed. Signal overlap most likely accounts for the detection of fewer than the theoretical number of trimethylsilyl carbon signals.

ESR Spectra. The spectra were obtained using sealed ESR tubes containing solutions of acylsilanes, or other species which had been degassed by means of three freeze-thaw cycles.

ESR Spectra of Pivaloyltris(trimethylsilyl)silane (9) **Photolysis Solutions.** Some experiments have been described in the Discussion section. Two ESR tubes containing degassed 0.23 M solutions of 9 in pentane were irradiated at about 10 °C for 6 h and then ESR spectra were recorded. One tube was placed in a freezer at −17 °C and the other tube was stored in the dark at room temperature. The intensity of the signal from a tube kept in the dark for 16 h had decayed to 75% of its original intensity. The intensity of the ESR spectrum of the sample stored in a freezer at −20 °C for 24 h was found to be about the same as before cooling.

An ESR tube containing a degassed 0.15 M solution of 9 in 1:1 ether-tetrahydrofuran was irradiated for about 6 h at 10 °C and the ESR spectrum was recorded at ambient temperature. The sample tube was then cooled to 77 K in the ESR probe and the ESR spectra of the products in the organic glass[32] were determined. After the sample was allowed to warm to room temperature, its ESR spectrum was identical with that obtained previously.

Thermolysis of Pivaloyltris(trimethylsilyl)silane (9) **in Alcohols.** The following is a typical procedure for the thermolyses summarized in Table IV. A frozen 0.2-g sample of 9 in 1 mL of dry isopropyl alcohol was sealed off under vacuum, and then heated at 180 °C for 20 h. The tube was opened, excess alcohol was removed under reduced pressure, and the residue was analyzed by GLC (SE-30 on Chromosorb W at 200 °C). One major peak, 88% of the total material, was collected and identified as 1-(isopropoxybis(trimethylsilyl)silyl)-1-trimethylsiloxy-2,2-dimethylpropane (**31**, R = Me$_2$CH). Crystalline material, 0.1 g (42%), was isolated with mp 97–98 °C.

Acknowledgment. The authors are grateful to the National Research Council of Canada for support of this research, and to Professor Colin Eaborn and the School of Molecular Sciences, University of Sussex, where some of the ESR work was done while A.G.B. was on sabbatical leave.

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