(2 × 50 mL). The organic layer was dried over Na_2SO_4 and oxidized with PbO_2 (0.5 g) under stirring. After 0.5 h, the insoluble salts were filtered off, the filtrate was evaporated to dryness, and the residue was chromatographed on a SiO_2 column, eluting with light petroleum/ethyl acetate (95:5).

HPLC Measurements. General Procedure. The Grignard reagents were prepared starting from the halides (0.5 mmol in 5 mL of THF or Et_2O) and magnesium (0.12 g, 0.5 mmol in 5 mL of THF or Et_2O) and adding to the solution of 1 (0.052 g, 0.125 mmol) and 5 (0.052 g, 0.125 mmol) in 10 mL of CH_2Cl_2 in the same conditions of the preparative reactions. After 1 h, the reaction mixture was hydrolyzed with a NH_4Cl solution (25 mL, 0.1 M) extracted with CH_2Cl_2 (2 × 25 mL), dried over Na_2SO_4, and oxidized with PbO_2 (0.2 g) under stirring. After 0.5 h, the mixture was filtered and evaporated to dryness. The residue was added to 10 mL of DMF and 90 mL of MeOH. The obtained solution was analyzed using HPLC. (Conditions: eluant = MeOH/H_2O 90:10; flow = 1.0 mL/min; temperature = 55 °C; column = Nucleosil-R C-18 5μ).

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Photooxygenation of Silyl Ketene Acetals: Dioxetanes as Precursors to α-Silylperoxy Esters in the Silatropic Ene Reaction

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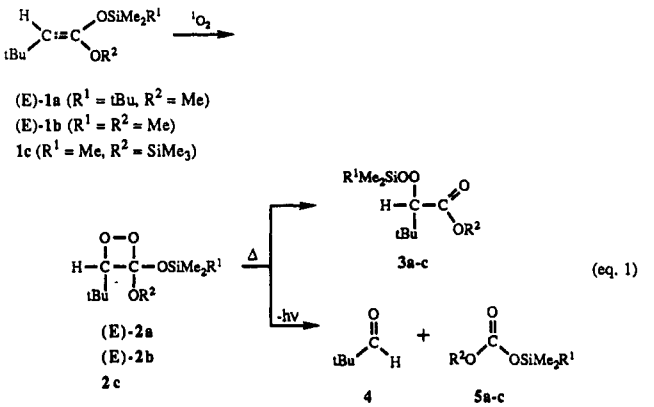
Photooxygenation of silyl ketene acetals afforded dioxetanes, which subsequently underwent secondary reactions to give rearrangement products (α-silylperoxy esters, major products) and cleavage products (pivalaldehyde, minor product). The kinetics of these reactions were studied by NMR and chemiluminescence. The activation energy of the chemiluminescent cleavage process was 2–3 kcal/mol higher than that of the rearrangement. In the presence of catalytic amounts of CF_3COCF_3 or CF_3COCH_3, the (*E*)-silyl ketene acetals rearranged into their *Z* isomers. Photooxygenation of the (*E*)- and (*Z*)-silyl ketene acetals showed that the [2 + 2] cycloaddition was rigorously diastereoselective. Trapping experiments with acetaldehyde confirmed the intermediacy of 1,4-zwitterions in the rearrangement of the (*E*)- and (*Z*)-dioxetanes into α-silylperoxy esters, but such intermediates were not detected during the photooxygenation of the silyl ketene acetals; the latter proceeds presumably via perepoxides.

The ene reaction of olefins bearing allylic hydrogens with $^1O_2$ produces allylic hydroperoxides via hydrogen migration.[1] Analogously, silyl enol ethers and ketene acetals form α-silylperoxy ketones and esters via silyl migration.[2-13] In this context, previously it was found[10] that silyl ketene acetals reacted with $^1O_2$ to give not only the expected α-silylperoxy esters, but also dioxetanes. A mechanism was proposed in which a common 1,4-dipolar intermediate served as precursor to both the dioxetanes and the silylperoxy esters. We now present evidence that esters **3** are not formed directly from the acetals **1**, but rather through rearrangement of the dioxetanes **2** (eq 1).



(eq. 1)

Results and Discussion

tert-Butylketene methyl *tert*-butyldimethylsilyl acetal ((*E*)-**1a**) was prepared by the published procedure as the sole isomer, and its configuration was determined by ^1H NOE[14] experiments (Figure 1). The NOE spectra of the (*E*)-**1a** isomer showed a large enhancement (8%) of the olefinic proton resonance during saturation of the $SiMe_2$ group, while no corresponding effect could be observed from the methoxy group. A reverse situation was obtained for the (*Z*)-**1a** isomer, for which saturation of the methoxy group enhanced the intensity of the olefinic proton by 11%.

It was discovered that the CF_3COCF_3 and CF_3COCH_3 ketones could be used as catalysts for the geometrical isomerization of the ketene silyl acetals (*E*)-**1a,b**. When a solution of silyl ketene acetal (*E*)-**1a** was heated with catalytic amounts of CF_3COCF_3 or CF_3COCH_3 in CCl_4 at 35 °C and the reaction monitored by ^1H NMR, after several minutes the characteristic signals of (*E*)-**1a** at δ 3.51 (OMe) and 3.73 (CH) decreased and two new signals for (*Z*)-**1a** at δ 3.43 and 3.35 (ratio of integration 3:1) appeared

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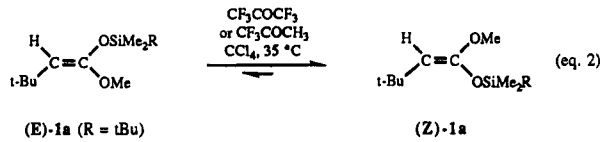
and increased gradually. After about 2 h, a mixture that consisted of 10% (*E*)-**1a** and 90% (*Z*)-**1a** isomers (eq 2)

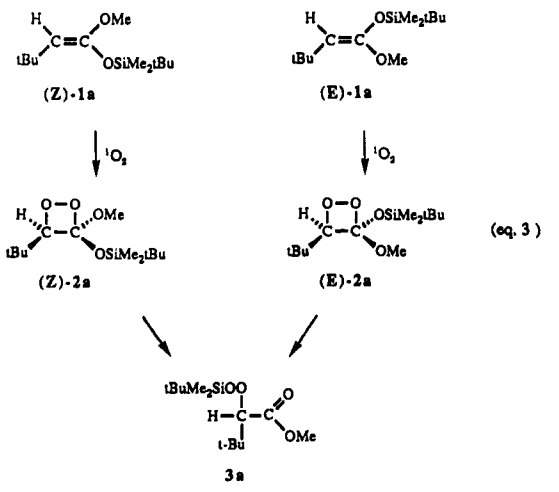


(*E*)-**1a** (R = tBu) (*Z*)-**1a**

was attained. Unfortunately, column chromatography on silica gel or Florisil or fractional distillation failed to separate the isomers. The characterization of the unknown (*Z*)-**1a** isomer was accomplished by comparison of its spectral data with that of the known (*E*)-**1a** isomer. The ^1H NOE results of the (*Z*)-**1a** isomer were also definitive for determining its stereochemistry (Figure 1). This unusual isomerization has precedence in that silyl ketene acetals were interconverted by $HgBr_2/Me_3SiBr$ as catalysts.[15]

A solution of the silyl ketene acetal (*E*)-**1a** and catalytic amounts of TPP (tetraphenylporphine) in CH_2Cl_2 was irradiated at −80 °C under an oxygen atmosphere and monitored by ^1H NMR. It was observed that the characteristic signals of (*E*)-**1a** (δ 3.51 (OCH_3), 3.73 (=CH)) decreased and those of the dioxetane (*E*)-**2a** (δ 3.32 (OCH_3) 4.84 (CH)) increased. After ca. 3 h (*E*)-**1a** was completely converted exclusively into the diastereoisomer (*E*)-**2a** and no α-silylperoxy ester **3a** was detected. Workup gave pure dioxetane (*E*)-**2a**, which was characterized by ^1H and ^{13}C NMR, IR, iodometry, and chemiluminescence measurements. While a sample of the dioxetane (*E*)-**2a** in CCl_4 was heated at 70 °C, ^1H NMR monitoring showed that the signals of (*E*)-**2a** decreased and those of the α-silylperoxy ester **3a** (δ 3.73 (OCH_3) and 4.13 (CH)) increased to afford **3a** (ca. 97% by NMR) and small amounts (ca. 3% by ^1H NMR) of pivalaldehyde (**4**, δ 9.8 (CH=O)). The silyl carbonates **5a–c** were detected by ^1H NMR but not characterized. By quantitative capillary GC analysis 3.2 ± 0.2% pivalaldehyde (**4**) was determined. The thermal reaction was accompanied by bright chemiluminescence. A control experiment indicated that the ester **3a** was stable toward heating at 70 °C in CCl_4 and thus not responsible for the light emission.

When a 90:10 diastereomeric mixture of the silyl ketene acetals (*Z*/*E*)-**1a** was photooxygenated, a 90:10 diastereomeric mixture of the dioxetanes (*Z*/*E*)-**2a** was also obtained. Like for the pure (*E*)-**1a** isomer, again complete diastereoselectivity occurred in the [2 + 2] cycloaddition of singlet oxygen to the (*Z*)-**1a** ketene acetal (eq 3). The



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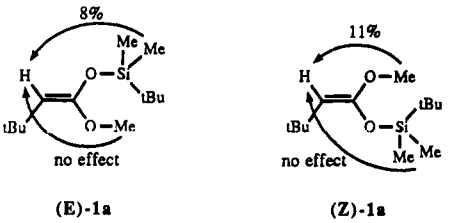

(*E*)-**1a** (*Z*)-**1a**

Figure 1. NOE results for the diastereomeric silyl ketene acetals (*E*)-**1a** and (*Z*)-**1a**.

Table I. Activation Parameters for the Rearrangement and Cleavage of Dioxetane (*E*)-2a

kinetic method	temp range (K)	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
isothermal (^1H NMR)[a]	322.6–338.3	23.4 ± 0.7	22.7 ± 0.7	−5.3 ± 0.3
isothermal (direct chemiluminescence)[b]	322.7–339.5	23.8 ± 0.9	23.1 ± 0.9	−4.2 ± 0.3
temp jump (direct chemiluminescence)[b]	313.3–328.2	26.5 ± 0.2		

[a] Monitoring the consumption of dioxetane (*E*)-**2a** and the formation of α-silylperoxy ester **3a**. [b] Monitoring the light emission by means of a Mitchell–Hastings photometer.

structure of the dioxetane (*Z*)-**2a** was confirmed by comparison of its ^1H and ^{13}C NMR spectra with those of the dioxetane (*E*)-**2a** and by the rearrangement to the α-silylperoxy ester. Thus, the isomer mixture of (*Z*/*E*)-**2a** in CCl_4 was allowed to warm from −20 to +20 °C, and ^1H and ^{13}C NMR monitoring showed that both (*Z*/*E*)-**2a** rearranged to the α-silylperoxy ester **3a**. It was noted that the dioxetane (*Z*)-**2a** was less stable than its isomer (*E*)-**2a**. At −20 °C the isomer (*E*)-**2a** could be stored for several days without significant change, while the isomer (*Z*)-**2a** was completely converted into the α-silylperoxy ester **3a** within 24 h. The instability of the (*Z*)-**2a** isomer should be due to the steric interaction of the two bulky groups located on the same side of the dioxetane ring.

When the silyl ketene acetals (*E*)-**1b** and **1c** were submitted to the photooxygenation conditions as described previously, analogous transformations were observed (eq 1), except that the rearrangement of the dioxetanes (*E*)-**2b** and **2c** to the α-silylperoxy ester **3b** and **3c** were faster than that of (*E*)-**2a** to **3a**. For example, upon termination of the photooxygenation of the ketene acetal **1c** at −20 °C in CCl_4, ca. 50% of the dioxetane **2c** had already been converted into the ester **3c**.

The paradoxical happenstance of observing pronounced direct chemiluminescence but only traces of cleavage product **4** (ca. 3%) in the thermolysis of dioxetane (*E*)-**2a** required experimental clarification. A kinetic investigation gave the activation parameters shown in Table I. Within the experimental error, ^1H NMR and direct isothermal chemiluminescence gave the same results, while temperature-jump chemiluminescence[16] gave consistently activation enthalpies about 2–3 kcal/mol higher. The latter method measures the activation enthalpy for the light emitting path, i.e., for the cleavage (*E*)-**2a** → **4** and **5a**, while the former encompasses all decomposition modes, of which the silatropic rearrangement (*E*)-**2a** → **3a** strongly predominates (ca. 97%). Assuming similar entropy factors (the temperature jump method[16] does not provide entropy

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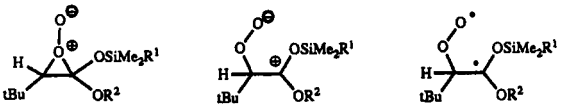
values) from the difference of about 2–3 kcal/mol in the activation enthalpies between cleavage and silatropic rearrangement, it can be estimated that ca. 2–4% pivalaldehyde (4) should be produced (via dioxetane cleavage at 60–70 °C). The observed yield of 3.2 ± 0.2% of 4 in the thermolysis of dioxetane (*E*)-**2a** provides a most satisfactory check on this kinetic data.

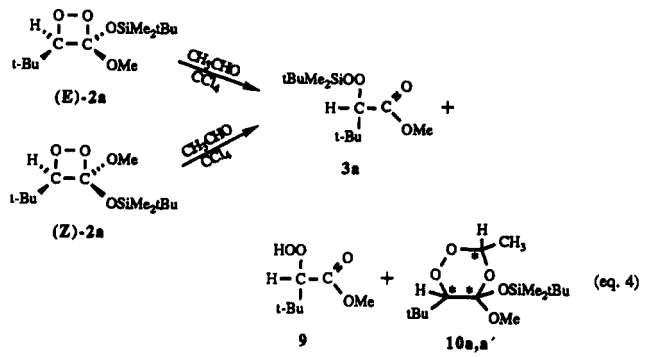
The interesting feature of the present case is that the more exothermic reaction (cleavage is by ca. 71 kcal/mol more exothermic than the silatropic rearrangement of the dioxetane (*E*)-**2a**) requires the higher (by ca. 2–3 kcal/mol) thermal activation; however, the chemiluminescent pathway[16b] leads to electronically excited carbonyl products whose n,π* excitation energies lie ca. 80 kcal/mol above the ground-state products. Consequently, adjusting for this excitation energy the dioxetane cleavage route is by ca. 10 kcal/mol more endothermic than the silatropic rearrangement and thus the latter is energetically preferred.

What is unusual about the present case is the lower activation enthalpy for the ring-opening process with preservation of the peroxide bond, i.e., the rearrangement (*E*)-**2a** → **3a**. Of the possible intermediates **6**–**8**, the most



6 **7** **8**

propitious is presumably the 1,4-dipole **7** because of efficient mesomeric stabilization of the positive charge at the acetal carbon atom. Indeed, zwitterion intermediates could be trapped by acetaldehyde during the rearrangement (*E*)-**2a** → **3a** (eq 4). A sample of (*E*)-**2a** in a 1:4 mixture



(eq. 4)

(by volume) of CH_3CHO and CCl_4 was heated at 35 °C and the reaction monitored by ^1H NMR. The dioxetane (*E*)-**2a** slowly disappeared, and besides the rearrangement product **3a** and its desilylation product **9**, the diastereomeric 1,2,4-trioxanes **10a** (characteristic signals: δ 5.44 (q, 1 H), 1.24 (d, 3 H)) and **10a′** (characteristic signals: δ 5.46 (q, 1 H), 1.27 (d, 3 H)) were also observed as trapping products (eq 4). After all dioxetane (*E*)-**2a** was consumed, the solvent was rotaevaporated and the residue chromatographed on Florisil to give the α-silylperoxy ester **3a**, the α-hydroperoxy ester **9**, and a mixture of the diastereomeric 1,2,4-trioxanes **10a** and **10a′** in relative proportions 35:25:23:17. Iodometric titration of the mixture of **10a** and **10a′** gave 88.7 ± 1.3% peroxide content, but further efforts to separate or purify rigorously these trapping products by column chromatography and/or fractional distillation failed in view of decomposition. When a 90:10 mixture of the dioxetane isomers (*Z*/*E*)-**2a** was submitted to this trapping experiment with acetaldehyde, the same products were obtained, except the relative proportions of **3a**, **9**, **10a**, and **10a′** were 61:16:15:8. The 1,2,4-trioxanes **10a** and **10a′** were identified by comparison of their spectral data with those of known analogues.[17–19] Unfortunately, due to the instability of these 1,2,4-trioxanes, their absolute configuration could not be determined. Nevertheless, in view of the fact that from the diastereomeric dioxetanes (*E*)-**2a** and (*Z*)-**2a** nearly the same amounts of diastereomeric trioxanes **10a** and **10a′** were formed in the acetaldehyde trapping experiments, presumably the same 1,4-zwitterion **7a** serves as the intermediate in the rearrangement of both dioxetanes (*E*)- and (*Z*)-**2a**.

Such trapping experiments were also conducted during the photooxygenation of silyl ketene acetal (*E*)-**1a** under a variety of conditions. Firstly, the photooxygenation was performed at −20 and −10 °C by using a 1:1 mixture (by volume) of CH_3CHO and CCl_4 as medium. After the silyl ketene acetal (*E*)-**1a** was completely consumed, the dioxetane (*E*)-**2a** and a trace of the α-silylperoxy ester **3a**, but no trapping product, were detected. Secondly, the photooxygenation was performed under the above conditions, but at 0, 10, and 20 °C. In these runs, besides the dioxetane (*E*)-**2a** and a trace of the α-silylperoxy ester **3a**, some higher molecular weight products derived from CH_3CHO were observed, but again no trapping product.

Mechanistically significant is the fact that during the photooxygenation of ketene acetal (*E*)-**1a** in the presence of acetaldehyde no trapping products **10a** and **10a′** were detected. Furthermore, the reaction of the ketene acetal isomer (*E*)-**1a** with singlet oxygen gave exclusively the dioxetane isomer (*E*)-**2a** and (*Z*)-**1a** only (*Z*)-**2a** (eq 3), thereby showing that the [2 + 2] cycloaddition proceeded with a high degree of diastereoselectivity. Had a dipolar intermediate intervened in the photooxygenation, e.g., the 1,4-zwitterion **7**, some isomerization would have been expected, leading to a mixture of the diastereomeric dioxetanes (*E*)-**2a** and (*Z*)-**2a**. Consequently, the present results demand that if an intermediate is involved in the photooxygenation of ketene acetals (*E*)-**1a**, it must be different from the 1,4-dipole **7** that is observed in the rearrangement of the dioxetanes (*E*)-**2a** to the peroxy esters **3a**. Although our results do not exclude a direct concerted [2 + 2] cycloaddition, the perepoxide **6a** is proposed as best qualifying for serving as intermediate, especially in view of the current trend of thinking.[1] Thus, the previous mechanism,[10] in which the 1,4-dipolar intermediate **7a** functions as common branching point in the formation of the dioxetane and silylperoxy ester products, must be revised, and we suggest that the mechanism in eq 5 accommodates more adequately the present experimental facts.

In summary, photooxygenation of silyl ketene acetals **1** gave the expected dioxetanes, which underwent subsequent reactions to afford rearrangement and cleavage products. Moreover, the dioxetane isomers (*E*)- and (*Z*)-**2a** were formed from the isomers (*E*)- and (*Z*)-**1a** in high diastereoselectivity. Trapping experiments with acetaldehyde confirmed the intermediacy of 1,4-zwitterions in the rearrangement of the (*E*)- and (*Z*)-**2a** into the α-silylperoxy ester **3a**, but such intermediates were not detected during attempted trapping in the photooxygenation of the silyl ketene acetals; in the latter process presumably a perepoxide intermediate intervenes.

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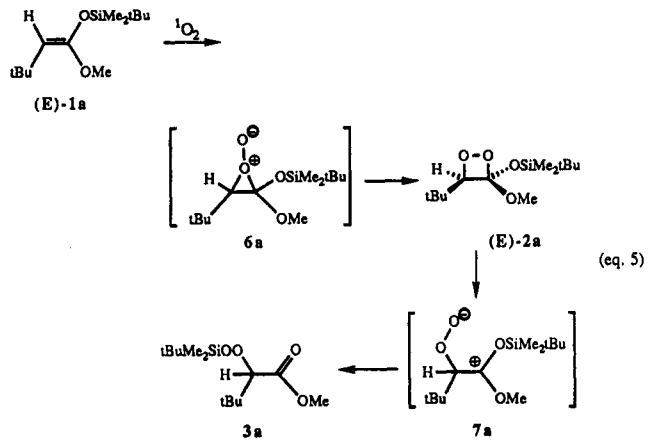

Experimental Section

Infrared (IR) spectra were measured on a Perkin-Elmer 1420 spectrophotometer. ^{1}H NMR spectra were obtained either on a Bruker AW 80 (80-MHz) or AC 200 (200-MHz) and ^{13}C NMR spectra on a Bruker AC 200 (50-MHz) spectrometer. The chemiluminescence intensities were measured by means of a Mitchell-Hastings photometer. Gas chromatographic analyses were performed on a Carlo Erba Strumentazione 4100 or on a Fractovap 2900 capillary instrument.

General Procedures for the Preparation of Silyl Ketene Acetals.[20] A 100-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a pressure-equalizing dropping funnel, and a reflux condenser, was flame dried while flushing with dry nitrogen gas. Under a nitrogen atmosphere, a solution of iPr_2NH (25 mmol) in dry THF (20 mL) was introduced and a solution of nBuLi (25 mmol) in hexane was added dropwise at 0 °C. The mixture was allowed to warm up to 20 °C after complete addition and further stirred for 15–30 min, then cooled to −78 °C. A solution of the carbonyl compound (22–25 mmol of ketone, aldehyde, or ester or 12 mmol of carboxylic acid) in dry THF (5–10 mL) was added dropwise within 10–20 min. The stirred mixture was maintained at −78 °C for 30–60 min and subsequently a solution of chlorosilane (25–50 mmol) in dry THF (5–10 mL) was added. In the case of *tert*-butyldimethylchlorosilane, 2 mL of HMPT was added after the addition of the chlorosilane was complete. The reaction mixture was warmed up to 20 °C, further stirred for 30–60 min, and then allowed to stand overnight. THF was removed by rotaevaporation. The resulting residue was taken up in ca. 50 mL of petroleum ether (bp 30–50 °C), and after addition of ca. 20 mL of cold, saturated, aqueous $NaHCO_3$ solution, the mixture was well shaken, the organic layer dried over anhydrous Na_2SO_4, and the solvent rotaevaporated (ca. 20 °C (15 Torr)). The crude product was purified by distillation or chromatography.

(*E*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal[21] ((*E*)-1a). The above general procedure was employed by using 6.10 g (60.0 mmol) of iPr_2NH in 16 mL of THF, 50.0 mL (59.0 mmol) of a 1.18 M nBuLi hexane solution, 7.80 g (60.0 mmol) of $tBuCH_2COOMe$ in 10 mL of THF, 9.00 g (60.0 mmol) of $tBuMe_2SiCl$ in 15 mL of THF, and 2.0 mL of HMPT. The crude product (13.5 g, 92% yield) was distilled under reduced pressure to yield 10.8 g (75%; lit.[21] 48%) of pure product as a colorless liquid: bp 94–104 °C (17 Torr), 53–55 °C (0.2 Torr) (lit.[21] bp 91–95 °C (3 Torr)); IR (CaF_2) ν 2940, 2886, 2844, 1660, 1455, 1240, 1225, 1140, 1070, 880 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.17 (s, 6 H, $SiMe_2$), 0.94 (s, 9 H, SitBu), 1.05 (s, 9 H, CtBu), 3.51 (s, 3 H, OMe), 3.73 (s, 1 H, =CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −5.1 (q, $SiMe_2$), 18.2 (s, SitBu), 25.7 (q, SitBu), 29.7 (s, CtBu), 31.0 (q, CtBu), 54.5 (q, OMe), 96.9 (d, C-2), 152.7 (s, C-1).

(*E*)-*tert*-Butylketene Methyl Trimethylsilyl Acetal[9,21] ((*E*)-1b). The above general procedure was employed by using 2.20 g (20.4 mmol) of iPr_2NH in 15 mL THF, 10 mL (20.4 mmol) of a 2.04 M nBuLi hexane solution, 2.34 g (18.0 mmol) of $tBuCH_2COOCH_3$, and 3.91 g (36.0 mmol) of Me_3SiCl in 5 mL of THF. The crude product was distilled under reduced pressure to yield 3.42 g (94%; lit.[21] 85%) of pure product as a colorless liquid, bp 60–64 °C (13 Torr) (lit.[21] bp 45 °C (0.5 Torr)); IR (CaF_2) ν 2958, 2900, 2860, 1668, 1460, 1440, 1324, 1250, 1232, 1148, 1076 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.21 (s, 9 H, $SiMe_3$), 1.05 (s, 9 H, tBu), 3.46 (s, 3 H, OMe), 3.61 (s, 1 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.3 (q, $SiMe_3$), 29.7 (s, tBu), 31.0 (q, tBu), 54.3 (q, OMe), 96.8 (d, C-2), 152.4 (s, C-1).

***tert*-Butylketene Bis(trimethylsilyl) Acetal[20b] (1c).** The above general procedure was employed by using 3.80 g (37.5 mmol) of iPr_2NH in 30 mL of THF, 20.0 mL (37.6 mmol) of a 1.88 M nBuLi hexane solution, 2.18 g (19.0 mmol) of $tBuCH_2COOH$ in 10 mL of THF, and 10.3 g (95.0 mmol) of Me_3SiCl. The crude product was distilled under reduced pressure to yield 4.11 g (83%; lit.[20b] 90%) of pure product as a colorless liquid, bp 85–88 °C (15 Torr) (lit.[20b] 42 °C (0.5 Torr)); IR (CCl_4) ν 2960, 2900, 1663, 1340, 1249, 1230, 1160, 1063, 1030, 881, 850 cm^{-1}; ^{1}H NMR (80 MHz, CCl_4) δ 0.1 (s, 18 H, 2 × $SiMe_3$), 0.9 (s, 9 H, tBu), 3.3 (s, 1 H, CH).

(*Z*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal ((*Z*)-1a). A solution of 2.20 g (9.00 mmol) of silyl ketene acetal (*E*)-1a and 0.220 g (2.00 mmol) of CF_3COCH_3 in 10 mL of CCl_4 was heated at 35 °C and the reaction progress monitored by ^{1}H NMR. After about 3 h, 90% of (*E*)-1a had been converted into the *Z* isomer, and the isomer composition did not change on further standing. Rotaevaporation (20 °C (17 Torr)) of the solvent and the CF_3COCH_3 gave a 10:90 mixture of (*E*/*Z*)-1a isomers. Attempts to separate the isomers failed, since they decomposed during silica gel as well as Florisil column chromatography and fractional distillation; IR (CaF_2) ν 2966, 2910, 2870, 1670, 1474, 1360, 1238, 1160, 1100, 977, 952, 915 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.16 (s, 6 H, $SiMe_2$), 0.94 (s, 9 H, SitBu), 1.08 (s, 9 H, CtBu), 3.35 (s, 1 H, =CH), 3.43 (s, 3 H, OMe); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.8 (q, $SiMe_2$), 18.2 (s, SitBu), 26.0 (q, SitBu), 29.5 (s, CtBu), 31.3 (q, CtBu), 54.5 (q, OMe), 85.1 (d, C-2), 155.9 (s, C-1).

General Procedure of Photooxygenation. A 15 × 3 cm Pyrex test tube was equipped with an oxygen inlet tube and charged with a solution of silyl ketene acetals (ca. 2 mmol) and catalytic amounts of TPP (1–2 mg) in 10 mL of CCl_4. The test tube was immersed in an ethanol bath, cooled by means of a cryostat (generally at −20 °C, except where indicated), and irradiated by two 150-W sodium lamps while passing a stream of oxygen through the reaction vessel. The process was monitored by ^{1}H NMR. After all starting material was consumed, the solvent was rotaevaporated (0 °C (17 Torr)) and the residue purified by column chromatography or used directly in further reactions.

Photooxygenation of (*E*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal ((*E*)-1a). The above general procedure was followed, except that CH_2Cl_2 was used as the solvent and the reaction mixture was maintained at −90 °C. A sample of 0.240 g (1.00 mmol) of silyl ketene acetal (*E*)-1a was completely converted within 2 h into the dioxetane (*E*)-2a,[21] as confirmed by ^{1}H NMR. On warm up to 30 °C, the dioxetane (*E*)-2a led within ca. 8 h to ca. 97% α-silylperoxy ester 3a[21] and ca. 3% pivalaldehyde. The products were isolated by column chromatography at −40 °C. (*E*)-2a: IR (CCl_4) ν 2956, 2930, 2858, 1462, 1363, 1302, 1245, 1130, 1050, 1002, 910, 840 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.24 (s, 3 H, SiMe), 0.37 (s, 3 H, SiMe), 0.91 (s, 9 H, SitBu), 1.00 (s, 9 H, CtBu), 3.28 (s, 3 H, OMe), 4.76 (s, 1 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −4.5 (q, SiMe), −3.0 (q, SiMe), 17.6 (s, SitBu), 24.6 (q, CtBu), 25.4 (q, SitBu), 32.8 (s, CtBu), 47.7 (q, OMe), 99.2 (d, C-4), 115.6 (s, C-3); iodometric titration of (*E*)-2a gave 99.3 ± 0.5% peroxide content. 3a: IR (CCl_4) ν 2958, 2930, 2900, 2858, 1757, 1740, 1460, 1365, 1276, 1248, 1212, 1162, 1100, 880, 835 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 3 H, SiMe), 0.17 (s, 3 H, SiMe), 0.90 (s, 9 H, SitBu), 0.97 (s, 9 H, CtBu), 3.75 (s, 3 H, OMe), 4.13 (s, 1 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −5.8 (2 × q, $SiMe_2$), 26.0 (q, SitBu), 26.4 (q, CtBu), 29.5 (s, SitBu), 34.5 (s, CtBu), 51.3 (q, OMe), 91.4 (d, C-2), 171.1 (s, C=O); iodometric titration of 3a gave 99.1 ± 0.6% peroxide content.

Photooxygenation of (*E*)- and (*Z*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetals [(*Z*/*E*)-1a]. The above general procedure was followed by using 0.490 g (2.00 mmol)

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of a 90:10 mixture of silyl ketene acetals (*Z*/*E*)-**1a** and completely converted within 40 min into the dioxetanes (*Z*/*E*)-**2a** (90:10, determined by NMR). On warming a sample of the dioxetane mixture (*Z*/*E*)-**2a** from −20 to +20 °C, both (*Z*)- and (*E*)-dioxetane rearranged into the α-silylperoxy ester **3a**. At −20 °C as shown by NMR, the time of rearrangement was about 1 d for the isomer (*Z*)-**2a** and several weeks for the (*E*)-**2a** isomer. (*Z*)-**2a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.10 (s, 3 H, SiMe), 0.12 (s, 3 H, SiMe), 0.89 (s, 9 H, SitBu), 1.02 (s, 9 H, CtBu), 3.71 (s, 3 H, OMe), 4.86 (s, 1 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.5 (2 × q, $SiMe_2$), 18.1 (s, SitBu), 24.4 (q, CtBu), 25.6 (q, SitBu), 29.6 (s, CtBu), 51.6 (q, OMe) 94.4 (d, C-4), 109.6 (s, C-3).

Photooxygenation of (*E*)-*tert*-Butylketene Methyl Trimethylsilyl Acetal ((*E*)-1b). The above general procedure was followed by employing 0.410 g (2.00 mmol) of silyl ketene acetal (*E*)-**1b**, which was completely converted within 50 min into a 70:30 mixture of dioxetane (*E*)-**2b** and α-silylperoxy ester **3b**.[9,21] ^{1}H NMR monitoring of the reaction progress revealed that the latter was formed by rearrangement of the dioxetane (*E*)-**2b**. A sample of the reaction mixture was allowed to stand at 20 °C for 1 d and all the dioxetane rearranged into the α-silylperoxy ester **3b**. (*E*)-**2b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.29 (s, 9 H, $SiMe_3$), 0.99 (s, 9 H, tBu), 3.27 (s, 3 H, OMe), 4.74 (s, 1 H, CH). **3b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.19 (s, 9 H, $SiMe_3$), 0.98 (s, 9 H, tBu), 3.75 (s, 3 H, OMe), 4.12 (s, 1 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.4 (q, $SiMe_3$), 26.5 (q, tBu), 34.6 (s, tBu), 51.4 (q, OMe), 91.5 (d, C-2), 171.0 (s, C=O).

Photooxygenation of *tert*-Butylketene Bis(trimethylsilyl) Acetal (1c). The above general procedure was followed by employing 0.780 g (3.00 mmol) of silyl ketene acetal **1c**, which was completely converted within 30 min into a 60:40 mixture (determined by ^{1}H NMR) of dioxetane **2c** and α-silylperoxy ester **3c**.[6,22] On rotaevaporation (0 °C (15 Torr)) the dioxetane was completely converted into the known[6,22] α-silylperoxy ester **3c**. **2c**: ^{1}H NMR (80 MHz, CCl_4) δ 0.1 (s, 9 H, $SiMe_3$), 0.2 (s, 9 H, $SiMe_3$), 0.9 (s, 9 H, tBu), 4.4 (s, 1 H, CH). **3c**: ^{1}H NMR (80 MHz, CCl_4) δ 0.1 (s, 9 H, $OSiMe_3$), 0.2 (s, 9 H, $OOSiMe_3$), 0.9 (s, 9 H, tBu), 3.9 (s, 1 H, CH).

Trapping Experiments with Acetaldehyde. In the Photooxygenation of (*E*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal ((*E*)-1a). The above general procedure was followed by using 0.240 g (1.00 mmol) of silyl ketene acetal (*E*)-**1a**, 5 mL of acetaldehyde, and 2 mg of TPP in 5 mL of CCl_4. The experiments were run at −20, −10, 0, 10, and 20 °C, and by ^{1}H NMR monitoring no trapping product was detected.

In the Rearrangement of (*E*)-4-*tert*-Butyl-3-[(*tert*-butyldimethylsilyl)oxy]-3-methoxy-1,2-dioxetane ((*E*)-2a). To a solution of 0.140 g (0.510 mmol) of dioxetane (*E*)-**2a** in 2 mL of CCl_4 was added 0.5 mL of acetaldehyde. The reaction mixture was allowed to stand at 35 °C while being monitored by ^{1}H NMR. After all the dioxetane was consumed, the solvent was rotaevaporated (20 °C (17 Torr)) and the residue chromatographed at −40 °C on Florisil by eluting with a 9:1 petroleum ether (bp 30–50 °C)/diethyl ether mixture to give α-silylperoxy ester **3a**, α-hydroperoxy ester **9**,[21] and the diastereomeric trioxanes **10a** and **10a′** in a total yield of 60% and the relative proportions of 35:25:23:17. Iodometry of the isomeric mixture of the trapping products gave a 88.6 ± 1.2% peroxide content. **10a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.26 (s, 6 H, $SiMe_2$), 0.92 (s, 9 H, SitBu), 1.01 (s, 9 H, CtBu), 1.27 (d, *J* = 6 Hz, 3 H, CMe), 3.77 (s, 3 H, OMe), 4.34 (s, 1 H, 6-H), 5.46 (q, *J* = 6 Hz, 1 H, 3-H). **10a′**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.09 (s, 6 H, $SiMe_2$), 0.94 (s, 9 H, SitBu), 1.01 (s, 9 H, CtBu), 1.24 (d, 3 H, CMe), 3.79 (s, 3 H, OMe), 4.22 (s, 1 H, 6-H), 5.44 (q, 1 H, 3-H). **9**: IR (CaF_2) ν 3520, 3380, 2960, 2868, 1741, 1432, 1370, 1355, 1337, 1215, 1171, 1090 cm^{-1}; ^{1}H NMR (80 MHz, CCl_4) δ 0.89 (s, 9 H, tBu), 3.68 (s, 3 H, OMe), 4.05 (s, 1 H, CH), 8.9 (s, 1 H, OOH).

In the Rearrangement of (*Z*/*E*)-4-*tert*-Butyl-3-[(*tert*-butyldimethylsilyl)oxy]-3-methoxy-1,2-dioxetanes ((*Z*/*E*)-2a). Following the above procedure, a solution of 0.600 mmol of dioxetane (*Z*/*E*)-**2a** and 0.5 mL of acetaldehyde in 2 mL of CCl_4 was allowed to stand at 20 °C while being monitored by ^{1}H NMR. After all of the dioxetane was consumed, the solvent was rotaevaporated (20 °C (17 Torr)) and the residue chromatographed at −40 °C on Florisil by eluting with a 9:1 petroleum ether (bp 30–50 °C)/diethyl ether mixture to give α-silylperoxy ester **3a**, α-hydroperoxy ester **9**, and the diastereomeric trioxanes **10a** and **10a′** in a total yield of 65% and the relative proportions of 61:16:15:8.

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Supplementary Material Available: ^{1}H NMR spectra of the compounds (*E*)-**1a**, (*Z*)-**1a**, (*E*)-**1b,c**, (*E*)-**2a**, (*Z*)-**2a**, (*E*)-**2b,c**, **3a**, **3b**, **3c**, **9**, **10a**, **10a′** (14 pages). Ordering information is given on any current masthead page.

A Laser Flash Photolysis Derived Study of a Glycosylidene Carbene

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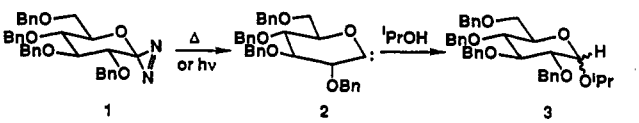
Laser flash photolysis of a glycosylidene-derived diazirine produces the corresponding carbene. The carbene can be intercepted with pyridine to form an ylide. The absolute rate constants for the reaction of the glycosylidene carbene with alcohols can be obtained by monitoring the absolute rate of formation of the pyridinium ylide. The kinetic data favors a mechanism involving a proton transfer from the alcohol to the carbene.

The preparation of the glycosylidene diazirine **1** and some of the chemistry of its corresponding carbene **2** have recently been reported.[1] Carbene **2** inserts into the OH bonds of alcohols and phenols to form mixtures of α- and β-D-glucopyranosides, such as **3**.



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Because of the obvious potential of glycosylidene-derived diazirines as glycosyl donors, the mechanism of the reaction of carbene **2** with alcohols was investigated by laser flash photolysis (LFP) techniques.[2] LFP (XeF excimer laser,

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