

Acylsilenes (3-Oxo-1-sila-1-propenes) from Acyl(disilanyl)carbenes

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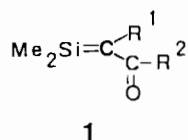
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UV photolysis of diazo(disilanyl)methyl ketones **2** in benzene generates acyl(disilanyl)carbenes **3**, which rearrange to 3-oxo-1-sila-1-propenes **4**. The latter compounds are reactive intermediates which either cyclize to 1-oxa-2-sila-3-cyclobutenes **5** or form the eight-membered cyclodimers **6**, depending on the

substituent of the acyl function. In a side reaction, isomerization of **4** to disilylketenes **7** takes place in some cases. On the other hand, photolysis of diazo ketone **13** yields both the 1-oxa-2-sila-3-cyclobutene **5a** (via the acylsilene **14**) and the adamantyl (trisilanyl)ketene **15** (by Wolff rearrangement).

The high reactivity of the Si=C double bond in most cases prevents the isolation of sila-ethene (silene) derivatives¹⁾. In a recent review^{1b)}, some 150 silenes are compiled which have been reported as reactive intermediates only, characterized by rapid subsequent reactions such as isomerization and dimerization or by appropriate trapping reactions. Acylsilenes **1** represent a rather little known subset of the reactive silene family. Compounds **1a, b** have been isolated in an argon matrix at 10–35 K (**1a**²⁾) or in a 3-MP glass at 77 K (**1a**^{2,3)}, **1b**³⁾). In solution, **1a** can be trapped by addition of an alcohol to the Si=C bond or with enolizable (ene reaction) and non-enolizable ketones ([2+2] cycloaddition)²⁾. Furthermore, **1a** undergoes a facile acylsilene→silylketene rearrangement by a 1,3(C→Si) ethoxy migration. Judging from the reactivity of **1a**, it may be concluded that the related acylsilenes **1c, d** are formed on photolysis or pyrolysis of (trimethylsilyl)- and (dimethylphenylsilyl)-diazoacetates respectively⁴⁾. On the other hand, cyclization of **1b** yielding a 1-oxa-2-sila-3-cyclobutene outweighs any isomerization or intermolecular trapping reaction⁵⁾.



	1 a	b	c	d
R ¹	SiMe ₃	SiMe ₃	Me	Ph
R ²	OEt	Ad	O-alkyl	OMe

Ad :



The diverging behavior of **1b** as compared to the (alkoxy-carbonyl)silenes **1a, c, d** prompted us to investigate a representative series of alkanoyl- and aroylsilenes. In this paper we describe the fate of such acylsilenes in the absence of trapping reagents. The results reported below illustrate that the behavior of acylsilenes **1** depends strongly on the steric bulk of the substituent R²⁶⁾.

Results

1,2(Si→C) migration in a silylcarbene is a well-established route to silenes^{1,2)}. It fails completely, however, in the case of acyl(trialkylsilyl)- or (alkyldiphenylsilyl)carbenes, which have a high preponderance to undergo Wolff rearrangement⁷⁾. On the other hand, it has already been demonstrated that acyl(pentamethylsilyl)carbenes rearrange exclusively by a 1,2(Si→C) trimethylsilyl shift^{2,3,5,6)}, the phenomenon being rationalized by efficient overlap of the Si-σ orbital and the empty carbenic p_z orbital⁸⁾. Therefore, (1-diazo-2-oxoalkyl)pentamethylsilylanes **2** were chosen as the appropriate precursors of acylsilenes (Scheme 1). They were prepared by silylation of the corresponding diazomethyl ketone with pentamethylsilyl triflate, a procedure that has been used successfully before with other silyl triflates^{7,9,10)}. Alternatively, compounds **2a, b, d** have been prepared by acylation of lithium (pentamethylsilyl)diazomethanide¹¹⁾.

Photolysis of **2a, b** in benzene produces 1-oxa-2-sila-3-cyclobutenes **5a, b** as the main product. Compound **5a** has been described before⁵⁾ as a highly reactive and thermally labile molecule, which was characterized in solution only. We have found that **5a** can be isolated as a moisture-sensitive solid by low-temperature crystallization from pentane. A benzene solution appears to be stable at least for several hours at room temperature. Ring cleavage by alcohols may serve as a chemical characterization (vide infra).

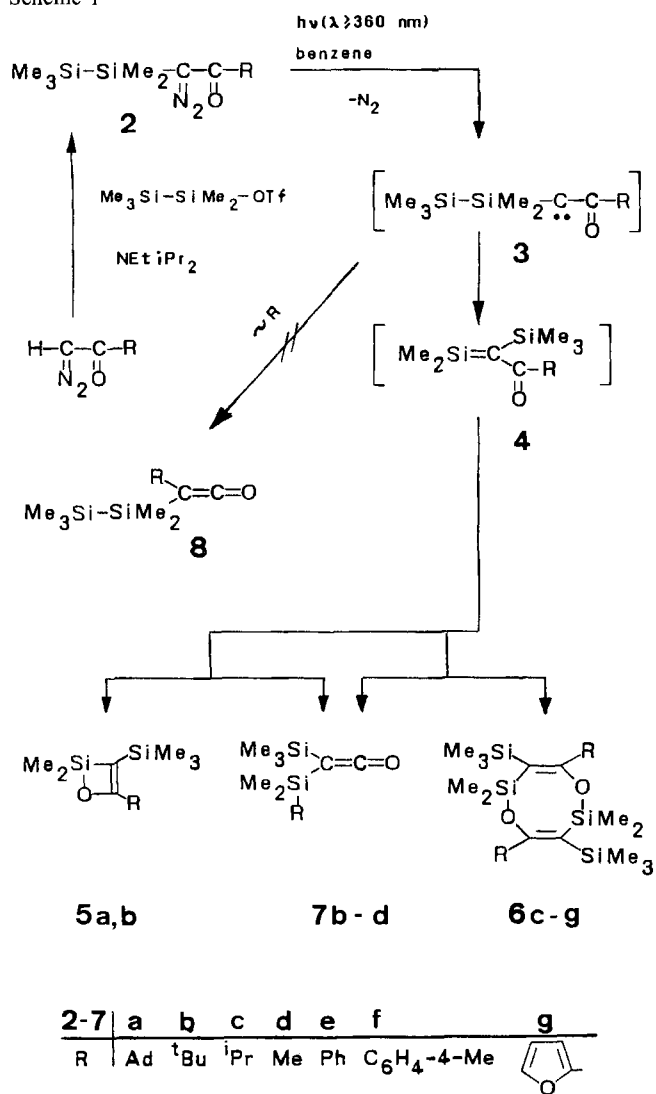
In contrast to **2a, b**, irradiation of **2c–g** furnished the eight-membered heterocycles **6c–g** as stable crystalline compounds. The nature of these rings has been established beyond doubt by an X-ray crystal structure analysis of **6d**⁶⁾. A synopsis of spectroscopic data relevant to differentiate between the four- and eight-membered rings **5** and **6** has been given⁶⁾; it is not repeated here. Clearly, the mass spectrum is the most important tool to elucidate the structure of the products (see Experimental).

In mechanistic terms, acylsilenes **4**, formed from **2** via carbenes **3**, are the precursors of both **5** and **6**. Whereas **5a**,

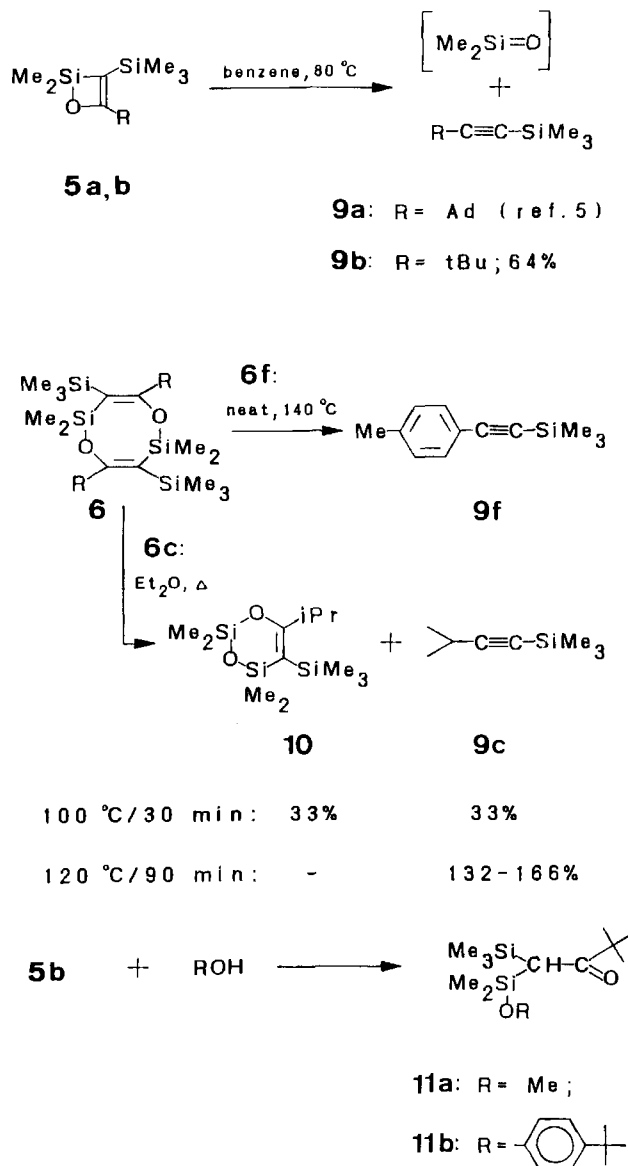
b are readily explained by cyclization of **4a, b**, the eight-membered rings **6** may be considered to be cyclodimers of either **4** or **5**^{12,13}. As a reason for the fast cyclization of **4a, b**, one could invoke the bulkiness of the adamantyl and *t*Bu groups, which certainly would enforce cyclization, if the silene is formed in the *s-cis*-conformation.

In the photolyzed reaction mixtures of **2b–d** weak IR absorptions in the cumulene region are found, which are assigned to ketenes **7b–d**. Being formed only in low yields, these ketenes were not isolated except in the case of **7d**. Clearly, this product stems from an acylsilene \rightarrow silylketene rearrangement (**4d** \rightarrow **7d**), which has precedent in the literature [**4**, R = OEt² (\equiv **1a**)]; it should be noted that Wolff rearrangement of carbene **3** would produce a different ketene **8**⁷. The assignment of ketenes **7b, c** rests on analogy with **7d**. During irradiation of the aryl-substituted diazo ketones **2e–g**, a deep-red to violet color developed which persisted as long as the solution was kept under argon; it was also observed when the photolysis was carried out in anhydrous THF rather than in benzene. The carrier of this color could not be identified.

Scheme 1



Scheme 2



The heterocycles **5** and **6** differ considerably in their thermal stability and chemical reactivity (Scheme 2). In solution, **5a, b** are unstable above ca. 50 °C. In a fragmentation process, alkynes **9a**, **b** are formed together with dimethylsilanone which oligomerizes (Scheme 2). The silanone has been trapped by insertion into Si–O bonds⁹, and one might expect that **5a, b** themselves can act as traps for dimethylsilanone. In fact, if **5a** is kept in benzene at 50 °C for 20 hours, it partly decomposes to a mixture that – according to GC/MS analysis – contains **9a** (61%) and presumably the products of insertion of two, three, or four Me₂Si=O units into the Si–O bond of **5a** (yields 2.9, 3.2, 3.0%, resp.). The 1-oxa-2-sila-3-cyclobutene, the signals of which were still visible in the ¹³C-NMR spectrum of the reaction mixture, and the insertion product of one dimethylsilanone molecule into **5a** probably do not survive the GC conditions (60–150 °C).

The eight-membered heterocycles are thermally more stable. At ca. 120–140°C, however, they also break down into two equivalents of the respective silylalkyne, e.g. **9c** and **9f**, and a silicon-containing polymer. As has been demonstrated for **6c**, the fragmentation occurs stepwise: Extrusion of one alkyne unit and ring contraction produces the six-membered heterocycle **10**, which on prolonged heating or at higher temperature undergoes further fragmentation. No clean reaction was observed, on the other hand, when neat **6g** was thermolyzed at 140°C.

Whereas **6d** does not react with methanol even after six hours at 65°C, **5a** has been reported to be readily ring-opened by methanol at room temperature⁹. In the same manner, the Si–O bond of **5b** is easily cleaved by alcohols to form α,α -disilyl ketones **11**.

We have also used diazo ketone **13** as an acylsilene precursor (Scheme 3). This compound was prepared from 1-(1-adamantyl)-2-diazo-1-ethanone and the hitherto unknown silyl triflate **12**. The photochemical decomposition of **13** furnished two major products. In line with the transformation **2a**→**5a**, the acylsilene **14** is generated, which cyclizes to the 1-oxa-2-sila-3-cyclobutene **5a**. The second product is a ketene, but, surprisingly enough, the one (**15**) resulting from Wolff rearrangement of **13** rather than from an acylsilene→silyl ketene rearrangement. The constitution of ketene **15** follows from the X-ray crystal structure analysis of the carboxylic acid **16** derived from the ketene (Figure 1). This seems to be the only known case in which Wolff rearrangement and a 1,2(Si→C) silyl migration to a carbene center occur competing. Perhaps, the steric bulk of the tris(trimethylsilyl)silyl group reduces its rate of 1,2 migra-

tion, despite of the high donating property of the $\sigma(\text{Si}-\text{Si})$ bond.

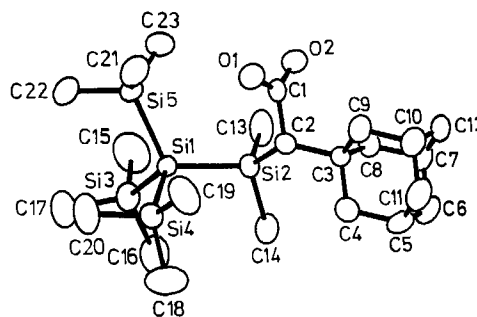


Figure 1. Molecular structure of **16** (ORTEP plot). Selected bond distances [Å]: Si1–Si2 2.357(2); Si1–Si3 2.364(2); Si1–Si4 2.337(2); Si1–Si5 2.352(2); Si–CH₃ 1.842(8)–1.869(8); Si2–C2 1.912(5); C1–O1 1.284(5); C1–O2 1.234(5). In the crystal, two molecules related by a center of symmetry are connected by a hydrogen bond, O1⋯H⋯O2' = 2.643(5) Å

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Experimental

IR spectra: Perkin-Elmer IR 394, Beckman IR 20A. — ¹H-NMR spectra: Varian EM 390 (90 MHz), Bruker WP 200 (200 MHz), CHCl₃ or CH₂Cl₂ as internal standards; δ values correspond to $\delta(\text{TMS})$. — ¹³C-NMR spectra: Bruker WP 200 (50.28 MHz), solvent peaks (C₆D₆ or CDCl₃) as internal standards; δ values correspond to $\delta(\text{TMS})$ [$\delta(\text{TMS}) = \delta(\text{CDCl}_3) + 77.0 = \delta(\text{C}_6\text{D}_6) + 128.0$]. — ²⁹Si NMR: Jeol GX 270 HL (53.54 MHz), TMS as internal standard. All NMR spectra were taken in CDCl₃ unless stated otherwise. — Elemental analyses: Perkin-Elmer EA 240. — Melting points: Heat block. Oven temperatures are reported for kugelrohr distillations. — Column chromatography: Merck Lobar columns (LiChroprep SI 60, 40–63 μm). — Photolyses: Pyrex glass vessel, high-pressure mercury lamp (Philips HPK 125 W). — All reactions involving synthesis and transformation of diazo ketones **2** and **13** were carried out in rigorously dried solvents.

Diazo Ketones 2a–g. — *General Procedure:* The solution of a diazomethyl ketone (10 mmol) and ethyldiisopropylamine (1.29 g, 1.74 ml, 10 mmol) in 50 ml of anhydrous ether is chilled to 0°C under argon, and pentamethyldisilanyl triflate¹⁴ (2.80 g, 10 mmol) is added dropwise. A white precipitate of ethyldiisopropylammonium triflate starts to form immediately. After 30 min at 0°C the mixture is brought to room temp. and stirred for another 2–5 h. The solid is filtered off with suction and washed with ether. The combined ethereal solutions are concentrated at 14 Torr/25°C, and the yellow residue is purified by Lobar column chromatography [**2a–d**: eluent chloroform; **2g**: ether/petrolether (30–75°C) (1:1); dry solvents were used] or used as crude product (**2e, f**).

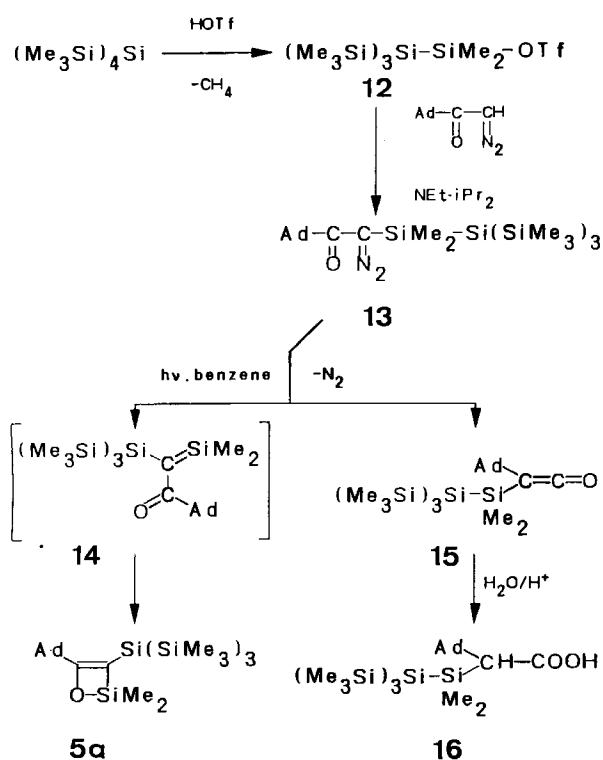
Diazo ketones **2a, b, d** have already been prepared by a different procedure¹¹.

1-(1-Adamantyl)-2-diazo-2-(pentamethyldisilanyl)ethanone (2a): From 1-(1-adamantyl)-2-diazo-1-ethanone²; yield 2.48 g (74%); yellow solid, m. p. 80–83°C (dec.). — IR (KBr): $\tilde{\nu} = 2045 \text{ cm}^{-1}$ (CN₂), 1608 (C=O). — ¹H NMR: $\delta = 0.10$ (SiMe₃), 0.21 (SiMe₂).

C₁₇H₃₀N₂OSi₂ (334.6) Calcd. C 61.02 H 9.04 N 8.37
Found C 61.0 H 8.95 N 7.6

1-Diazo-3,3-dimethyl-1-(pentamethyldisilanyl)-2-butanone (2b): From 1-diazo-3,3-dimethyl-2-butanone¹⁵; 1.48 g (58%) of a yellow

Scheme 3



oil. — IR (film): $\tilde{\nu}$ = 2055 cm^{-1} (CN_2), 1615 ($\text{C}=\text{O}$). — ^1H NMR: δ = 0.15 (SiMe_3), 0.25 (SiMe_2), 1.25 ($t\text{Bu}$).

$\text{C}_{11}\text{H}_{24}\text{N}_2\text{OSi}_2$ (256.5) Calcd. C 51.51 H 9.43 N 10.92
Found C 50.9 H 9.33 N 10.2

1-Diazo-3-methyl-1-(pentamethyldisilanyl)-2-butanone (2c): From 1-diazo-3-methyl-2-butanone¹⁵; 1.36 g (56%) of a yellow oil. — IR (film): $\tilde{\nu}$ = 2060 cm^{-1} (CN_2), 1625 ($\text{C}=\text{O}$). — ^1H NMR: δ = 0.15 (SiMe_3), 0.25 (SiMe_2), 1.20 (CHMe_2), 3.00 (CHMe_2).

$\text{C}_{10}\text{H}_{22}\text{N}_2\text{OSi}_2$ (242.5) Calcd. C 49.54 H 9.15 N 11.55
Found C 49.4 H 9.3 N 8.2

1-Diazo-1-(pentamethyldisilanyl)-2-propanone (2d): From 1-diazo-2-propanone¹⁶; 1.58 g (74%) of a yellow oil. — IR (film): $\tilde{\nu}$ = 2063 cm^{-1} (CN_2), 1632 ($\text{C}=\text{O}$). — ^1H NMR: δ = 0.15 (SiMe_3), 0.25 (SiMe_2), 2.28 (Me).

$\text{C}_8\text{H}_{18}\text{N}_2\text{OSi}_2$ (214.4) Calcd. C 44.81 H 8.46 N 13.06
Found C 44.5 H 8.42 N 11.2

2-Diazo-2-(pentamethyldisilanyl)-1-phenylethanone (2e): From 2-diazo-1-phenyl-1-ethanone¹⁵; 2.32 g (84%) of a yellow solid, which is very moisture-sensitive¹⁷ (protodesilylation). — IR (KBr): $\tilde{\nu}$ = 2060 cm^{-1} (CN_2); 1605 ($\text{C}=\text{O}$). — ^1H NMR: δ = 0.21 (SiMe_3), 0.38 (SiMe_2).

2-Diazo-1-(4-methylphenyl)-2-(pentamethyldisilanyl)ethanone (2f): From 2-diazo-1-(4-methylphenyl)-1-ethanone¹⁸; 2.21 g (76%) of a yellow solid, which is very moisture-sensitive¹⁷ (protodesilylation). — IR (KBr): $\tilde{\nu}$ = 2065 cm^{-1} (CN_2), 1610 ($\text{C}=\text{O}$). — ^1H NMR: δ = 0.12 (SiMe_3), 0.30 (SiMe_2), 2.38 ($\text{C}_6\text{H}_4\text{CH}_3$).

2-Diazo-1-(2-furyl)-2-(pentamethyldisilanyl)ethanone (2g): From 2-diazo-1-(2-furyl)-1-ethanone¹⁵; 1.50 g (56%) of an orange oil. — IR (film): $\tilde{\nu}$ = 2070 cm^{-1} (CN_2), 1594 ($\text{C}=\text{O}$). — ^1H NMR: δ = 0.10 (SiMe_3), 0.26 (SiMe_2), 6.46 (dd), 7.07 (d), 7.50 (d).

$\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_2\text{Si}_2$ (266.5) Calcd. C 49.59 H 6.81 N 10.51
Found C 49.5 H 6.72 N 10.2

4-(1-Adamantyl)-2,2-dimethyl-3-(trimethylsilyl)-1-oxa-2-sila-3-cyclobutene (5a): The solution of 1.50 g (4.5 mmol) of **2a** in benzene (50 ml) is irradiated for 6 h. The solvent is removed at 20°C/0.01 Torr, and the residue is recrystallized from pentane at -78°C: 0.81 g (59%) of **5a** as a colorless, moisture-sensitive solid, m.p. 50–52°C. — IR (KBr): $\tilde{\nu}$ = 1532 cm^{-1} ($\text{C}=\text{C}$). — ^1H NMR: δ = 0.15 (SiMe_3), 0.45 (SiMe_2), 1.65–2.10 (m, 15H). — ^{13}C NMR: δ = 0.5 (SiMe_2), 1.9 (SiMe_3); 28.0 (d), 36.6 (t), 39.6 (t), 40.1 (s) (C adamantyl); 103.9 (C-3), 184.2 (C-4). — ^{29}Si NMR (C_6D_6): δ = -5.23 (SiMe_3), 38.2 (SiMe_2). — MS (70 eV): m/z (%) = 306.7 (4) [M^+], 291.6 (27) [$\text{M}^+ - \text{Me}$], 232.6 (3) [$\text{Ad}-\text{C}\equiv\text{C}-\text{SiMe}_3$], 217.6 (100) [$\text{Ad}-\text{C}\equiv\text{C}-\text{SiMe}_2$], 135.5 (10) [Ad], 73 (7) [SiMe_3].

$\text{C}_{17}\text{H}_{30}\text{OSi}_2$ (306.6) Calcd. C 66.59 H 9.86
Found C 65.7 H 9.65

4-tert-Butyl-2,2-dimethyl-3-(trimethylsilyl)-1-oxa-2-sila-3-cyclobutene (5b): The solution of 2.70 g (10.5 mmol) of **2b** in benzene (50 ml) is irradiated for 4 h. The solvent is removed at 20°C/0.01 Torr, and the residual oil is purified by crystallization from pentane (5 ml) at -78°C. (The solid melts above ca. -30°C.) Yield: 1.46 g (61%) of a labile, moisture-sensitive oil¹⁷. — IR (film): $\tilde{\nu}$ = 1540 cm^{-1} ($\text{C}=\text{C}$). — ^1H NMR: δ = 0.22 (SiMe_3), 0.45 (SiMe_2), 1.15 ($t\text{Bu}$). — ^{13}C NMR: δ = 0.3 (SiMe_2), 1.9 (SiMe_3), 28.0 (CMe_3), 38.3 (CMe_3), 103.9 (C-3), 185.5 (C-4). — MS (70 eV): m/z = 228.5 (8) [M^+], 213.5 (9) [$\text{M}^+ - \text{Me}$], 154 (13) [$t\text{Bu}-\text{C}\equiv\text{C}-\text{SiMe}_3 - \text{Me}$], 139 (19) [$t\text{Bu}-\text{C}\equiv\text{C}-\text{SiMe}_2$], 73 (100) [SiMe_3].

Photolysis of 2c–g in Benzene; General Procedure: A solution of **2c–g** in benzene (50 ml) is purged with argon and irradiated until

N_2 evolution has ceased (95–100% N_2 , 3–5 h). In the course of photolysis, the color changes to pale-red (**2c, d**) or violet (**2e–g**). The solvent is evaporated at 20°C/0.01 Torr, and the solid residue is recrystallized from petroleum ether/ether (10 ml, 5:1, **2c, d**) or ether (**2e–g**) at -78°C.

4,8-Diisopropyl-2,2,6,6-tetramethyl-3,7-bis(trimethylsilyl)-1,5-dioxo-2,6-disila-3,7-cyclooctadiene (6c): From 1.09 g (4.05 mmol) of **2c**; 0.59 g (61%) of a colorless powder, m.p. 94–95°C. — IR (KBr): $\tilde{\nu}$ = 1555/1548 cm^{-1} ($\text{C}=\text{C}$). — ^1H NMR: δ = 0.09 (SiMe_3), 0.22 (SiMe_2), 1.10 (d, CHMe_2), 2.90 (sept, CHMe_2). — ^{13}C NMR: δ = 1.7 (SiMe_2), 1.9 (SiMe_3), 20.6 (CHMe_2), 37.3 (CHMe_2), 105.1 (C-3), 175.9 (C-4). — ^{29}Si NMR (C_6D_6): δ = -10.4 (SiMe_3), 4.3 (SiMe_2). — MS (70 eV): m/z (%) = 429 (1.5) [M^+], 288.5 (11) [$\text{M}^+ - i\text{Pr}-\text{C}\equiv\text{C}-\text{SiMe}_3$], 273.5 [$\text{M}^+ - i\text{Pr}-\text{C}\equiv\text{C}-\text{SiMe}_3 - \text{Me}$], 245 (6) [$\text{M}^+ - i\text{Pr}-\text{C}\equiv\text{C}-\text{SiMe}_3 - i\text{Pr}$], 140 (7) [$i\text{Pr}-\text{C}\equiv\text{C}-\text{SiMe}_3$], 125 (100) [$i\text{Pr}-\text{C}\equiv\text{C}-\text{SiMe}_3 - \text{Me}$], 97 (8) [$\text{C}\equiv\text{C}-\text{SiMe}_3$], 73 (30) [SiMe_3].

$\text{C}_{20}\text{H}_{44}\text{O}_2\text{Si}_4$ (428.9) Calcd. C 56.00 H 10.34
Found C 55.5 H 10.14

2,2,4,6,6,8-Hexamethyl-3,7-bis(trimethylsilyl)-1,5-dioxo-2,6-disila-3,7-cyclooctadiene (6d): From 1.26 g (5.9 mmol) of **2d**, 0.63 g (58%) of colorless crystalline **6d** is obtained, m.p. 70–71°C. — IR (KBr): $\tilde{\nu}$ = 1565/1555 cm^{-1} ($\text{C}=\text{C}$). — ^1H NMR: δ = 0.18 (SiMe_3), 0.28 (SiMe_2), 1.99 (Me). — ^{13}C NMR: δ = 2.1/2.2 ($\text{SiMe}_3 + \text{SiMe}_2$), 25.1 (Me), 107.5 (C-3), 170.0 (C-4). — ^{29}Si NMR (C_6D_6): δ = -8.1 (SiMe_3), 7.8 (SiMe_2). — MS (70 eV): m/z (%) = 373 (1) [M^+], 260.5 (25) [$\text{M}^+ - \text{Me}-\text{C}\equiv\text{C}-\text{SiMe}_3$], 245.5 (100) [$\text{M}^+ - \text{Me}-\text{C}\equiv\text{C}-\text{SiMe}_3 - \text{Me}$], 112 (4) [$\text{Me}-\text{C}\equiv\text{C}-\text{SiMe}_3$], 97 (83) [$\text{Me}-\text{C}\equiv\text{C}-\text{SiMe}_3 - \text{Me}$], 73 (9) [SiMe_3].

$\text{C}_{16}\text{H}_{36}\text{O}_2\text{Si}_4$ (372.8) Calcd. C 51.55 H 9.73
Found C 51.1 H 9.42

For the isolation of also formed *bis(trimethylsilyl)ketene* (**7d**), crystallization of **6d** was carried out in pentane. From the remaining solution pentane was distilled off carefully at 36°C. The residue was distilled at 30°C/0.01 Torr to yield **7d**, which was identified by comparison of IR and ^1H -NMR data with reported values¹⁹.

2,2,6,6-Tetramethyl-4,8-diphenyl-3,7-bis(trimethylsilyl)-1,5-dioxo-2,6-disila-3,7-cyclooctadiene (6e): From 2.76 g (10 mmol) of **2e** 0.85 g (34%) of colorless crystalline **6e** is obtained, m.p. 138°C. — IR (KBr): $\tilde{\nu}$ = 1542 cm^{-1} ($\text{C}=\text{C}$). — ^1H NMR: δ = -0.21 (SiMe_3), 0.11 (SiMe_2), 7.35 (phenyl). — ^{13}C NMR: δ = 1.6 (SiMe_2 , SiMe_3), 111.4 (C-3), 171.0 (C-4).

$\text{C}_{26}\text{H}_{40}\text{O}_2\text{Si}_4$ (494.9) Calcd. C 63.09 H 7.74
Found C 61.4 H 8.15

2,2,6,6-Tetramethyl-4,8-bis(4-methylphenyl)-3,7-bis(trimethylsilyl)-1,5-dioxo-2,6-disila-3,7-cyclooctadiene (6f): From 2.90 g (10 mmol) of **2f** 0.85 g (32%) of yellow **6f** is obtained, m.p. 149°C. — IR (KBr): $\tilde{\nu}$ = 1542 cm^{-1} ($\text{C}=\text{C}$). — ^1H NMR: δ = -0.23 (SiMe_3), -0.08 (SiMe_2), 2.42 ($\text{C}_6\text{H}_4\text{CH}_3$), 7.16/7.30 (AA'BB', C_6H_4). — ^{13}C NMR: δ = 1.8 (SiMe_2 , SiMe_3), 21.6 ($\text{C}_6\text{H}_4\text{CH}_3$), 111.2 (C-3), 128.5, 129.6, 139.0, 139.5 (C-aryl), 171.2 (C-4). — MS (70 eV): m/z (%) = 525 (0.1) [M^+], 336.5 (16) [$\text{M}^+ - \text{MeC}_6\text{H}_4-\text{C}\equiv\text{C}-\text{SiMe}_3$], 321.5 (100) [$\text{M}^+ - \text{MeC}_6\text{H}_4-\text{C}\equiv\text{C}-\text{SiMe}_3 - \text{Me}$], 188.3 (6) [$\text{Me}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{SiMe}_3$], 173 (100) [$\text{MeC}_6\text{H}_4-\text{C}\equiv\text{C}-\text{SiMe}_3 - \text{Me}$], 73 (3) [SiMe_3].

$\text{C}_{28}\text{H}_{44}\text{O}_2\text{Si}_4$ (525.0) Calcd. C 64.06 H 8.45
Found C 63.3 H 8.27

4,8-Di-2-furyl-2,2,6,6-tetramethyl-3,7-bis(trimethylsilyl)-1,5-dioxo-2,6-disila-3,7-cyclooctadiene (6g): From 1.00 g (3.8 mmol) of **2g** 0.53 g (59%) of colorless crystalline **6g** is obtained, m.p. 133°C. —

IR (KBr): $\nu = 1595 \text{ cm}^{-1}$, 1525 (C=C, 8-membered ring), 1468. — $^1\text{H NMR}$: $\delta = -0.08$ (SiMe₃), 0.18 (SiMe₂), 6.40–6.47 (m, 3,4-H, furyl), 7.42 (dd, 5-H, furyl). — MS (70 eV): m/z (%) = 477 (1) [M^+], 312.6 (6) [$\text{M}^+ - \text{C}_4\text{H}_3\text{O} - \text{C}\equiv\text{C} - \text{SiMe}_3$], 297.5 (28) [$\text{M}^+ - \text{C}_4\text{H}_3\text{O} - \text{C}\equiv\text{C} - \text{SiMe}_3 - \text{Me}$], 164 (5) [$\text{C}_4\text{H}_3\text{O} - \text{C}\equiv\text{C} - \text{SiMe}_3$], 149 (31) [$\text{C}_4\text{H}_3\text{O} - \text{C}\equiv\text{C} - \text{SiMe}_2$], 73 (100) [SiMe₃].

$\text{C}_{22}\text{H}_{36}\text{O}_4\text{Si}_4$ (476.9) Calcd. C 55.4 H 7.61
Found C 54.7 H 7.54

Thermolysis of 5b: A solution of **2b** (0.70 g, 2.7 mmol) in benzene (40 ml) is irradiated for 4 h (95% N₂). The reaction mixture is then heated at 80°C for 1 h. The solvent is removed at 80°C, and the residue is distilled at 50°C/0.01 Torr (kugelrohr): 0.30 g (64%) of 3,3-dimethyl-1-(trimethylsilyl)-1-butyne (**9b**), identified by comparison (IR, $^1\text{H NMR}$) with an independently prepared sample²⁰.

Thermolysis of 6c: In a thick-walled Schlenk tube the solution of **6c** (0.620 g, 1.45 mmol) in ether (3 ml) is kept at 100°C for 30 min. After cooling the solvent is evaporated, and the residual oil is carefully distilled in a kugelrohr apparatus. At 45°C/0.01 Torr 3-methyl-1-(trimethylsilyl)-1-butyne²¹ (**9c**) is obtained in 33% yield. Further distillation at 70°C/0.01 Torr yields 0.144 g (34%) of 6-isopropyl-2,2,4,4-tetramethyl-5-(trimethylsilyl)-1,3-dioxo-2,4-disila-5-cyclohexene (**10**). — IR (film): $\tilde{\nu} = 1538 \text{ cm}^{-1}$ (C=C). — $^1\text{H NMR}$: $\delta = 0.08$ (SiMe₃), 0.10 (SiMe₂), 0.15 (SiMe₂), 0.96 (d, CHMe₂), 2.65 (sept, CHMe₂). — MS (70 eV): m/z (%) = 288.5 (8) [M^+], 273.5 (16) [$\text{M}^+ - \text{Me}$], 245.5 (7) [$\text{M}^+ - i\text{Pr}$], 221.5 (52), 133 (28) [$\text{M}^+ - i\text{Pr} - \text{C}\equiv\text{C} - \text{SiMe}_3 - \text{Me}$], 125 (23) [$i\text{Pr} - \text{C}\equiv\text{C} - \text{SiMe}_3 - \text{Me}$], 73 (100) [SiMe₃].

$\text{C}_{12}\text{H}_{28}\text{O}_2\text{Si}_3$ (288.6) Calcd. C 49.94 H 9.78
Found C 48.1 H 9.86

If the thermolysis of **6c** (0.480 g, 1.12 mmol) is carried out at 120°C for 90 min, 1.48–1.86 mmol (132–166%) of **9c** is obtained as the only distillable product.

Thermolysis of 6f: 0.28 g (0.53 mmol) of **6f** is placed in a kugelrohr set-up and heated to 140°C at 0.01 Torr. The yellow powder melts, and a colorless oil starts to distill, which is identified as 4-methylphenyl(trimethylsilyl)ethyne (**9f**) by comparison with reported spectral data²²; yield 0.17 g (85%).

Reaction of 5b with Alcohols. — 1-(Dimethylmethoxysilyl)-3,3-dimethyl-1-(trimethylsilyl)-2-butanone (**11a**): **5b** is prepared by photolysis of 1.31 g (5.1 mmol) of **2b** in benzene (50 ml) as described above. To this solution methanol (10 ml) is added. After stirring for 2 h the solvent is removed at 20°C/0.01 Torr, and the residue is distilled at 55°C/0.01 Torr (kugelrohr): 0.86 g (64% based on **5b**) of **11a**. — IR (film): $\tilde{\nu} = 1655 \text{ cm}^{-1}$ (C=O). — $^1\text{H NMR}$: $\delta = 0.12$ (SiMe₃), 0.20 (SiMe₂), 1.12 (tBu), 2.85 (1-H), 3.43 (OMe). — $^{13}\text{C NMR}$ (C₆D₆): $\delta = -0.42/-0.26$ (SiMe₂), 1.05 (SiMe₃), 27.8 (CMe₃), 37.4 (CH), 44.9 (CMe₃), 50.2 (OMe), 213.6 (C=O).

$\text{C}_{12}\text{H}_{28}\text{O}_2\text{Si}_2$ (260.5) Calcd. C 55.32 H 10.83
Found C 54.5 H 10.58

1-[(4-tert-Butylphenoxy)dimethylsilyl]-3,3-dimethyl-1-(trimethylsilyl)-2-butanone (**11b**): **5b** is prepared by photolysis of 1.53 g (6.0 mmol) of **2b** in benzene (50 ml) as described above. To this solution is added 4-tert-butylphenol (0.80 g, 5.3 mmol). After stirring for 3 h the solvent is removed, and the residue is distilled twice at 100°C/0.01 Torr (kugelrohr): 0.63 g (28% based on **5b**) of **11b**. — IR (film) $\tilde{\nu} = 1665 \text{ cm}^{-1}$ (C=O). — $^1\text{H NMR}$: $\delta = 0.25$ (SiMe₃), 0.38/0.41 (diastereotopic SiMe₂), 1.15 (tBuCO), 1.35 (tBu-aryl), 3.15 (1-H). — $^{13}\text{C NMR}$: $\delta = 0.77$, 0.88 (SiMe₂ + SiMe₃), 27.7 (CO-CMe₃), 31.6 (aryl-CMe₃), 34.1 (aryl-CMe₃), 45.2

(CO-CMe₃); 121.4 (d), 126.5 (d), 142.7 (s), 154.5 (s) (C₆H₄); 217.7 (C=O). $\text{C}_{21}\text{H}_{38}\text{O}_2\text{Si}_2$ (378.7) Calcd. C 66.60 H 10.11
Found C 65.3 H 9.83

[1,1,3,3,3-Pentamethyl-2,2-bis(trimethylsilyl)trisilanyl]-trifluoromethanesulfonate (**12**): To a solution of 3.20 g (10 mmol) of tetrakis(trimethylsilyl)silane²³ in dichloromethane (20 ml), kept under argon, trifluoromethanesulfonic acid (1.50 g, 10 mmol) is added dropwise. Gas evolution (CH₄) starts immediately. After 15 h at room temp. the solvent is removed at 20°C/0.01 Torr, and the solid residue is recrystallized from dichloromethane: 3.98 g (87%) of very moisture-sensitive **12**, m.p. 126–128°C. — IR (KBr): $\tilde{\nu} = 1255 \text{ cm}^{-1}$ (br), 1177, 1028, 835–795 (br.). — $^1\text{H NMR}$: $\delta = 0.21$ (SiMe₃), 0.68 (SiMe₂).

$\text{C}_{12}\text{H}_{33}\text{F}_3\text{O}_3\text{Si}_5$ (454.9) Calcd. C 31.68 H 7.31
Found C 31.4 H 7.22

1-(1-Adamantyl)-2-diazo-2-[1,1,3,3,3-pentamethyl-2,2-bis(trimethylsilyl)trisilanyl]ethanone (**13**): Preparation according to the general procedure for **2a–g** given above from 2.04 g (10 mmol) of 1-(1-adamantyl)-2-diazo-1-ethanone and 4.55 g (10 mmol) of **12**. Yield: 2.75 g (54%); yellow powder, m.p. 74°C. — IR (KBr): $\tilde{\nu} = 2057 \text{ cm}^{-1}$ (CN₂), 1615 (C=O). — $^1\text{H NMR}$: $\delta = 0.28$ (27H, SiMe₃), 0.42 (6H, SiMe₂), 1.75–2.20 (m, 15H).

$\text{C}_{23}\text{H}_{48}\text{N}_2\text{OSi}_5$ (509.1) Calcd. C 54.26 H 9.50 N 5.50
Found C 54.1 H 9.39 N 4.6

Photolysis of 13: A solution of 2.04 g (4.01 mmol) of **13** in benzene (40 ml) is irradiated for 75 min. The solvent is evaporated at 0.01 Torr/20°C, and the remaining oil (1.80 g) is dissolved in pentane (2 ml)/ether (1 ml). After 15 h at –78°C 0.85 g of a solid has separated, which is recrystallized three times from ether (3 ml): 0.75 g (39%) of 4-(1-adamantyl)-2,2-dimethyl-3-[tris(trimethylsilyl)silyl]-1-oxa-2-sila-3-cyclobutene (**5a**): m.p. 138°C (dec). — IR (KBr): $\tilde{\nu} = 1528 \text{ cm}^{-1}$ (C=C). — $^1\text{H NMR}$: $\delta = 0.17$ [s, 27H, Si(SiMe₃)₃], 0.47 (s, 6H, SiMe₂), ca. 0.6–2.1 (m, 15H). — $^{13}\text{C NMR}$: $\delta = 0.2$ (SiMe₂), 2.0 (SiMe₃), 27.9 (d), 36.7 (t), 39.7 (t), 40.7 (s) (adamantyl); 91.0 (3-C), 184.3 (4-C).

$\text{C}_{23}\text{H}_{48}\text{OSi}_5$ (481.1) Calcd. C 57.43 H 10.04
Found C 56.8 H 10.06

The mother liquid of the first crystallization is separated by Lobar column chromatography (CHCl₃ as eluent): 0.82 g of still impure ketene **15** [$\nu(\text{C}=\text{C}=\text{O}) = 2075 \text{ cm}^{-1}$] as a viscous yellow oil. Addition of acetone (10 ml) and water (1 ml), stirring for 12 h, evaporation to dryness (0.01 Torr), recrystallization from ether (3 ×), and washing with CH₂Cl₂ (1 ml) yields 0.66 g (33%, based on **13**) of (1-adamantyl)[1,1,3,3,3-pentamethyl-2,2-bis(trimethylsilyl)trisilanyl]acetic acid (**16**), m.p. 196°C. — $^{13}\text{C-NMR}$ (CDCl₃): $\delta = 2.9$ (SiMe₂), 3.5 (SiMe₃); 29.0 (d), 36.7 (t), 37.6 (s), 42.4 (t) (all adamantyl); 51.4 (d, CHCO₂H), 179.7 (CO₂H). — No correct elemental analysis was obtained (uncombustible residue).

X-ray Crystal Structure Analysis of 16: $\text{C}_{23}\text{H}_{50}\text{O}_2\text{Si}_5$, molecular mass 499.08, triclinic, space group $P\bar{1}$, $a = 13.128(7)$, $b = 13.299(4)$, $c = 9.287(5)$ Å, $\alpha = 107.76(4)$, $\beta = 92.24(4)$, $\gamma = 93.26(3)^\circ$, $Z = 2$, $d_{\text{calc}} = 1.08 \text{ g cm}^{-3}$. — **Data collection:** Crystal size 0.5 × 0.3 × 0.2 mm, diffractometer Enraf-Nonius CAD4, monochromatized Mo-K α radiation, 2948 independent reflections in the range $2.0 \leq \theta \leq 21.0^\circ$, $\theta/2\theta$ scan, scan width (0.90 + 0.35 tan θ) $^\circ$, scan speed 1.22–4.02 $^\circ \text{ min}^{-1}$. — **Structure solution and refinement**²⁴: Structure solution by direct methods (MULTAN), refinement by a full-matrix least-squares method. H atoms were partly located in a ΔF map and partly calculated; they were included in the refinement with fixed B values (taken from their bond neigh-

Table 1. Atom coordinates and B_{eq} of non-hydrogen atoms of **16**

Atom	x/a	y/b	z/c	$B_{eq} [Å^2]$
Si1	0.2679(1)	0.2247(1)	0.4469(1)	3.5(1)
Si2	0.3076(1)	0.4013(1)	0.5985(2)	4.3(1)
Si3	0.4138(1)	0.1702(1)	0.3103(2)	5.5(1)
Si4	0.2332(1)	0.1157(1)	0.5971(1)	5.3(1)
Si5	0.1323(1)	0.1981(1)	0.2632(1)	4.5(1)
O1	0.0315(3)	0.4075(2)	0.5965(4)	5.7(1)
O2	0.1178(3)	0.5453(2)	0.5655(4)	5.4(1)
C1	0.1115(4)	0.4719(3)	0.6209(5)	3.8(1)
C2	0.1968(4)	0.4538(3)	0.7212(5)	3.8(1)
C3	0.2153(3)	0.5512(3)	0.8699(5)	3.6(1)
C4	0.2736(4)	0.5191(4)	0.9918(5)	5.1(1)
C5	0.2879(4)	0.6120(4)	1.1403(5)	5.7(1)
C6	0.3446(4)	0.7035(4)	1.1118(6)	5.9(2)
C7	0.2850(5)	0.7372(4)	0.9946(5)	5.7(1)
C8	0.2724(4)	0.6461(3)	0.8469(5)	4.6(1)
C9	0.1112(4)	0.5817(4)	0.9309(6)	5.5(1)
C10	0.1251(4)	0.6729(5)	1.0807(6)	6.9(2)
C11	0.1852(5)	0.6400(5)	1.1975(6)	7.0(2)
C12	0.1803(5)	0.7661(4)	1.0491(6)	7.8(2)
C13	0.3397(5)	0.4870(4)	0.4789(6)	7.0(2)
C14	0.4250(4)	0.4019(5)	0.7184(7)	7.5(2)
C15	0.4293(5)	0.2407(6)	0.1676(8)	9.9(2)
C16	0.5357(5)	0.1981(6)	0.4279(9)	9.7(2)
C17	0.4030(5)	0.0259(5)	0.2092(8)	8.7(2)
C18	0.3479(7)	0.1092(6)	0.7176(8)	11.5(2)
C19	0.1232(6)	0.1596(5)	0.7173(6)	9.0(2)
C20	0.1953(6)	-0.0216(5)	0.4777(7)	9.1(2)
C21	0.0063(5)	0.1775(5)	0.3342(7)	7.2(2)
C22	0.1479(5)	0.0785(5)	0.0991(6)	6.7(2)
C23	0.1316(4)	0.3126(4)	0.1887(6)	6.2(2)

bors). The proton of the CO_2H group was not found (it is involved in a $O \cdots H \cdots O$ hydrogen bond and probably disordered). With 2431 reflections [$I > 2 \sigma(I)$] and 467 variables, refinement converged at $R = 0.0458$, $R_w = [\sum \Delta^2 F / \sum F_o^2]^{1/2} = 0.0451$ (unit weights, maximum shift/error ratio 1.34).

Atom parameters are given in Table 1. Further details of the structure are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2. These data are available with quotation of the registry number CSD-54048, the authors, and the reference to this publication.

CAS Registry Numbers

2a: 87594-05-6 / **2b**: 87594-03-4 / **2c**: 118096-53-0 / **2d**: 87594-01-2 / **2e**: 123725-17-7 / **2f**: 123725-18-8 / **2g**: 123725-19-9 / **5a**:

88703-87-1 / **5b**: 118096-54-1 / **6c**: 118107-32-7 / **6d**: 118096-55-2 / **6e**: 123725-20-2 / **6f**: 123725-21-3 / **6g**: 123725-22-4 / **7d**: 19061-00-8 / **9b**: 14630-42-3 / **9c**: 18388-07-3 / **9f**: 4186-14-5 / **10**: 118096-56-3 / **11a**: 123725-23-5 / **11b**: 123725-24-6 / **12**: 123725-25-7 / **13**: 123725-26-8 / **15**: 123725-27-9 / **16**: 123725-28-0 / $Me_3SiSi(Me_2)OTf$: 105445-53-2 / $MeOH$: 67-56-1 / $(Me_3Si)_4Si$: 4098-98-0 / 4-*tert*-butylphenol: 98-54-4 / 1-(1-adamantyl)-2-diazo-1-ethanone: 5934-69-0 / 1-diazo-3,3-dimethyl-2-butanone: 6832-15-1 / 1-diazo-3-methyl-2-butanone: 14088-55-2 / 1-diazo-2-propanone: 2684-62-0 / 2-diazo-1-phenyl-1-ethanone: 3282-32-4 / 2-diazo-1-(4-methylphenyl)-1-ethanone: 17263-64-8 / 2-diazo-1-(2-furyl)-1-ethanone: 21443-46-9

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