Photolysis of Diazo(pentamethyldisilanyl)methyl Ketones in the Presence of Carbonyl Compounds: Trapping of the Acylsilene Intermediates☆

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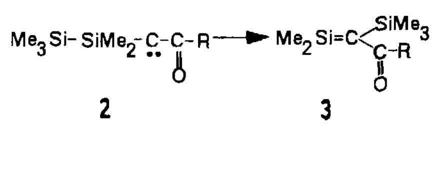
UV photolysis of diazo(pentamethyldisilanyl)methyl ketones **1b**–**d** generates acylsilenes (3-oxo-1-sila-1-propenes) **3** as reactive intermediates, which can be trapped by enolizable carbonyl compounds in an ene-type reaction. With non-enolizable carbonyl compounds or ethyl acetate, they undergo a [4 + 2] cycloaddition. In contrast to the photolysis in the absence of these carbonyl compounds, a Wolff rearrangement of **1b**–**d** (or the derived carbenes) to silyl ketenes **5b**–**d** is observed as a competitive reaction.

Acylsilenes (3-oxo-1-sila-1-propenes) **3** are reactive intermediates, which can be generated from pentamethyldisilanyl-substituted diazocarbonyl compounds **1** on the carbene route. In the absence of trapping reagents, subsequent reactions of **3** take place. Thus, photolysis of **3a**–**d** in benzene yields cyclic isomers (of **3a,b**) of [4 + 4] cyclodimers (of **3c,d**) as the major products[1,2]. An acylsilene→silylketene rearrangement is the exclusive reaction pathway in both gas-phase thermolysis and solution photolysis of ethyl diazo(pentamethyldisilanyl)acetate (**1e**)[3]. In general, silaethenes readily react with various kinds of carbonyl compounds[4]. 3-Silaacrylate **3e** is no exception since it can be trapped by enolizable (ene reaction[3,5]) and non-enolizable ketones ([4 + 2] cycloaddition[6], [2 + 2] cycloaddition followed by fragmentation of the 1,2-silaoxetanes thus formed[3,5]); however, the rearrangement to a silylketene remains the dominant reaction pathway. On the other hand, the fast cyclization of adamantyl-substituted acylsilene **3a** prevents any intermolecular reaction with carbonyl compounds such as acetone and benzophenone[1b,2].

In this paper, we show that the behavior of **3a** is an exception, since acylsilenes **3b**–**d** can be trapped by both enolizable and non-enolizable carbonyl compounds.



$$\underset{\mathbf{1}}{Me_3Si{-}SiMe_2{-}\underset{\underset{N_2}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}R} \xrightarrow[-N_2]{h\nu}$$

$$\underset{\mathbf{2}}{Me_3Si{-}SiMe_2{-}\underset{\cdot\cdot}{C}{-}\underset{\underset{O}{\|}}{C}{-}R} \longrightarrow \underset{\mathbf{3}}{Me_2Si{=}C(SiMe_3){-}\underset{\underset{O}{\|}}{C}{-}R}$$

1-3	a	b	c	d	e
R	Ad[a)]	tBu	iPr	Me	OEt

a) Ad = 1-adamantyl

Results

Photolysis of diazo compounds **1b**–**d** in acetone yields the siloxyalkenes **6a,c,d** as major products (Scheme 1, Table 1). Their formation is rationalized as an ene-type reaction between acylsilenes **3** and the enolizable ketone. Notably, the cyclization of **3b** (→ **8b**), or cyclodimerization of **3c,d** (→ **12c,d**), is largely (or totally) suppressed in acetone, in contrast to the photolyses in benzene (see above). Only in the crude product mixture from **1c**, a small amount of **12c** is detected by its characteristic[1a] ^{1}H-NMR signals; this thermolabile[1] compound does not survive the workup conditions, however.

In all photolysis mixtures, ketenes (IR: 2075–2080 cm^{-1}) are formed as byproducts, which can be isolated by distillation in a low-boiling fraction. Because of silicon-containing impurities, the constitution of the ketenes cannot be established unequivocally from the ^{13}C-NMR data. Therefore, they have been converted into carboxylic esters which, according to their ^{1}H- and ^{13}C-NMR spectra, clearly have the constitution of **10** rather than **13**. The multiplicity of the signals[7] of 2-H and 3-H (in **10c,d**) as well as the chemical shift of the *ipso*-C atom of group R (which would be at a lower δ value if bound to silicon) are the most significant hints to this assignment. Esters **10** are derived from ketenes **5**, the products expected to be formed from a Wolff rearrangement of either **1** or **2**, rather than from the isomeric ketenes **9**, the rearrangement products of acylsilenes **3**. Whereas ketene **9d** has been identified definitely as a product of the photolysis of **1d** in benzene, photolysis of **1b**–**d** in acetone triggers the formation of ketenes **5**[8].

In the presence of acetophenone, acylsilenes **3b,d** can also be trapped in an ene-type reaction, and siloxyalkenes **6b,e** are obtained. Compound **6b** is partially hydrolyzed during chromatographic workup; unfortunately, we have not succeeded in removing the resulting disiloxane **11b** from **6b**. In order to identify **11b** unambiguously by its NMR signals, it has been synthesized independently by hydrolytic cleavage

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Scheme 1

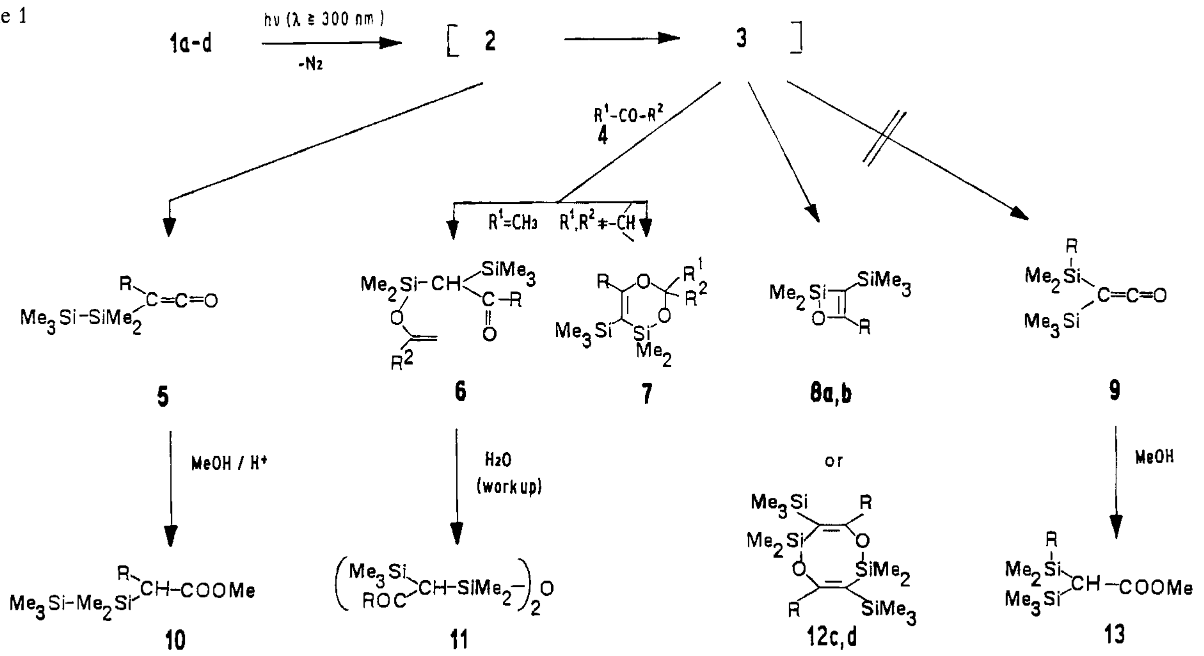


Table 1. Products and yields for reactions of Scheme 1

1 R	4 R¹	R²	Solvent/ [4]:[1]	Products (yield [%])[a]			
*t*Bu (**1b**)	Me	Me	[b]	**6a** (41)		[c]	
	Me	Ph	benzene/ 3:1	**6b** (≤42)[d]		[c]	
*i*Pr (**1c**)	Me	Me	[b]	**6c** (43)		**10c** (23)	**12c**[e]
	Ph	Ph	benzene/ 11:1		**7a**[f]	[c]	**12c** (>23[f])
	H	(*E*)- MeCH=CH	benzene/ 33:1		**7b** (36[g])	**10c** (9)	
	Me	OEt	[b]		**7c** (28)	**10c** (48)	
Me (**1d**)	Me	Me	[b]	**6d** (67)		**10d** (29)	
	Me	Ph	benzene/ 3:1	**6e** (41)		[c]	**12d** (51)
	Me	OEt	[b]		**7d**[h]	**10d** (36)	

[a] Yields are given for isolated products; attempts to analyze the reaction mixtures directly by analytical HPLC (Merck columns, LiChrospher SI-60, LiChrospher 100CN, LiChrospher 100RP-18, 5 µm) proved unsuccessful. — [b] Carbonyl compound as solvent. — [c] Small amounts of a ketene were detected by IR (2075–2080 cm^{-1}) in the product mixture, but were not isolated. — [d] Accompanied by varying amounts of a hydrolysis product (**11b**). — [e] Detected by ^{1}H NMR as a minor product in the reaction mixture, but not isolated. — [f] Besides pure **12c** (23%) an unseparable mixture of **7a**/**12c** was obtained. Because of extensive loss of material during purification by column chromatography, true yields cannot be given. — [g] Accompanied by an unidentified compound (6%). — [h] See text.

of **8b** in wet acetone. Small amounts of a ketene are detected by IR spectroscopy of the reaction mixtures obtained from **1b,d**, but are lost during workup. As before, it is assumed that ketenes **5b,d** are formed once again.

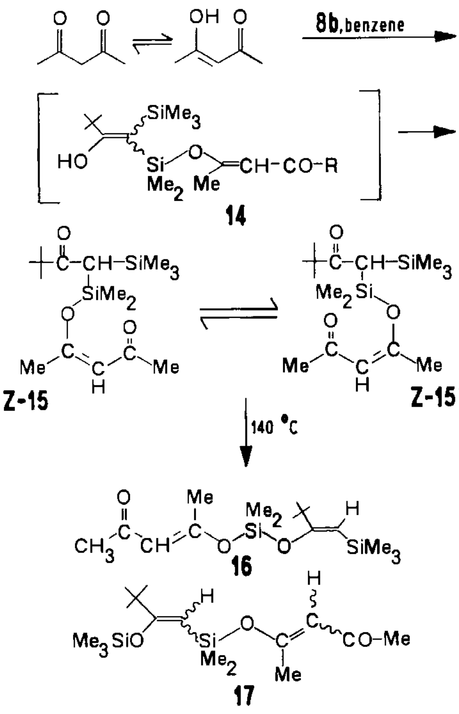
The formation of the acylsilene cyclodimer **12d** cannot be totally suppressed if **1d** is photolyzed in the presence of three equivalents of acetophenone. With a larger excess of the ketone, however, chromatographic separation of the products from excess ketone becomes increasingly difficult if not impossible.

With non-enolizable carbonyl compounds such as benzophenone and crotonaldehyde, acylsilene **3c** undergoes a [4 + 2] cycloaddition to form the rather moisture-sensitive heterocyclic compounds **7a,b** (Table 1). Similarly, **3c** is trapped by ethyl acetate to form **7c**. The analogous cycloadduct **7d** is detected by NMR spectroscopy as a minor component of the product mixture from **1d** and ethyl acetate, but cannot be obtained in a pure state; it is possible that this compound partly decomposes by extrusion of $Me_2Si=O$ on attempted Kugelrohr distillation at 65 °C[1a]. Furthermore, we have not succeeded in isolating the pure cycloadduct **7a**, since the acylsilene cyclodimer **12c** — formed to a considerable extent in spite of a large excess (11:1) of benzophenone — cannot be separated completely. The nature of **7a–c** follows from IR [absence of $\nu(C=O)$] as well as from ^{13}C-NMR data [δ(C-5) = 95.2–97.0, δ(C-

6) = 175.3–178.8, δ(C-2) = 101.3 (**7a**), 94.7 (**7b**), 113.2 (**7c**)]. With ethyl acetate as the trapping reagent for **3c,d**, the [4 + 2] cycloaddition is less efficient than the formation of ketenes **5c,d**, but with the carbonyl compounds mentioned, it becomes the major pathway.

1-Oxa-2-sila-3-cyclobutene **8b** has not been detected among the photolysis products of **1b** in the presence of acetone or acetophenone. Since the Si–O bond of **8b** is readily cleaved by alcohols[1a], the possibility exists that siloxyalkenes **6a,b** result from a similar ring cleavage of **8b** by the enols of both ketones. However, a control experiment shows that **8b** is stable in *dry* acetone. Therefore, it seems clear that **6a,b** are direct trapping products of the respective acylsilenes **3**. On the other hand, **8b** does react smoothly with acetylacetone in benzene solution. By a ring cleavage process analogous to the one with alcohols, silylenol ether **15** is formed, probably via enol **14** (Scheme 2). According to the ^{1}H- and ^{13}C-NMR spectra, only the (*Z*) diastereomer is present. Magnetic equivalence of both methyl groups and of both C(O) atoms of the acetylacetonate subunit points to a fast degenerate rearrangement (*Z*)-**15** $\rightleftharpoons$ (*Z*)-**15′**, which is caused by a rapid 1.5(O→O′) silyl shift and proceeds most likely through an intermediate in which the migrating silicon atom is pentacoordinated. Similar silatropic equilibria have been observed earlier for other *O*-silyl acetylacetonates[9–12]. The exclusive formation of the (*Z*) isomer of **15** is surprising, since (*E*) isomers of such compounds are known to be thermodynamically more stable and a slow (*Z*)→(*E*) isomerization usually takes place already at room temperature within several days[9,10]. Attempts to accelerate this isomerization have ultimately led to a ketosilane→siloxyalkene isomerization[13] which is complete after 2 h at 140°C. After distillation, only one compound is obtained to which structure **16** is assigned. In particle, either the Me$_3$Si or the Me$_2$SiOR group in **15** can undergo the 1,3(C→O) shift. Considering the fact that such intramolecular rearrangements most likely proceed through pentacoordinated silicon intermediates[13] and that pentacoordination at silicon is stabilized by electronegative substituents such as N, O, Hal[14], we have anticipated siloxyalkene **16** rather than **17** to be formed. In fact, the ^{29}Si-NMR spectrum shows signals at $\delta = -10.9$ and -11.1. These values corroborate structure **16**, since the typical values for trimethylvinylsilanes are $\delta \approx -5$ to -12[15,16], and Me$_2$Si(OPh)$_2$, as a model for Me$_2$Si($-$O$-$C$_{sp^2}$)$_2$, shows $\delta(^{29}\text{Si}) = -6.1$[16]. For **17**, on the other hand, we would expect $\delta(\text{Me}_3Si-\text{O}-\text{C}=\text{C}) \approx 16 \pm 2$[17] and $\delta(\text{O}-Si\text{Me}_2-\text{C}=\text{C})_2 \approx -1 \pm 4$[18]. The configuration of the acetylacetonate C=C bond in **16** is (*E*), since the methyl groups and the C(O) carbon atoms are not equivalent in the NMR spectra; for the (*Z*) configuration we would expect a fast, degenerate 1,5(O→O) silyl shift as in (*Z*)-**15** $\rightleftharpoons$ (*Z*)-**15′**, and hence time-averaged signals. Furthermore, the chemical shift of the vinylic proton in the acetylacetonate subunit (δ = 5.7) is closer to the value found in (*E*)-O-trimethylsilyl acetylacetonate[9] [(*E*)-form: δ = 5.47; (*Z*)-form: δ = 5.19). The (*Z*)-configuration of the second double bond in **16** has been established by a NOE experiment; saturation of the ^{1}H NMR signal of *t*Bu produces a 20% enhancement of the =CH resonance at δ = 4.52.

Scheme 2



Discussion

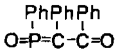
The preceding results show that acylsilene intermediates **3b–d** may be trapped by carbonyl compounds. In the presence of a sufficient excess of the latter, the reactions occurring in the absence of a suitable trapping reagent, i.e. cyclization of **3b** or cyclodimerization of **3c,d**, are suppressed completely or at least to a large extent. With enolizable ketones (acetone, acetophenone), the Si=C bond of **3b–d** undergoes an ene-type reaction leading to silylenol ethers **6**; this reflects the normal behavior of silenes having a "naturally" polarized Si=C bond[4a,19–21], including acylsilene **3e**[3,5]. Towards ethyl acetate and non-enolizable carbonyl compounds, acylsilenes **3c,d** behave as 4-π systems in a nominal [4 + 2] cycloaddition. So far, this reaction mode of an acylsilene has only been reported for the combination of **3e** with 7-norbornanone[6]. Normally, the Si=C bond of **3e** as well as those of non-conjugated silenes undergo a nominal [2 + 2] cycloaddition with non-enolizable carbonyl compounds to form 1,2-siloxetanes, which in many cases decompose spontaneously to an alkene and a silanone[3–5], but can be isolated in certain other cases[20b,22–24]. Another well-known reaction between Si=C and an aryl ketone, namely [2 + 4] cycloaddition[20b,23,24], cannot be observed either for acylsilenes **3b–d**. Furthermore, the [4 + 2] cycloaddition between **3c** and the carbonyl group of ethyl acetate had not been expected, since Me$_2$Si=C(SiMe$_3$)$_2$ reacts with ethyl acetate exclusively by an ene reaction[20b].

In summary, acylsilenes **3b–d** behave as 2-π systems (Si=C) towards enolizable carbonyl compounds, but as 4-

π systems towards non-enolizable ones. For comparison, 1-sila-1,3-butadiene **18**, another conjugated silene, but with a less polarized 4-π system, reacts with acetone under photochemical conditions to give a [4 + 2] cycloadduct rather than an ene-reaction product[25]. Another interesting comparison concerns a phosphorus analog of **3b–d**, namely the reactive intermediate **19**. This species yields only [4 + 2] cycloadducts with both enolizable and non-enolizable (including α,β-unsaturated) carbonyl compounds; in the absence of trapping partners, it forms nominal [4 + 4] cyclodimers analogous to **12**[26].

$Me_2Si{=}C(Ph){-}CH{=}CH_2$

18



$\overset{Ph}{O{=}P}{=}\overset{Ph}{C}{-}\overset{Ph}{C}{=}O$

19

Formation of ketenes **5b–d**, identified (**5c,d**) by their derived esters **10c,d**, comes as a surprise. For **1c,d**, this reaction path is followed to a considerable extent, when the photolysis is carried out in acetone or ethyl acetate. In contrast, photolysis of **1b–d** in benzene is dominated by subsequent reactions of acylsilenes **3**, and no hints to ketenes **5** have been obtained[1]. The direct conversion of acylsilenes **3** into ketenes **5** under the influence of added carbonyl compounds is most unlikely. Thus, we must conclude that these ketenes result from a Wolff rearrangement which originates either from an excited singlet state of diazo compounds **1** or from the singlet state of carbenes **2**[27]. The presence of benzophenone or acetophenone, representing typical sensitizers for triplet reactions of diazo compounds or the derived carbenes, is expected to suppress reactions of the singlet manifold. However, we have not optimized the reaction conditions (molar excess of sensitizer, wavelength of irradiation) so as to ensure that an excited singlet state of **1** is totally circumvented. For carbene **2**, rapid triplet→singlet intersystem crossing could provide singlet reactions even under conditions where the triplet state is populated in the first place[28,29].

According to Tomioka et al.[29], the Wolff rearrangement of an excited singlet state of a diazocarbonyl compound is controlled by the conformation at the $C(N_2)-C(=O)$ bond. Accordingly, the rearrangement of **1** should occur in the (*s*-*E*) conformation, i.e. with the N_2 and R substituents in a *trans* relationship. For steric reasons, this conformation becomes increasingly unfavorable in the sequence **1d** < **1c** < **1b**. This fact correlates with the observation of only traces of a ketene in the photolyses of **1b**.

Notwithstanding the preceding basic considerations, it is not obvious how the presence of a carbonyl compound should favor the Wolff rearrangement of either diazo compounds **1** or carbenes **2** at the expense of the carbene→silene rearrangement (**2**→**3**). Further investigations are needed to clarify this problem.

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Experimental

IR: Perkin-Elmer IR 397. – ^1H NMR: Varian EM 390 (90 MHz), Bruker WP 200 (200 MHz), Bruker AM 400 (400 MHz); internal standard TMS (δ = 0) or $CHCl_3$ (δ = 7.24). – ^{13}C NMR: Bruker WP 200 (50.28 MHz), AM 400 (100.56 MHz); internal standard $CHCl_3$ (δ = 77.0) or C_6H_6 (δ = 128.5). – ^{29}Si NMR: Bruker AM 400 (79.5 MHz), TMS as internal standard. The solvent used for all NMR spectra was $CDCl_3$ if not stated otherwise. – Elemental analyses: Perkin-Elmer EA 2400. – The experimental values for some products described below are not satisfactory. This is due to one or more of the following facts: the moisture sensitivity of compounds **6** and **7**; the failure to remove side-products and impurities completely by Kugelrohr distillation; the limited usefulness of column chromatography for product purification because of hydrolysis, incomplete or no separation, extensive loss of material on the column.

All reactions were carried out in dried solvents under argon, using rigorously dried glassware. – Photolyses: Pyrex glass, high-pressure mercury lamp (Philips HPK 125 W). – Column chromatography: Merck Lobar columns, LiChroprep Si-60, 40–63 μm. – Synthesis of diazo ketones **1b–d**: ref.[1a]

Photolyses of 1b–d *in the Presence of Carbonyl Compounds*

1b *and Acetone:* A solution of **1b** (2.36 g, 9.20 mmol) in acetone (50 ml) is irradiated for 3 h (100% N_2 evolution). The solvent is evaporated at 12 Torr, and the residue is fractionated by Kugelrohr distillation. Some volatile products, including a ketene, are removed at 30°C/0.01 Torr. Further distillation at 95°C/0.01 Torr yields 1.08 g (41%) of *1-[dimethyl(1-methylvinyloxy)silyl]-3,3-dimethyl-1-(trimethylsilyl)-2-butanone* (**6a**), b.p. 95°C/0.01 Torr. – IR (film): $\tilde{\nu}$ = 1655 cm^{-1} (C=O). – ^1H NMR: δ = 0.08 ($SiMe_3$), 0.12/0.18 (diastereotopic $SiMe_2$), 1.08 (*t*Bu), 1.73 (=CMe), 2.90 (CH), 4.00/4.06 (=CH_2).

$C_{14}H_{30}O_2Si_2$ (286.6)	Calcd.	C 58.68	H 10.55
	Found	C 57.9	H 10.24

1b *and Acetophenone:* A solution of **1b** (1.16 g, 4.52 mmol) and acetophenone (1.65 g, 13.73 mmol) in benzene (50 ml) is irradiated for 3 h (100% N_2 evolution). The solvent is removed at 15°C/0.5 Torr, and the residue is fractionated by Lobar column chromatography (ether/petroleum ether, 1:9 v/v). A fraction (0.10 g) which contains a ketene (IR: $\tilde{\nu}$ = 2080 cm^{-1}) and other products is eluted first. The second fraction is an unseparable mixture (0.67 g) of *1-[dimethyl(1-phenylvinyloxy)silyl]-3,3-dimethyl-1-(trimethylsilyl)-2-butanone* (**6b**) and, in different runs, varying amounts of **11b** (identified by NMR comparison with an authentic sample, see below). Attempted distillation resulted in decomposition at ca. 140°C. – Spectroscopic data for **6b**: – IR (film): $\tilde{\nu}$ = 1645 cm^{-1} (vs, C=O), 1610 (m), 1255 (vs). – ^1H NMR (400 MHz): 0.15 ($SiMe_3$), 0.30/0.34 (diastereotopic $SiMe_2$), 1.12 (*t*Bu), 3.05 (s, CH), 4.43/4.91 (AB system, $|^2J|$ = 1.8 Hz, =CH_2), 7.28–7.56 (m, Ph). – ^{13}C NMR (100.6 MHz): δ = 0.42/0.71 ($SiMe_2$), 0.87 ($SiMe_3$), 27.51 (CMe_3), 37.36 (CH), 44.98 (CMe_3), 91.96 (=CH_2), 155.17 (OC=), 215.81 (C=O).

1,3-Bis[3,3-dimethyl-2-oxo-1-(trimethylsilyl)butyl]-1,1,3,3-tetramethyldisiloxane (**11b**): Wet acetone (1 ml) is added to a solution of **8b** in benzene (50 ml), obtained[1b] by photolysis of **1b** (1.25 g, 4.87 mmol). After 5 h, the solvent is evaporated, and the residual oil is dissolved in pentane. At –78°C, colorless crystals of **11b** (0.49 g, 42%) are obtained, m.p. 73°C. – IR (KBr): $\tilde{\nu}$ = 1645 cm^{-1} (vs, C=O), 1245 (vs), 1195 (s), 1045 (s), 1025 (s). – ^1H NMR (400 MHz): δ = 0.10 ($SiMe_3$), 0.14/0.23 ($SiMe_2$), 1.09 (*t*Bu), 2.75 (s, CH).

– ^{13}C NMR (100.6 MHz): δ = 1.02 (SiMe$_3$), 2.62/3.19 (SiMe$_2$), 27.65 (C*Me*$_3$), 38.47 (CH), 44.73 (*C*Me$_3$), 215.84 (C=O).

$C_{22}H_{50}O_3Si_4$ (475.0) Calcd. C 55.63 H 10.61
Found C 54.2 H 10.8

1c *and Acetone:* A solution of **1c** (1.45 g, 5.98 mmol) in acetone (50 ml) is irradiated for 2 h (100% N_2 evolution). The solvent is evaporated at 15°C/0.5 Torr, and the residue is subjected to Kugelrohr distillation.

a) A fraction boiling at 30°C/0.01 Torr is treated with methanol (3 ml) and conc. HCl (2 drops) for 2 h. Kugelrohr distillation yields 0.34 g (23%) of *methyl 3-methyl-2-(pentamethyldisilanyl)butanoate* (**10c**) as a colorless oil, b.p. 95°C/0.07 Torr. – IR (film): $\tilde{\nu}$ = 1715 cm^{-1} (C=O). – ^{1}H NMR (400 MHz): δ = 0.095 (SiMe$_3$), 0.097/0.100 (SiMe$_2$), 0.97/0.99 (each 3H, d, CH*Me*$_2$), 1.89 (d, 2H, 2-H, ^3J = 10 Hz), 2.13 (m, 1H, 3-H), 3.62 (s, OMe). – ^{13}C NMR (100.6 MHz): δ = −4.23/−3.28 (SiMe$_2$), −1.70 (SiMe$_3$), 11.72/12.54 (CH*Me*$_2$), 28.73 (C-3), 45.01 (C-2), 50.68 (OMe), 175.69 (C=O).

$C_{11}H_{26}O_2Si_2$ (246.5) Calcd. C 53.60 H 10.63
Found C 52.7 H 10.1

b) 0.69 g (43%) of *1-[dimethyl(1-methylvinyloxy)silyl]-3-methyl-1-(trimethylsilyl)-2-butanone* (**6c**), b.p. 95°C/0.03 Torr, colorless oil. – IR (film): $\tilde{\nu}$ = 1670 cm^{-1} (vs, C=O), 1635 (m), 1550 (w), 1275 (s), 1250 (vs), 1225 (s). – ^{1}H NMR (400 MHz): δ = 0.16 (SiMe$_3$), 0.28/0.32 (diastereotopic SiMe$_2$), 0.94/1.14 (each 3H, d, CH*Me*$_2$), 1.78 (s, =C–CH$_3$), 2.57 (sept, C*H*Me$_2$), 2.71 (s, 1-H), 4.00, 4.10 (each 1H, =CH$_2$). – ^{13}C NMR (100.6 MHz): δ = 0.05/0.48 (SiMe$_2$), 0.18 (SiMe$_3$), 18.02/18.47 (CH*Me*$_2$), 22.76 (*Me*–C=), 41.94 and 43.57 (C-1 and C-3), 91.46 (=CH$_2$), 155.50 (OC=), 213.77 (C=O).

$C_{13}H_{28}O_2Si_2$ (272.5) Calcd. C 57.29 H 10.36
Found C 56.5 H 10.1

1c *and Benzophenone:* A solution of **1c** (1.50 g, 6.20 mmol) and benzophenone (12.50 g, 68.68 mmol) in benzene (30 ml) is irradiated for 3 h (100% N_2 evolution). The solvent is removed at 20°C/0.5 Torr, pentane (30 ml) is added to the solid residue, and the solution is cooled to −78°C, whereupon more crystalline benzophenone separates. The pentane layer is decanted, and the solid is extracted with more pentane (30 ml). The combined pentane solutions are concentrated to a volume of 1 ml, from which crystalline **12c**[1a] (0.30 g, 23%) is obtained at −78°C. The filtrate is concentrated, and the remaining oil (1.50 g) is purified by column chromatography (silica gel, 25 g, eluant chloroform/petroleum ether, 7:3). Extensive loss of products occurs, and only 0.11 g of a mixture (4:5 by ^{1}H NMR) of **12c** and **7a** is obtained. – NMR data of **7a**: ^{1}H NMR (90 MHz): δ = 1.45 (d, 6H, CH*Me*$_2$), 7.1–7.6 (m, 10H). – ^{13}C NMR (100.6 MHz): δ = 1.95/2.24 (SiMe$_3$ and SiMe$_2$), 21.13 (CH*Me*$_2$), 37.71 (CHMe$_2$), 96.80 (C-5), 101.32 (C-2), 126.32 (d), 127.75 (d, *p*-C$_{\text{phenyl}}$), 127.69 (d), 144.81 (*ipso*-C$_{\text{phenyl}}$), 175.87 (C-6).

1c *and Crotonaldehyde:* A solution of **1c** (2.22 g, 9.20 mmol) in crotonaldehyde (25 ml, 0.30 mol) and benzene (10 ml) is irradiated for 2 h (90% N_2 evolution). The solvents are removed at 20°C/1 Torr, and the residual oil is separated into two fractions by Kugelrohr distillation. The fraction boiling at 30–60°C/0.02 Torr contains a ketene, which is transformed into ester **10c** (0.18 g, 9%) as described above (for **1c** and acetone).

The fraction boiling at 90°C/0.02 Torr (1.10 g) is a mixture (85:15 by ^{1}H NMR) of *6-isopropyl-4,4-dimethyl-2-[(E)-1-propenyl]-5-(trimethylsilyl)-1,3-dioxa-4-sila-5-cyclohexene* (**7b**) and an unidentified compound; yield of **7**: 36%. – IR (film): $\tilde{\nu}$ = 1572 cm^{-1}, 1270, 1240. – ^{1}H NMR (400 MHz): δ = 0.15 (SiMe$_3$), 0.23/0.25 (s each, SiMe$_2$), 1.05/1.11 (d each, CH*Me*$_2$), 1.77 (d, =CH*Me*), 2.62 (mc, C*H*Me$_2$), 5.39 (d, ^3J = 4.8 Hz, 2-H), 5.60–5.68 (m, 1H, CHC*H*=), 5.93 (dq, $^3J_{trans}$ = 16.0 Hz, =C*H*Me). – ^{13}C NMR (100.6 MHz): δ = 0.20 (SiMe), 1.47 (SiMe$_3$), 2.24 (SiMe), 17.58 (=CH*Me*), 20.59 (CH*Me*$_2$), 36.75 (*C*HMe$_2$), 94.68 (C-2), 97.04 (C-5), 128.83/129.43 (CH=CH), 178.81 (C-6). – NMR data of impurity (assignment based on a comparison with **7b**): ^{1}H NMR: δ = 1.03/1.09 (d each, CH*Me*$_2$), 1.75 (d, CH*Me*), ca. 2.58 (C*H*Me$_2$), 4.68 (mc), 5.59 (mc). – ^{13}C NMR: δ = 18.23 (=CH*Me*), 20.59 (CH*Me*$_2$), 34.09 (*C*HMe$_2$), 74.38 (d), 91.18 (d), 126.16 (d), 132.66 (d), 163.01 (s).

$C_{14}H_{28}O_2Si_2$ (284.5) Calcd. C 59.10 H 9.92
Found C 57.9 H 9.6

1c *and Ethyl Acetate:* A solution of **1c** (2.53 g, 10.43 mmol) in ethyl acetate (40 ml) is photolyzed for 2 h (100% N_2 evolution). The solvent is removed at 15°C/0.8 Torr, and the residue is subjected to Kugelrohr distillation.

a) The fraction boiling at 30–40°C/0.01 Torr is treated with methanol (5 ml) and conc. HCl (2 drops) for 2 h. The solvent is evaporated, and the residue is distilled (Kugelrohr) at 95°C/0.07 Torr: 1.24 g (48%) of ester **10c** (for spectroscopic data see above).

b) 0.88 g (28%) of *2-ethoxy-6-isopropyl-2,4,4-trimethyl-5-(trimethylsilyl)-1,3-dioxa-4-sila-5-cyclohexene* (**7c**), b.p. 65°C/0.01 Torr. – IR (film): $\tilde{\nu}$ = 1562/1555 cm^{-1} (C=C). – ^{1}H NMR (90 MHz): δ = 0.14 (SiMe$_3$), 0.28 (SiMe$_2$), 1.08 (d, CH*Me*$_2$), 1.20 (t, CH$_2$*CH*$_3$), 1.58 (2-Me), 2.55 (C*H*Me$_2$), 3.63 (q, OCH$_2$). – ^{13}C NMR (C_6D_6, 50.28 MHz): δ = 95.2 (C-5), 113.2 (C-2), 175.3 (C-6).

$C_{14}H_{30}O_3Si_2$ (302.6) Calcd. C 55.6 H 9.99
Found C 56.3 H 10.04

1d *and Acetone:* A solution of **1d** (1.25 g, 5.83 mmol) in acetone (50 ml) is photolyzed for 2 h (100% N_2 evolution). Workup as described above (for **1c** and acetone) yields:

a) 0.37 g (29%) of *methyl 2-(pentamethyldisilanyl)propanoate* (**10d**), b.p. 50°C/0.01 Torr. – IR (film): $\tilde{\nu}$ = 1715 cm^{-1} (C=O). – ^{1}H NMR (90 MHz); δ = 0.10/0.11 (SiMe$_2$), 0.13 (SiMe$_3$), 1.21 (d, CH–*Me*), 2.17 (q, C*H*–Me), 3.63 (OMe). – ^{13}C NMR (100.6 MHz): δ = −2.19/0.96 (SiMe$_2$), 1.59 (SiMe$_3$), 11.53 (C-3), 28.40 (C-2), 50.78 (OMe), 176.65 (C=O).

$C_9H_{22}O_2Si_2$ (218.4) Calcd. C 49.49 H 10.15
Found C 51.5 H 9.5

b) 0.96 g (67%) of *1-[dimethyl(1-methylvinyloxy)silyl]-1-(trimethylsilyl)-2-propanone* (**6d**), b.p. 80°C/0.08 Torr (Kugelrohr). – IR (film): $\tilde{\nu}$ = 1668 cm^{-1} (vs, C=O), 1633 (m, br), 1555/1545 (m). – ^{1}H NMR (90 MHz): δ = 0.18 (SiMe$_3$), 0.34/0.37 (SiMe$_2$), 1.83 (=CMe), 2.18 (COMe), 2.60 (s, CH), 4.08 (m, =CH$_2$). – ^{13}C NMR (100.6 MHz); δ = −0.25/0.27 (SiMe$_2$), −0.21 (SiMe$_3$), 22.66 (*Me*–C=), 34.20 (CO*Me*), 44.80 (CHCO), 91.28 (=CH$_2$), 155.41 (C=CH$_2$), 208.04 (C=O).

$C_{11}H_{24}O_2Si_2$ (244.5) Calcd. C 54.04 H 9.89
Found C 52.5 H 9.60

1d *and Acetophenone:* A solution of **1d** (1.16 g, 5.41 mmol) and acetophenone (2.00 g, 16.65 mmol) in benzene (50 ml) is irradiated for 2 h. The solvent is removed at 15°C/0.4 Torr, and the residue is separated by Lobar column chromatography (ether/petroleum ether, 3:7 v/v) to give the following three fractions and unreacted acetophenone:

a) A fraction which consists mainly of **12d**[1a] [after recrystallization from pentane 0.51 g (51%)] and traces of a ketene [most likely *methyl(pentamethyldisilanyl)ketene* (**5d**), IR: $\tilde{\nu}$ = 2075 cm^{-1}].

b) 0.68 g (41%) of *1-[dimethyl(1-phenylvinyloxy)silyl]-1-(trimethylsilyl)-2-propanone* (**6e**) as a colorless oil. – IR (film): $\tilde{\nu}$ = 1680 cm^{-1} (s, C=O), 1611 (m), 1567 (w). – ^{1}H NMR (400 MHz): δ = 0.14 (SiMe$_3$), 0.33/0.35 (SiMe$_2$), 2.13 (COMe), 2.68 (s, CH–CO), 4.42/4.90 (AB system, ^2J = 2.4 Hz, $=CH_2$), 7.27–7.56 (m, Ph). – ^{13}C NMR (100.6 MHz): δ = −0.34/0.51 ($SiMe_2$), −0.12 ($SiMe_3$), 34.44 (CO*Me*), 44.70 (C-1), 91.51 ($=CH_2$), 155.32 ($O-C=$), 208.16 ($C=O$).

$C_{16}H_{26}O_2Si_2$ (306.5) Calcd. C 62.69 H 8.55
Found C 61.2 H 8.8

1d *and Ethyl Acetate:* A solution of **1d** (1.20 g, 5.60 mmol) in ethyl acetate (50 ml) is photolyzed for 2 h (100% N_2 evolution). Workup as described above (for **1c** and ethyl acetate) yields ester **10d**, 0.44 g (36%), b.p. 50°C/0.01 Torr; for spectroscopic data see above.

(Z)-4-{[3,3-Dimethyl-2-oxo-1-(trimethylsilyl)butyl]dimethylsilyloxy}pent-3-en-2-one (*Z*-**15**): The solution of **1b** (1.39 g, 5.42 mmol) in benzene (50 ml) is irradiated for 3 h (100% N_2 evolution). The solvent is evaporated at 20°C/0.01 Torr, and the residue is dissolved in pentane (3 ml). At −78°C, crystalline **8b** separates to which benzene (10 ml) and acetylacetone (0.50 g, 4.99 mmol, dried[30] and distilled) are added after removal of the supernatant liquid. After 5 h, the volatile components are removed at 20°C/12 Torr. A colorless oil (1.02 g) is left, which consists mainly of *Z*-**15** and an unidentified compound in a ratio of 4.5:1 [^1H-NMR signals of the impurity: δ = 2.02 (s, 6H), 4.40 (s, 1H), 5.37 (s, 1H)]. Further purification of *Z*-**15** by column chromatography (silica gel, CN-modified silica gel) has been unsuccessful, whereas attempted vacuum distillation leads to isomerization (see below). Spectroscopic data of *Z*-**15**: IR (film): $\tilde{\nu}$ = 1671 (vs) cm^{-1}, 1650 (vs), 1615 (s), 1590 (vs), 1379 (s), 1252 (vs), 1210 (s). – ^1H NMR (400 MHz): δ = 0.03 (s, $SiMe_3$), 0.22/0.31 (diastereotopic $SiMe_2$), 0.98 (*t*Bu), 1.95 (CO*Me* and $Me-C=$), 3.06 ($CO-CH$), 5.23 (s, CH). – ^{13}C-NMR (100.6 MHz): δ = 26.55 (*Me*CO and $Me-C=$), 27.58 (C*Me*$_3$), 38.51 ($CO-CH$), 44.76 (*C*Me$_3$), 100.41 ($CH=$), 191.15 ($Me-C=$ and COMe).

(3E)-4-{[(Z)-1-tert-Butyl-2-(trimethylsilyl)vinyloxy]dimethylsilyloxy}pent-3-en-2-one (**16**): A solution of **1b** (1.41 g, 5.5 mmol) in benzene (50 ml) is photolyzed for 2 h. Acetylacetone (0.55 g, 5.5 mmol, dried[30] and distilled) is added, and the mixture is stirred for 3 h. The solvent is evaporated at 20°C/0.01 Torr, and the residue is kept at 140°C for 2 h, then distilled twice in a Kugelrohr apparatus at 140°C/0.01 Torr to give 1.13 g (63%) of **16**. – IR (film): $\tilde{\nu}$ = 1675 cm^{-1} (s), 1590 (vs), 1380 (s), 1260 (vs). – ^1H NMR (400 MHz): δ = 0.08 ($SiMe_3$), 0.38 ($SiMe_2$), 1.08 (*t*Bu), 2.12 (s, $=CMe$), 2.29 (s, MeCO), 4.52 (s, $=CHOSi$), 5.71 (s, $=CHCO$*Me*). – ^{13}C-NMR (100.6 MHz): δ = −1.13 ($SiMe_2$), −0.02 ($SiMe_3$), 20.98 (*Me*$-C=C$), 28.86 (C*Me*$_3$), 31.89 (CO*Me*), 38.07 (*C*Me$_3$), 100.72 ($C=$*C*HCOMe), 108.98 (*C*H$=$COSi), 167.62, 171.01, 197.61 ($C=O$). – ^{29}Si NMR: δ = −10.92, −11.13.

$C_{16}H_{32}O_3Si_2$ (328.6) Calcd. C 58.48 H 9.82
Found C 57.8 H 9.70

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1b: 87594-03-4 / **1c**: 118096-53-0 / **1d**: 87594-01-2 / **5d**: 132409-04-2 / **6a**: 132408-95-8 / **6b**: 132408-96-9 / **6c**: 132408-99-2 / **6d**: 118096-57-4 / **6e**: 132409-05-3 / **7a**: 132409-00-8 / **7b**: 132409-01-9 / **7c**: 132409-02-0 / **8b**: 118096-54-1 / **10c**: 132408-98-1 / **10d**: 132409-03-1 / **11b**: 132408-97-0 / **12c**: 118107-32-7 / **12d**: 118096-55-2 / (Z)-**15**: 132409-06-4 / **16**: 132409-07-5 / acetone: 67-64-1 / acetophenone: 98-86-2 / benzophenone: 119-61-9 / (*E*)-crotonaldehyde: 123-73-9 / ethyl acetate: 141-78-6

☆ Dedicated to Professor *Paul Binger* on the occasion of his 60th birthday.

[1] [1a] K. Schneider, B. Daucher, A. Fronda, G. Maas, *Chem. Ber.* **123** (1990) 589. – [1b] G. Maas, K. Schneider, W. Ando, *J. Chem. Soc., Chem. Commun.* **1988**, 72.

[2] A. Sekiguchi, W. Ando, *J. Am. Chem. Soc.* **106** (1984) 1486.

[3] A. Sekiguchi, T. Sato, W. Ando, *Organometallics* **6** (1987) 2337.

[4] [4a] G. Raabe, J. Michl, *Chem. Rev.* **85** (1985) 419. – [4b] A. G. Brook, K. M. Baines, *Adv. Organomet.Chem.* **25** (1986) 1.

[5] W. Ando, A. Sekiguchi, T. Sato, *J. Am. Chem. Soc.* **104** (1982) 6830.

[6] T. J. Barton, G. P. Hussmann, *Organometallics* **2** (1983) 692.

[7] For NMR data of related α-silyl esters see: R. Brückmann, K. Schneider, G. Maas, *Tetrahedron* **45** (1989) 5517.

[8] Assignment of bis(trimethylsilyl)ketene as a product of photolysis of **1d** in acetone (ref. [1b]) has to be revised.

[9] T. J. Pinnavaia, W. T. Collins, J. J. Howe, *J. Am. Chem. Soc.* **92** (1970) 4544.

[10] I. K. Kusnezowa, K. Rühlmann, E. Gründemann, *J. Organomet. Chem.* **47** (1973) 53.

[11] H. J. Reich, D. A. Murcia, *J. Am. Chem. Soc.* **95** (1973) 3418.

[12] H. Shanan-Atidi, Y. Shvo, *Tetrahedron Lett.* **1971**, 603.

[13] A. G. Brook, A. R. Bassindale in *Rearrangements in Ground and Excited States* (P. de Mayo, Ed.), vol. 2, p. 149, Academic Press, New York 1980.

[14] R. J. P. Corriu, J. C. Young, in *The Chemistry of Organic Silicon Compounds* (S. Patai, Z. Rappoport, Eds.), part 2, chapter 20, Wiley, Chichester 1989. – See also: A. R. Bassindale, P. G. Taylor, *ibid.*, part 1, chapter 12.

[15] M. Grignon-Dubois, M. Laguerre, *Organometallics* 7 (1988) 1443.

[16] H. Marsmann, in *NMR: Basic Principles and Progress* (P. Diehl, E. Fluck, R. Kosfeld, Eds.), vol. 17, p. 65, Springer, Berlin 1981.

[17] J. Schraml, J. Šraga, P. Hrnčiar, *Collect. Czech. Chem. Commun.* **48** (1983) 3097.

[18] $Me_2Si(OtBu)CH=CH_2$ shows δ(^{29}Si) = −5.6, $Me_2Si(OEt)$-$CH=CH_2$ δ = 2.7: J. Schraml, V. Chvalovský, M. Mägi, E. Lipmaa, *Collect. Czech. Chem. Commun.* **42** (1977) 306.

[19] D. N. Roark, L. H. Sommer, *J. Chem. Soc., Chem. Commun.* **1973**, 167.

[20] [20a] N. Wiberg, G. Wagner, *Angew. Chem.* **95** (1983) 1027; *Angew. Chem., Int. Ed.Engl.* **22** (1983) 1005. – [20b] N. Wiberg, G. Preiner, G. Wagner, H. Köpf, *Z. Naturforsch., Teil B*, **42** (1987) 1062.

[21] A. Sekiguchi, W. Ando, *Chem. Lett.* **1983**, 871; *Organometallics* **6** (1987) 1857.

[22] G. Märkl, M. Horn, *Tetrahedron Lett.* **24** (1983) 1477.

[23] [23a] N. Wiberg, *J. Organomet. Chem.* **273** (1984) 141. – [23b] N. Wiberg, G. Preiner, O. Scheida, *Chem. Ber.* **114** (1981) 3518.

[24] A. G. Brook, W. J. Chatterton, J. F. Sawyer, D. W. Hughes, K. Vorspohl, *Organometallics* **6** (1987) 1246.

[25] P. B. Valkovich, W. P. Weber, *Tetrahedron Lett.* **1975**, 2153.

[26] M. Regitz, W. Illger, G. Maas, *Chem. Ber.* **111** (1978) 705.

[27] For the mechanism of the Wolff rearrangement see: [27a] H. Meier, K.-P. Zeller, *Angew.Chem.* **87** (1975) 52; *Angew. Chem. Int. Ed. Engl.* **14** (1975) 32. – [27b] W. Ando, in *The Chemistry of Diazonium and Diazo Groups* (S. Patai, Ed.), vol. I, p. 341, Wiley, New York 1978. – [27c] G. Maas, in *Methoden der organischen Chemie*, Houben-Weyl (M. Regitz, Ed.), vol. E19, part 2, p. 1022, Thieme, Stuttgart 1989.

[28] [28a] H. D. Roth, M. L. Manion, *J. Am. Chem. Soc.* **98** (1976) 3392. – [28b] H. D.Roth, *Acc. Chem. Res.* **10** (1977) 85.

[29] [29a] H. Tomioka, H. Okuno,Y. Izawa, *J. Org. Chem.* **45** (1980) 5278. – [29b] H. Tomioka, H. Okuno, S. Kondo, Y. Izawa, *J. Am. Chem. Soc.* **102** (1980) 7123.

[30] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd edition, p. 70, Pergamon Press, Oxford 1988.

[415/90]