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WOLFF REARRANGEMENT OF (1-DIAZO-2-OXOALKYL) SILANES

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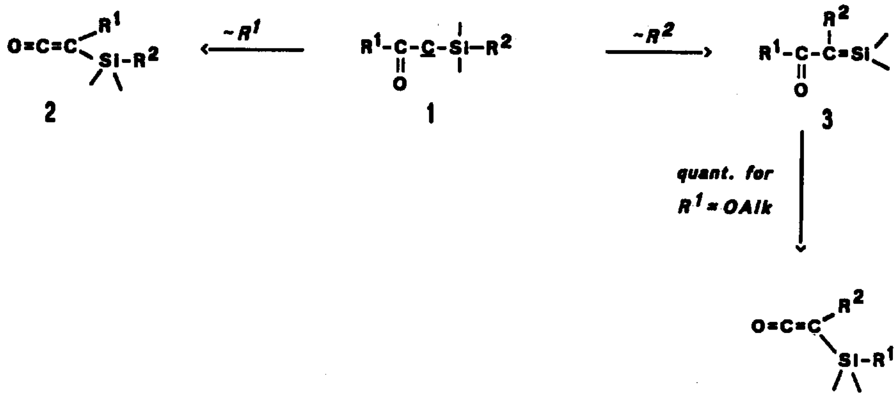
Summary: Photochemical decomposition of (1-diazo-2-oxoalkyl) silanes **6a-l** results in Wolff rearrangement yielding silyl ketenes **8a-l**. From (1-diazo-3,3-dimethyl-2-oxobutyl) silanes **6c-f**, 2-silyl-cyclobutanones **9c-f** are formed as by-products, arising from intramolecular C/H insertion of the acyl carbene intermediate. Irradiation of diazo-triisopropylsilyl-acetamide **6m** yields only β-lactam **16** and γ-lactam **17**. Wolff rearrangement also takes place on copper triflate catalyzed decomposition of **6a,c,l**, whereas the 1-oxa-2-sila-4-cyclopentene **19** is obtained from **6f**, probably as the result of SiC/H insertion of a copper carbene intermediate.

INTRODUCTION

Wolff rearrangement (WR) yielding ketenes is the most common result of the photochemical or thermal decomposition of α-diazoketones, and to a lesser extent, of α-diazoesters.[1] The acyl carbene, which is formed by loss of dinitrogen from the diazo compound and which may or may not be an intermediate in the WR, can undergo several intra- or intermolecular reactions in competition with the WR.

This general statement also applies for acyl silyl carbenes **1**. Both solution photolysis and gas phase pyrolysis of alkyl (trimethylsilyl or dimethylphenylsilyl)diazoacetates yield products derived from WR (1 → 2, R^1=alkoxy, R^2=Me, Ph) and 1,2(Si → C) migration of R^2 (1 → 3, followed by spontaneous isomerization to ketene **4**) in addition to other carbene reactions.[2] The migratory tendency of R^2 increases in the sequence Me < Ph < $SiMe_3$,[2,3] such that in the latter case, the acylsilene 3 (R^1 = OEt, R^2 = $SiMe_3$) is formed exclusively.[3]

Since alkyl and aryl groups have a higher migratory tendency than alkoxy groups in the WR,[1] the chance for acylsilene formation is expected to be smaller, when α-silylated diazoketones rather than diazoesters are chosen as starting materials. Nevertheless, the silene pathway is observed exclusively for (1-oxoalkyl) pentamethyldisilanyl carbenes (1, R^1 = ^{t}Bu or 1-adamantyl, R^2 = $SiMe_3$).[4,5] No information seems to exist about acylsilenes 1 with R^1,R^2 = alkyl, aryl. Therefore, we have investigated the photochemical and copper catalyzed decomposition of appropriate α-silylated diazoketones.



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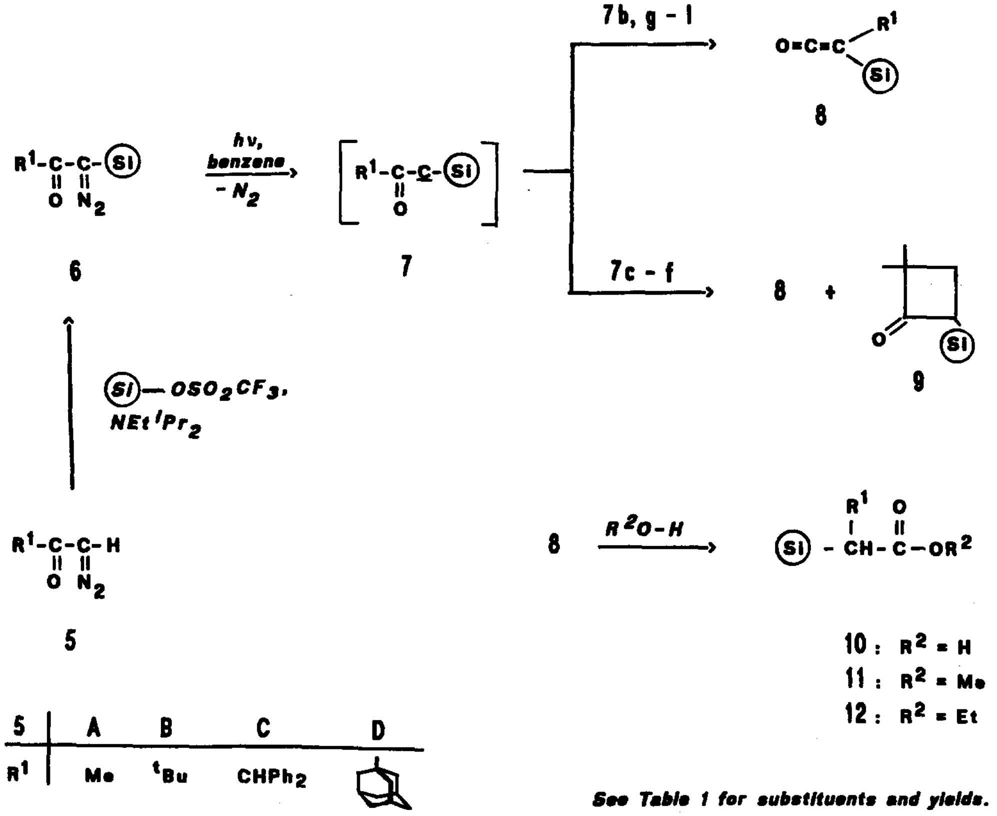
Scheme 1

RESULTS

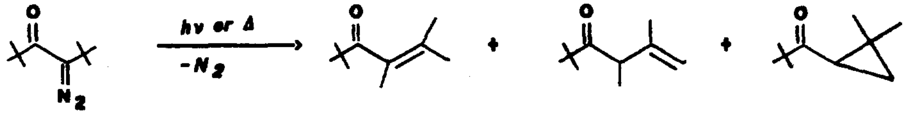
(1-Diazo-2-oxoalkyl) silanes 6 are prepared conveniently by silylation of primary α-diazoketones 5 with silyl trifluoromethanesulfonates in the presence of diisopropylethylamine.[6,7] Because of easy protiodesilylation, they cannot be handled in the lower alcohols as solvents. When 6a-l are photolyzed (λ ≥ 280 nm) in benzene, silyl ketenes 8 are formed in all cases in medium to high isolated yields (Scheme 2 and Table 1). Some of the ketenes could not be freed of impurities completely and were, therefore, transformed into the corresponding α-silyl carboxylic acids (10) or esters (11,12). In the cases of 6c-f, 2-silyl-cyclobutanones 9 were obtained concomitantly; obviously, they result from a γ-C/H insertion of the ketocarbene intermediate 7. Some attention has to be paid to the elucidation of the constitution of the silyl ketenes. The cumulene absorptions in the IR spectrum (ca. 2065-2080 cm^{-1}) and characteristic high-field values for δ(C=C=O) in the ^{13}C NMR spectrum (e.g. 8e: 19.1 ppm; 8j: 24.3 ppm) are not sufficient to define the exact constitution of the silyl ketene. As Scheme 1 indicates, the WR and the acylsilene pathway will transform an acyl silyl carbene into isomeric silyl ketenes if R^1 and R^2 are different. For **8a,b,f,g,j-l**, the assigned constitution follows definitely from the number of signals in the ^{1}H and ^{13}C NMR spectra (eventually those of the derivatives **10-12**) and it is then clear that WR has occurred. Decomposition of **6h** is expected to yield ketene **8h** by Wolff rearrangement, whereas the acylsilene pathway would produce $O{=}C{=}C(Me){-}SiMe^tBuAd$ or $O{=}C{=}C(^tBu){-}SiMe_2Ad$, depending on whether Me or ^{t}Bu migrates at the carbene stage. The ^{13}C NMR spectrum allows to distinguish between the three isomers. Whereas the latter ketene is readily excluded based on the number of signals, a decision in favor of **8h** is derived from δ(C1-adamantyl), which is virtually identical with the value found in ketene **8j**; silyl substitution at this carbon atom would have resulted in a high-field shift of this resonance. Thus, we have no reason to assume that the acylsilene pathway is operating in the remaining cases of **6c-e,i**.



See Table 1 for substituents and yields.

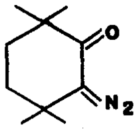
Scheme 2

A variety of mechanistic pathways exists for the WR.[1,8] There is much evidence that the WR occurs in a singlet state, either of the diazoketone or of the acyl carbene.[1,9,10] From the observation of conformational control of the WR of diazoketones, it has been concluded[9,11] that the photochemical version can take place in an excited singlet state of *s-cis* diazoketone, in which the diazo group and the migrating substituent are *trans* with respect to the (O=)C—C(=N_2) bond. In this case, a ketene can be formed without the intermediacy of an acyl carbene. In fact, diazoketone 13, which for steric reasons assumes the *s-trans* conformation practically exclusively,[11] does not undergo WR to an appreciable extent in solution[11,12,13] (eq. 1), contrary to its *s-cis* locked relative 14.[11]



(eq. 1)

13



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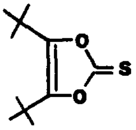

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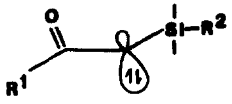
Further experiments by Strausz et al.[14] indicate that conformational control can originate not only in the *s-cis* diazoketone, but also in the *s-E*[15] acyl carbene. As an example, the result that di-*tert*-butyl-ketene is obtained on photochemical decomposition of 15, but not of 13, is explained most conveniently by the intermediacy of *s-E* acyl carbene in the former case, and of the *s-Z* form in the latter.[16] No such conformational control seems to dominate the photochemical decomposition of (1-diazo-2-oxoalkyl) silanes 6. Even though there cannot be any doubt that 6c-j are closely related structurally to 13, i.e. the fragment O=C—C=N_2 also adopts the *s-trans* conformation, the WR does occur. This is inconsistent with the concerted mechanism in which the diazoketone rather than the acyl carbene is the direct precursor of the ketene. Triplet-sensitized irradiation of 6f ($Ph_2C=O$, $\lambda \geq 280$ nm), which circumvents the excited singlet state of the diazoketone, supports this view, since the products are the same and the yields are nearly identical to those of direct irradiation (Table 1). As in other cases,[9,17,18] this is explained by assuming that a primarily formed triplet carbene rapidly interconverts with the singlet carbene which then goes on to the ketene and to the C/H insertion product.

Table 1. Products of photochemical or copper catalyzed decomposition of (1-diazo-2-oxoalkyl) silanes.

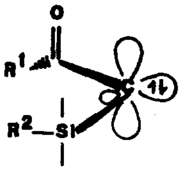
6-12	R¹	(Si)	Conditions a)	[%] 8 b)	[%] 9	Derivative of 8
a	Me	$\mathrm{SiEt_3}$	A	n.i.		$\mathrm{Et_3Si{-}CH(Me){-}COOMe}$ **11a**; 54 %
b	Me	$\mathrm{Si^iPr_3}$	B	49		
c	$^t\mathrm{Bu}$	$\mathrm{SiMe_2{}^tBu}$	B	n.i.	13	$\mathrm{Me_2{}^tBuSi{-}CH({}^tBu){-}COOH}$ **10c**; 50 %
			A	n.i.	-	$\mathrm{Me_2{}^tBuSi{-}CH({}^tBu){-}COOEt}$ **12c**; 72 %
d	$^t\mathrm{Bu}$	$\mathrm{SiMe^tBu_2}$	B	n.i.	25	$\mathrm{Me^tBu_2Si{-}CH({}^tBu){-}COOH}$ **10d**; 39 %
e	$^t\mathrm{Bu}$	$\mathrm{SiPh_2{}^tBu}$	B	26	17	
f	$^t\mathrm{Bu}$	$\mathrm{Si^iPr_3}$	B	21	24(14 c))	$\mathrm{{}^iPr_3Si{-}CH({}^tBu){-}COOMe}$ **12f**; 38 % c)
			C	n.i.	16	$\mathrm{{}^iPr_3Si{-}CH({}^tBu){-}COOH}$ **10f**; 46 %
g	$\mathrm{CHPh_2}$	$\mathrm{Si^iPr_3}$	B	n.i.		$\mathrm{{}^iPr_3Si{-}CH(CHPh_2){-}COOH}$ **10g**; 71 %
h	1-Ad d)	$\mathrm{SiMe_2{}^tBu}$	B	55		$\mathrm{Me_2{}^tBuSi{-}CH(1\text{-}Ad){-}COOH}$ **10h**; 72 % e)
i	1-Ad d)	$\mathrm{SiPh_2{}^tBu}$	B	71		
j	1-Ad d)	$\mathrm{Si^iPr_3}$	B	62		$\mathrm{{}^iPr_3Si{-}CH(1\text{-}Ad){-}COOH}$ **10j**; 90 % e)
k	Ph	$\mathrm{SiEt_3}$	B	49		
l		$\mathrm{Si^iPr_3}$	B A	94 93		

a) A: $\mathrm{CuO_3SCF_3}$ x 0.5 $\mathrm{C_6H_6}$ (4 mol-%), benzene, 20 °C; B: hν (λ ≥ 280 nm), benzene; C: hν (λ ≥ 320 nm), tenfold molar excess of benzophenone.
b) Isolated yields; n.i. = not isolated. In the latter case, the ketene was quenched, see last column.
c) The yield is given for a run in which the ketene was quenched with MeOH.
d) 1-Ad = 1-adamantyl.
e) Yield refers to isolated ketene.

Following the suggestion of Strausz¹⁴⁾ (see above), one would expect that the singlet carbenes *s-Z*-**7c-j**, derived from **6c-j** with retention of conformation, are not prone to WR.



s-Z-7

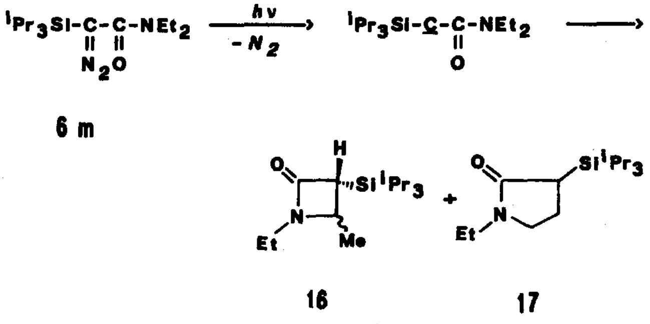


s-Z-7'

R^1 = ᵗBu, 1-adamantyl

Since the contrary is observed, we assume that 1,2(Si ⟶ C) migration of R^2 (alkyl or phenyl) is much slower than the 1,2-methyl shift in the carbene derived from 13, so that there is enough time for *s-Z*-7 to adopt a conformation which is more favorable to WR. By a simple 90° rotation around C—C, the conformation of *s-Z*-7' is reached, in which the substituent R^1 and the vacant carbenic p-orbital appear perfectly aligned (syn-periplanar) for the WR.[19]

We have also briefly examined the photochemical behavior of the silylated diazoacetamide 6m. In benzene, β-lactam 16 and γ-lactam 17 were the only isolated products, formed in a ratio of roughly 1:2 (Scheme 3). The same reactivity has been observed for N,N-diethyl diazoacetamide in inert solvents.[20,21] According to Tomioka,[21,22] only the γ-lactam results from carbenic C/H insertion, whereas the β-lactam is formed directly from the *s-cis* form of the singlet excited state of the diazoacetamide. Since we have no information about the preferred conformation of 6m, this point was not investigated further.



6 m

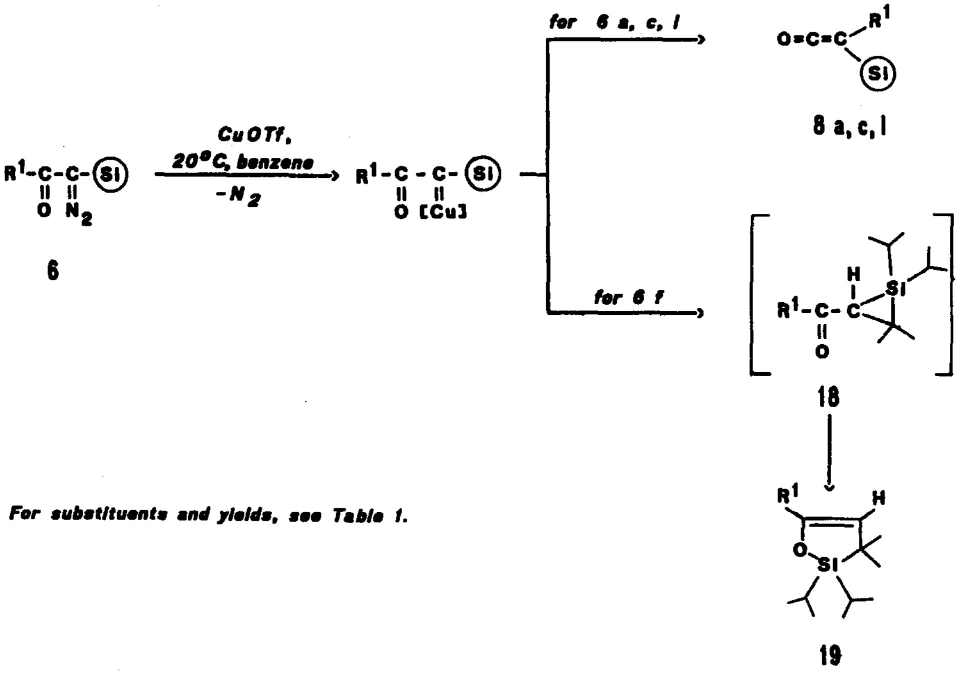
16

(2 isomers)

17

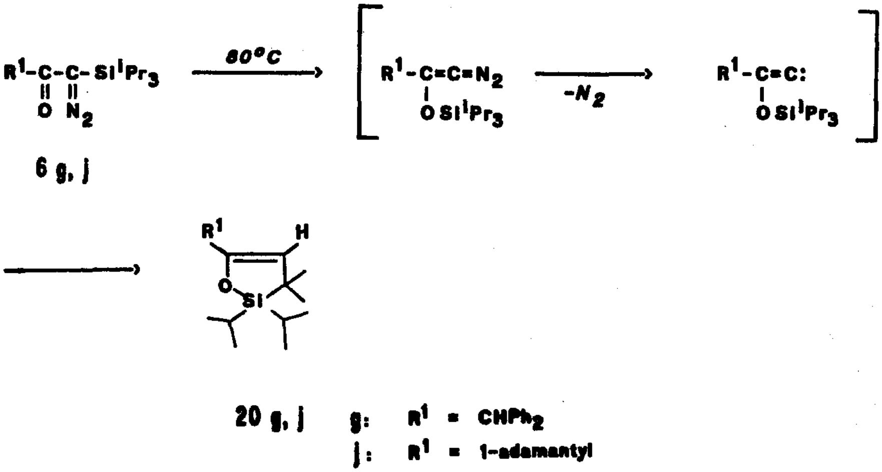
Scheme 3

The WR can often be suppressed by transition metal catalyzed decomposition of diazoketones.[23] Dirhodium tetraacetate normally is the catalyst of choice, but it does not decompose diazoketones 6a-l at a temperature well below that of purely thermal decomposition. With copper(I) triflate, smooth decomposition occurs at room temperature, but again WR leading to ketenes 8 takes place in the case of 6a,c,l (Scheme 4). Contrary to the photochemical result, the carbenoid mode suppresses the intramolecular C/H insertion in the case of 6c, although this is a well documented reaction of copper carbenoids.[23] It is possible that a β-C/H insertion does take place, however, when 6f is decomposed by copper triflate. It seems likely that the acyl silane 18 thus formed rearranges spontaneously to the cyclic siloxy alkene 19. For a plausible explanation of the unique behavior of 6f, it should be noted that ketene 8f has the most steric strain of the whole series 8a-l. This situation probably slows down the rate of formation of 8f to an extent, where another carbenoid reaction can take over.



Scheme 4

An analogous transformation had been observed when 6a was heated in boiling cyclohexane in the presence of copper powder.[24] We have presented evidence, however, that under these conditions purely thermal decomposition of 6a takes place, and that the mechanism does not include a ketocarbenoid intermediate.[7] The thermal mode of decomposition is exemplified further by the transformations of 6g,j to 20g,j (Scheme 5). It begins with 1,3(C → O) silyl migration to form a diazoalkene intermediate which then decomposes to a βsiloxyalkylidene carbene.



6 g, j

20 g, j

g: R^1 = $CHPh_2$
j: R^1 = 1-adamantyl

Scheme 5

In summary, we have shown that (1-diazo-2-oxoalkyl) silanes undergo photochemical Wolff rearrangement to silyl ketenes with secondary alkyl, tertiary alkyl or aromatic groups as migrating substituents. 1,2-Shift of alkyl or phenyl groups from silicon to the carbenic center cannot compete with the WR. Copper triflate catalyzed decomposition at room temperature normally also results in WR, the sterically demanding diazoketone **6f** being an exception.

Contrary to many other diazoketones, the WR cannot be induced thermally, since a 1,3-silyl migration is faster than N_2 loss from the silylated diazoketones.

EXPERIMENTAL

General information. IR spectra: Perkin-Elmer IR 394, Beckman IR 20A; reported values are in cm^{-1}. 1H NMR spectra: Varian EM 390 (90 MHz), Bruker WP 200 (200 MHz); tetramethylsilane or chloroform was used as internal standard; δ(TMS) values are given. ^{13}C NMR spectra: Bruker WP 200 (50.28 MHz), $CDCl_3$ or C_6D_6 as internal standard; δ(TMS) = δ($CDCl_3$) + 77.0 = δ(C_6D_6) + 128.0 [ppm]. All NMR spectra were taken in $CDCl_3$, unless stated otherwise. Elemental analyses: Perkin-Elmer EA 240. GC/MS: Perkin-Elmer F22, open split, Finnigan MAT CH 7A. Melting points: heat block, uncorrected. Oven temperatures are reported for Kugelrohr distillations.

All silylated diazoketones were synthesized and decomposed in dried solvents under an argon atmosphere. - Column chromatography: Merck Lobar columns (Lichroprep SI 60, 40-63 µm). - Preparative GC: Gerstel AMPG-60/3, column 200x2 cm, 20 % SE-30 on Volaspher A4, 100-120 mesh, 220 °C, carrier gas N_2, 750 ml min^{-1}.

3-Diazo-1,1-diphenyl-2-propanone (**5C**): Diphenylacetyl chloride (16.13 g, 0.07 mol) in ether (30 ml) is added dropwise to a stirred solution of diazomethane (from 30.6 g (0.3 mol) of N-methyl-N-nitrosourea[25]), kept at -5 °C. The solution is brought to room temperature and stirred for another 12 h. The solvent is replaced by 30 ml of ether-pentane (1:1). At -78 °C, yellow needles are obtained (12.38 g, 73 %), m.p. 42 °C. - IR (KBr): 2095 (CN_2), 1620 (C=O). - ^{1}H-NMR: 4.93 (s, HCN_2), 5.20 (s, CPh_2), 7.30 (10 H). - Anal. Calcd for $C_{15}H_{12}N_2O$ (236.3): C, 76.25; H, 5.12; N, 11.85. Found: C, 75.9; H, 5.25; N, 11.2.

1-(1-Adamantyl)-2-diazo-1-ethanone[26] (**5D**): 1-Adamantanecarboxylic acid chloride (10.0 g, 0.05 mol) in ether (60 ml) is added dropwise with stirring to a solution of diazomethane (from 20 g (0.2 mol) of N-methyl-N-nitrosourea[25]) in ether, kept at -10 °C. After 30 min, the solution is brought to room temperature, stirred for another 12 h and concentrated to ca. 25 % of its volume. At -78 °C, the diazoketone is precipitated; it can be purified by repeated recrystallization from ether or by column chromatography (Lobar column, pentane-chloroform (3:7); 9.05 g (88 %), yellow crystals, m.p. 61 °C. - IR (KBr): 2095 (CN_2), 1615 (C=O). - ^{1}H NMR: 1.65-2.20 (m, 15 H), 5.35 (s, 1 H, HCN_2). - ^{13}C NMR (C_6D_6): 28.5(d), 36.7(t), 39.0(t), 44.9(s, 1-adamantyl); 50.8 (CN_2), 199.3 (C=O). - Anal. Calcd. for $C_{12}H_{16}N_2O$ (204.3): C, 70.55; H, 7.89; N, 13.71. Found: C, 70.5; H, 7.85; N, 13.8.

(1-Diazo-2-oxoalkyl)silanes 6

According to the procedure given in ref.7, the following new compounds have been prepared.

1-Diazo-1-(di-*tert*-butylmethylsilyl]-3,3-dimethyl-2-butanone (**6d**): From **5B**[27] and di-*tert*-butylmethylsilyl trifluoromethanesulfonate;[28] yellow oil (1.00 g, 46 %). - IR (film): 2060 (CN_2), 1625 (C=O). - ^{1}H NMR: 0.15 (s, 3 H, SiMe), 1.10 (s, 18 H, Si- ^{t}Bu), 1.30 (s, 9 H, ^{t}Bu). - Anal. Calcd. for $C_{15}H_{30}N_2OSi$ (282.5): C, 63.77; H, 10.70; N, 9.92. Found: C, 62.9; H, 10.53; N, 8.8.

1-Diazo-3,3-diphenyl-1-(triisopropylsilyl)-2-propanone (**6g**): From **5C** and triisopropylsilyl trifluoromethanesulfonate;[29] 2.82 g (72 %) of a yellow solid, m.p. 38 °C. - IR (KBr): 2045 (CN_2), 1625 (C=O). - ^{1}H NMR: 1.00-1.62 (m, 21 H, ^{i}Pr), 5.45 (s, 1 H, $CHPh_2$), 7.30 (m, 10 H). - Anal. Calcd. for $C_{24}H_{32}N_2OSi$ (392.6): C, 73.42; H, 8.21; N, 7.14. Found: C, 72.5; H, 8.11; N, 6.7.

2-(1-Adamantyl)-1-(*tert*-butyldimethylsilyl)-1-diazo-2-ethanone (**6h**): From **5D** and *tert*-butyldimethylsilyl trifluoromethanesulfonate;[29] yellow crystals (2.12 g, 67 %), m.p. 63 °C. - IR (KBr): 2050 (CN_2), 1620 (C=O). - ^{1}H NMR: 0.20 (s, 6 H, Me), 0.90 (s, 9 H, ^{t}Bu), 1.60-2.20 (m, 15 H, adamantyl). - Anal. Calcd. for $C_{18}H_{30}N_2OSi$ (318.54): C, 67.87; H, 9.49; N, 8.79. Found: C, 66.7, H, 9.30; N, 8.6.

2-(1-Adamantyl)-1-(*tert*-butyldiphenylsilyl)-1-diazo-2-ethanone (**6i**): From **5D** and *tert*-butyldiphenylsilyl trifluoromethanesulfonate;[30] yellow solid (1.78 g, 40 %), m.p. 57 °C. - IR (KBr): 2060 (CN_2), 1620 (C=O). - ^{1}H NMR: 1.16 (s, 9 H, ^{t}Bu), 1.65-2.21 (m, 15 H, adamantyl), 7.15-7.65 (m, 10 H). - Anal. Calcd. for $C_{28}H_{34}N_2OSi$ (442.7): C, 75.97; H, 7.74; N, 6.33. Found: C, 75.1; H, 8.03; N, 5.9.

2-(1-Adamantyl)-1-diazo-1-(triisopropyl)-2-ethanone (**6j**): From **5D** and triisopropyl trifluoromethanesulfonate;[29] purification by column chromatography (ether - petrolether, 8:2); yellow solid (2.38 g, 68 %), m.p. 52 °C. - IR (KBr): 2050 (CN_2), 1618 (C=O). - ^{1}H NMR: 0.90-1.35 (m, 21 H, ^{i}Pr), 1.60-2.12 (m, 15 H, adamantyl). - ^{13}C-NMR (C_6D_6): 11.5 (*C*HMe$_2$), 18.5 (CH(*C*H$_3$)$_2$; 28.7(d), 36.6(t), 38.1(t), 46.2 (CN_2), 48.8 (1-adamantyl), 201.7 (CO). - Anal. Calcd. for $C_{21}H_{36}N_2OSi$ (360.6): C, 69.94; H, 10.06; N, 7.76. Found: C, 69.7; H, 9.86; N, 7.8.

N,N-Diethyl α-diazo-α-(triisopropylsilyl)acetamide (**6m**): From N,N-diethyl α-diazo-acetamide[20] and triisopropyl trifluoromethanesulfonate;[29] yellow oil (1.49 g, 50 %). - IR (film): 2060 (CN_2), 1618 (C=O). - ^{1}H NMR: 1.04-1.21 (m,

$NCH_2C\mathit{H}_3$ and $CH(C\mathit{H}_3)_2$), 1.31 (m, $C\mathit{H}Me_2$), 3.38 (q, 4 H, NCH_2). - Anal. Calcd. for $C_{15}H_{31}N_3OSi$ (297.5): C, 60.56; H, 10.50; N, 14.12. Found: C, 60.1; H, 10.35; N, 13.5.

Photolysis of 6a-m

General procedure: A solution of the diazo compound (3 - 9 mmol) in benzene (50 ml) is placed in a Pyrex glass irradiation vessel. After flushing with argon for 5 min, the solution is irradiated with a high-pressure mercury lamp (Philips HPK 125 W, $\lambda \geq 280$ nm), until no more dinitrogen is evolved (3 -12 h). The solvent is removed at 20 °C/≤0.01 mmHg, and the residue is subjected to Lobar column chromatography (eluent chloroform-pentane (7:3)) if not stated otherwise.
Methyl-triisopropyl-ketene (8b): By irradiation of **6b**;[7] pale-yellow oil; 46 % yield. - IR (film): 2085 (C=C=O). - ^1H NMR: 1.10 (21 H, ^iPr), 1.63 (3 H, Me). - Anal. Calcd. for $C_{12}H_{24}OSi$ (212.4): C, 67.9; H, 11.39. Found: C, 67.2; H, 11.09.
Photolysis of 6c: From 4.30 g (17.8 mmol) of **6c**,[7] an oil is obtained to which is added acetonitrile (10 ml), water (3 ml) and three drops of conc. hydrochloric acid. After 30 min at reflux, dichloromethane (30 ml) is added, and extraction is done with a saturated aqueous solution of potassium carbonate. The aqueous layer is acidified and extracted with dichloromethane (20 ml) to yield **2-(*tert*-butyldimethylsilyl)-3,3-dimethyl-butanoic acid (10c**; 50 %), m.p. 69 °C. - IR (KBr): 3100-2600 (OH), 1670 (C=O). - ^1H NMR: 0.12 (3 H, SiMe), 0.22 (3 H, SiMe), 0.90 (9 H, Si-^tBu), 1.15 (9 H, C-^tBu), 2.15 (s, 1 H, CH). - Anal. Calcd. for $C_{12}H_{26}O_2Si$ (230.1): C, 62.58; H, 11.30. Found: C, 62.4; H, 11.11.
From the organic layer, **4-(tert-butyldimethylsilyl)-2,2-dimethyl-cyclobutanone (9c)** is obtained as a colorless oil (0.49 g, 13 %), b.p. 65 °C /0.01 mmHg (Kugelrohr). - IR (film): 1745 (C=O). - ^1H NMR (200 MHz): 0.03 and 0.10 (3 H each, SiMe), 0.91 (9 H, ^tBu), 1.11 (s, 3 H, 2-Me), 1.22 (s, 3 H, 2-Me), 1.77 (dd, 1 H, 3-H^a, ^3J(3-H^a,3-H^b)=10.7, ^3J(3-H^a,4-H)=7.7 Hz), 1.97 (t, 1 H, 3-H^b, ^3J(3-H^b,4-H)=10.7 Hz), 3.19 (dd, 1 H, 4-H). - Anal. Calcd. for $C_{12}H_{24}OSi$ (212.1): C, 67.89; H, 11.32. Found: C, 67.0; H, 11.20.
Photolysis of 6d: The reaction mixture is concentrated, and 3 ml of $HCl_{conc.}$ is added. After 15 min, one extracts with dichloromethane (3x10 ml). The residue obtained after removal of the organic solvent is separated by Kugelrohr distillation at 55 °C/0.004 mmHg, which yields **4-(di-*tert*-butylmethylsilyl)-2,2-dimethyl-cyclobutanone (9d)** as a colorless liquid in 25 % yield. - IR (film): 1755 (C=O). - ^1H NMR: 0.15 (3 H, SiMe), 1.03 (s, 9 H, ^tBu), 1.08 (s, 9 H, ^tBu), 1.19 and 1.26 (s, 3 H each, 2-CH_3), 1.99 (d, 2 H, CH_2, ^2J(3-H^a,3-H^b) = ^3J(3-H^a,4-H) = 9.5 Hz), 3.30 (t,4-H). - Anal. Calcd. for $C_{15}H_{30}OSi$ (254.5): C, 70.79; H, 11.88. Found: C, 69.3; H, 11.61.
The residue of the distillation consists mainly of ketene **8d** (IR: 2070), which cannot be purified completely. Addition of water (see preparation of **10c**) yields **2-(di-*tert*-butylmethylsilyl)-3,3-dimethyl-butanoic acid (10d**, 39 %), m.p. 72 °C (from pentane). - IR (KBr): ca. 3500-2400 (OH), 1700 (C=O). - ^1H NMR: 0.33 (3 H, SiMe), 1.06 (18 H, Si-^tBu), 1.15 (9 H, C-^tBu), 2.33 (1 H, CH). - Anal. Calcd. for $C_{15}H_{32}O_2Si$ (272.5): C, 66.11; H, 11.84. Found: C, 65.3; H,11.52.
Photolysis of 6e: From 1.89 g (5.20 mmol) of **6e**[31], 0.78 g of a thick oil is obtained after Kugelrohr distillation at 80-85 °C/0.01 mmHg. Separation by preparative GC yields the following: a) An unknown compound (2.9 %). - Mass spectrum (70 eV): *m/z* 297 (82 %), 241 (10), 199 (100), 180 (8), 133 (10), 102 (6), 77 (14), 57 (22).
b) 3.3 % of a compound to which the structure of **1-[(*tert*-butyldiphenylsilyl)oxy]-3,3-dimethyl-1-butyne** is assigned tentatively based on the mass spectrum (70 eV): *m/z* 336 (≤1 %), 279 (100, $M^+-{}^tBu$), 199 (61, Ph_2SiO), 181 (15), 105 (17), 77 (13). No IR or NMR spectra were obtained, but the presence of this compound in the product mixture is compatible[32] with the following trace signals: (IR: 2250 ($C\equiv C$); ^{13}C NMR: 44.6 ($\mathit{C}\equiv C$-O), 86.7 ($C\equiv\mathit{C}$-O),

c) **4-(*tert*-Butyldiphenylsilyl)-2,2-dimethyl-cyclobutanone** (**9e**); colorless oil, 39 % yield. - IR (film): 1758 (C=O). - ^{1}H NMR: 0.32 (3 H, 2-Me), 1.12 (9 H, ^{t}Bu), 1.15 (2-Me), 1.70 and 2.03 (AB part of ABX system, 3-H^a, 3-H^b, ^3J(3-H^a,3-H^b) = ^3J(H-3^b,4-H) = 10.3 Hz, ^3J(3-H^a,4-H) = 8.3 Hz), 3.82 (dd, 1 H, 4-H), 7.25-7.84 (10 H). - ^{13}C NMR: 18.7 (Me), 19.7 (Me), 24.2 (CH$_2$), 28.2 (C(*C*H$_3$)$_3$), 29.1 (*C*(CH$_3$)$_3$), 44.0 (4-C), 59.3 (2-C), 217.0 (C=O). - Mass spectrum (70 eV): *m/z* 336 (≤ 1 %), 280 (3, M$^+$ - C$_4$H$_8$), 223 (100, M$^+$ - C$_4$H$_8$ - ^{t}Bu), 136 (6), 106 (10). - Anal. Calcd. for $C_{22}H_{28}OSi$ (336.6): C, 78.51; H, 8.38. Found: C, 77.5; H, 8.29.

d) ***tert*-Butyl-(*tert*-butyldiphenylsilyl)-ketene** (**8e**), 59 % yield, m.p. 49 °C. - IR (KBr): 2079 (C=C=O). - ^{1}H NMR: 0.96 and 1.02 (9 H each, Si-^{t}Bu and C-^{t}Bu), 7.28-7.96 (10 H). - ^{13}C NMR: 19.1 (*C*=C=O), 21.7 (Si-*C*(CH$_3$)$_3$), 27.9 (C-*C*(CH$_3$)$_3$ and Si-C(*C*H$_3$)$_3$), 33.1 (C-C(*C*H$_3$)$_3$), 128.0, 129.9, 134.7, 136.6, 184.7 (C=*C*=O). - Mass spectrum (70 eV): *m/z* 336 (5 %), 279 (100, M$^+$ - ^{t}Bu), 223 (74, M$^+$ - ^{t}Bu - C$_4$H$_8$), 197 (17), 137 (15), 105 (28), 57 (12). - Anal. Calcd. for $C_{22}H_{28}OSi$ (336.6): C, 78.51; H, 8.38. Found: C, 77.8; H, 8.22.

Photolysis of 6f:[7)] To the product mixture is added dichloromethane (20 ml), methanol (10 ml) and a few drops of HCl$_{conc}$. After 1 h, the solvent is evaporated, and the residue is separated by Lobar column chromatography. a) 0.18 g (14 %) of **2,2-dimethyl-4-triisopropylsilyl-cyclobutanone** (**9f**). - IR (film): 1755 (C=O). - ^{1}H NMR: 1.0-1.1 (m, 21 H, ^{i}Pr), 1.13 (s, 3 H, Me), 1.23 (s, 3 H, Me), 1.90 ("d", 2 H, 3-H^a, 3-H^b, ^3J(3-H^a,3-H^b) = ^3J(3-H^a,4-H) = 10.5 Hz), 3.20 (t, 1 H, 4-H). - Anal. Calcd. for $C_{13}H_{30}OSi$ (254.1): C, 70.84; H, 11.81. Found: C, 70.5; H, 11.59.

b) 0.54 g (38 %) of **methyl 3,3-dimethyl-2-triisopropylsilyl-butanoate** (**12f**). - IR (film): 1720 (C=O). - ^{1}H NMR: 1.00-1.20 (m, 30 H, ^{i}Pr and ^{t}Bu), 2.35 (s, 1 H, CH), 3.70 (s, 3 H, OMe). - Anal. Calcd. for $C_{16}H_{34}O_2Si$ (286.1): C, 67.11, H, 11.88. Found: C, 67.1; H, 11.24.

Sensitized photolysis of 6f: A solution of **6f**[7)] (1.71 g, 6.06 mmol) and benzophenone (10.92 g, 60 mmol) in benzene (100 ml) is irradiated for 17 h at $\lambda \geq 320$ nm (Gräntzel photoreactor, model 400). The solution is concentrated to ca. 20 ml, and pentane (20 ml) is added. Benzophenone is removed by repeated crystallization at -30 °C. The residual product mixture is treated as described above for **6c**. a) 0.76 g (46 %) of **3,3-dimethyl-2-triisopropylsilyl-butanoic acid** (**10f**), m.p. 85 °C. IR (KBr): 3300-2400 (OH), 1660 (C=O). - ^{1}H NMR: 1.10-1.20 (30 H, ^{i}Pr and ^{t}Bu), 2.30 (1 H, 2-H). Anal. Calcd. for $C_{15}H_{32}O_2Si$ (272.1): C, 66.15; H, 11.76. Found: C, 66.4; H, 11.48.

Photolysis of 6g: The resulting **diphenylmethyl-triisopropylsilyl-ketene** (**8g**) cannot be purified completely. A mixture of **8g**, acetonitrile (10 ml), water (5 ml) and two drops of HCl$_{conc}$. is refluxed for 2 h. Extraction with dichloromethane (3x10 ml), drying, replacing the solvent by ether-petrolether (3:1) and cooling to -78 °C yields a solid, which is recrystallized from petrolether: 1.45 g (71 %) of **3,3-diphenyl-2-triisopropylsilyl-propanoic acid** (**10g**), m.p. 176-178 °C. - IR(KBr): ca. 3300-2400 (OH), 1680 (C=0). - ^{1}H NMR: 0.9-1.2 (m, 21 H, ^{i}Pr), 3.37 (d, 1 H, 2-H, ^3J = 12 Hz), 4.50 (d, 1 H, CHPh$_2$, ^3J = 12 Hz), 6.95-7.32 (m, 10 H). - Anal. Calcd. for $C_{24}H_{34}O_2Si$ (382.6): C, 75.34; H, 8.96. Found; C, 75,3; 8.84.

(1-Adamantyl)-(*tert*-butyldimethylsilyl)-ketene (**8h**): By irradiaton of **6h**; purification by column chromatography (ether - petrolether, 1:1), pale-yellow viscous oil, 55 % yield. - IR (film): 2075 (C=C=O). - ^{1}H NMR: 0.15 (6 H, Me), 0.90 (9 H, ^{t}Bu), 1.55-2.10 (15 H, adamantyl). ^{13}C NMR: -2.9 (SiMe$_2$), 18.5 (*C*=C=O), 26.9 (C(*C*H$_3$)$_3$), 28.0 (*C*Me$_3$), 29.4 (d), 36.4 (t), 38.5 (1-adamantyl), 45.8, 184.1 (C=*C*=O). - Anal. Calcd. for $C_{18}H_{30}SiO$ (290.5): C, 74.42; H, 10.41. Found: C, 74.9; H, 10.21.

(1-Adamantyl)-(*tert*-butyldimethylsilyl)-acetic acid (**10h**): A solution of **8h** in acetone-water (10:1) is stirred for 2 h. Work-up yields **10h** as a colorless powder, m.p. 178-180 °C (from ether) in 72 % yield. - IR (KBr): ca. 3300-2400 (OH), 1685 (C=O). - ^{1}H NMR: 0.13 and 0.20 (3 H each, SiMe), 0.92, (9 H, ^{t}Bu), 1.50-2.05 (m, 16 H). - Anal. Calcd. for $C_{18}H_{32}O_2Si$ (308.5): C, 70.07; H, 10.45. Found: C, 69.9; H, 10.43.

(1-Adamantyl)-(*tert*-butyldiphenylsilyl)-ketene (8i): By irradiation of 6i; viscous yellow oil, 71 % yield. - IR (film): 2067 (C=C=O). - ^{1}H NMR: 1.00 (9 H, ^{t}Bu), 1.2-2.1 (15 H), 7.30-7.50 (6 H), 7.70-7.95 (4 H).
(1-Adamantyl)-triisopropylsilyl-ketene (8j): By irradiation of 6j; pale-yellow viscous oil; 62 % yield. IR (film): 2070 (C=C=O). - ^{1}H NMR: 1.10 (21 H, ^{i}Pr), 1.55-2.12 (15 H). - ^{13}C NMR: 13.5 (*C*H(CH$_3$)$_2$), 19.3 (CH(*C*H$_3$)$_2$), 24.3 (*C*=C=O), 29.9(d), 36.7(t), 38.6 (1-adamantyl), 46.2(t), 183.6 (C=*C*=O). - Anal. Calcd. for $C_{21}H_{36}OSi$ (332.6): C, 75.83; H, 10.91. Found: C, 73.6; H, 10.58.
(1-Adamantyl)-(triisopropylsilyl)-acetic acid (10j): A solution of 8j is stirred in acetone-water (10:1) for 2 h; yield: 90 %; m.p. 180-183 °C. - IR (KBr): ca. 3300-2400 (OH), 1680 (C=O). - ^{1}H NMR: 1.22 (21 H, ^{i}Pr), 1.65-2.10 (15 H, adamantyl), 2.20 (s, 1 H, C*H*-COOH). - Anal. Calcd. for $C_{21}H_{38}O_2Si$ (350.6): C, 71.94; H, 10.92. Found: C, 71.6; H, 10.69.
Phenyl-triethylsilyl-ketene (8k): From 6k[6] as a yellow oil, 49 % yield. - IR (film): 2080 (C=C=O). - Anal. Calcd. for $C_{14}H_{20}OSi$ (232.4): C, 72.4; H, 8.67. Found: C 72.0; H, 9.04.
(2-Thienyl)-triisopropylsilyl-ketene (6l): The product obtained by irradiation of 6l[6] is purified by Kugelrohr distillation at 140 °C/0.25 mmHg; 94 % yield. - IR (film): 2085 (C=C=O). - ^{1}H NMR: 1.03-1.30 (21 H), 6.63-7.16 (3 H). - Anal. Calcd. for $C_{15}H_{24}OSSi$ (280.5): C, 64.2; H, 8.62. Found: C, 64.0; H, 8.45.
Photolysis of 6m: The solution of **6m** (1.49 g, 5.00 mmol) in benzene (65 ml) is irradiated for 12 h. The solvent is removed and the residue is separated by Lobar column chromatography. The first major fraction consists of unreacted **6m** (15 %). The second major fraction (0.74 g, 55 %) is a mixture of **1-ethyl-4-methyl-3-triisopropylsilyl-2-azetidinone 16** (2 isomers, IR: ν(C=O) = 1740 cm^{-1}) and **1-ethyl-3-triisopropylsilyl-2-pyrrolidinone 17** (IR: 1670 cm^{-1}) in a ratio of 27:6:61 as determined by GC. Identification of **16**/**17** by analytical GC/MS: Mass spectrum of **16** (70 eV): *m/z* 269 (1 %, M$^+$), 226 (18, M$^+$ - ^{i}Pr), 155 (10), 113 (15), 96 (100, M$^+$ - Me - Si^{i}Pr$_3$), 68 (21, M+ - Me - Si^{i}Pr$_3$ - C_2H_5 or C_2H_4). Both isomers give virtually identical mass spectra. - Mass spectrum of **17** (70 eV): *m/z* 269 (1 %, M$^+$), 254 (1, M$^+$ - Me), 226 (100, M$^+$ - ^{i}Pr).

Copper(I) triflate catalyzed decomposition of 6a, c, 1

Methyl 2-(triethylsilyl)propanoate (11a): Crude diazoketone **6a**, obtained from 1-diazo-2-propanone (0.84 g, 10 mmol), triethylsilyl trifluoromethanesulfonate (10 mmol) and ethyldiisopropylamine (10 mmol) in ether,[7] is added dropwise with stirring to a solution of 0.20 g (0.4 mmol) of CuO_3SCF_3 x 0.5 C_6H_6[33] in benzene (60 ml). After 10 min, methanol (2 ml) is added, and stirring is continued for 1 h. The mixture is filtered through a pad of $MgSO_4$, the solvent is evaporated, and the residue is distilled at 65 °C/0.02 mmHg (Kugelrohr): 1.10 g (50 %) of 11a. - IR (film): 1725 (C=O). - ^{1}H NMR: 0.48-1.02 (m, 15 H), 1.19 (d, 3 H, ^3J = 7.5 Hz, CH-C*H*$_3$), 2.10 (q, 1 H, CH), 3.64 (s, 3 H). Anal. Calcd. for $C_{10}H_{22}O_2Si$ (202.4): C, 59.4; H, 10.96. Found: C, 59.5; H, 10.84.
Ethyl 2-(*tert*-butyldimethylsilyl)-3,3-dimethyl-butanoate (12c): A solution of 6c (1.73 g, 7.2 mmol) in benzene (5 ml) is added dropwise to CuO_3SCF_3 x 0.5 C_6H_6[33] (0.15 g, 0.3 mmol) in benzene (60 ml). When gas evolution has ceased (10 min), ethanol (2ml) is added. After 1 h, the solvent is removed and the residue is chromatographed over silica gel (30 g) with chloroform: 0.71 g (38 %) of **12d**, b.p. 70 °C/0.01 mmHg. - IR (film): 1710 (C=O). - ^{1}H NMR: 0.15 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe), 0.88 (s, 9 H, Si-^{t}Bu), 1.07 (s, 9 H, C-^{t}Bu), 1.32 (t, 3 H, CH$_2$C*H*$_3$), 2.10 (s, 1 H, 2-H), 4.03 (dq, C*H*$_2$CH$_3$). - Anal. Calcd. for $C_{14}H_{30}O_2Si$ (258.5): C, 65.1; H, 11.69. Found: C, 65.2; H, 11.40.
5-*tert*-Butyl-2,2-diisopropyl-3,3-dimethyl-1-oxa-2-sila-4-cyclopentene (19): 6f is decomposed as described for **6d**. When evolution of dinitrogen is over (2 h), the mixture is filtered over a pad of $MgSO_4$. Kugelrohr distillation

at 90 °C/0.01 mmHg yields **16**[7] (46 %). - Anal. Calcd. for $C_{15}H_{30}OSi$ (254.5): C, 70.8; H, 11.88. Found: C, 70.8; H, 11.76.
(2-Thienyl)-triisopropylsilyl-ketene (81): **61**[6] is decomposed as described above for **6c**. When gas evolution is finished, the solvent is evaporated, and **81** is purified by Kugelrohr distillation at 125 °C/0.25 mmHg; yield: 93 %. See above for spectroscopic data.

Thermolysis of 6g, j

General procedure: A solution of diazoketone **6** (5-10 mmol) in benzene (50-60 ml) is refluxed for 4,5 h. The solvent is removed and the residue is purified.
2,2-Diisopropyl-3,3-dimethyl-5-diphenylmethyl-1-oxa-2-sila-4-cyclopentene (20g): From **6g**, purification by Lobar column chromatography; 78 % yield. - IR (film): 1605 (C=C), 1125 (SiOC?[7]). - ^1H NMR: ca. 0.9-1.3 (14 H, Si^iPr_2), 4.35 (s, 1 H, =CH), 4.73 (s, 1 H, Ph_2CH), 7.20 (10 H). - Anal. Calcd. for $C_{24}H_{32}OSi$ (364.6): C, 79.06; H, 8.85. Found: C, 77.9; H, 8.65.

5-(1-Adamantyl)-2,2-diisopropyl-3,3-dimethyl-1-oxa-2-sila-4-cyclopentene (20j): From **6j**; purification by Kugelrohr distillation at 155 °C/ 0.01 mmHg; 68 % yield. - IR (film): 1623 (C=C). - ^1H NMR: 1.0-1.2 (20 H, ^iPr and CMe_2), 1.5-2.1 (15 H, adamantyl), 4.28 (s, 1 H, =CH). -^{13}C NMR: 12.1 ($CHMe_2$), 17.6, 17.7 ($CH(\mathit{CH_3})_2$), 25.9 (C-3), 26.3 ($C(\mathit{CH_3})_2$), 28.4 (d), 35.9 (1-adamantyl), 37.1 (t), 39.9 (t), 109.4 (=CH), 164.1 (C-5). - Anal. Calcd. for $C_{21}H_{36}OSi$ (332.6): C, 75.83; H, 10.9. Found: C, 74.7; H, 10.83.

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