Regioselectivity of the Singlet Oxygen Ene Reaction (Schenck Reaction) with Vinylsilanes

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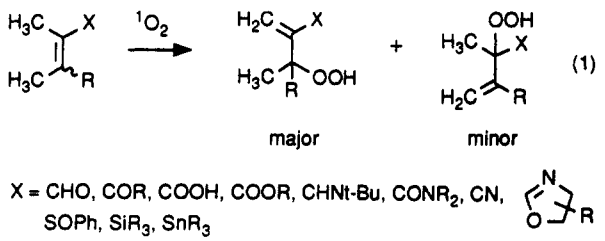
The ene reaction of singlet oxygen and vinylsilanes 1 with various substitution patterns and double-bond geometry has been studied. β-Silyl allylic hydroperoxides 2 were the major products of the photooxygenation, accompanied by smaller amounts of α,β-unsaturated ketones 3. The latter derive from decomposition of the regioisomeric α-hydroperoxy silanes 4 by elimination of silanol. Regioselectivities up to 97:3 were observed for vinylsilanes with a methyl group *geminal* to the silyl group and with cyclic derivatives. *Z*-Configurated substrates showed lower regioselectivity and reactivity. Elongation of the carbon chain at the *geminal* position also increased the amount enone formed. These results are rationalized in terms of stereoelectronic effects imposed by the silyl group on the ring-opening of the perepoxide intermediate.

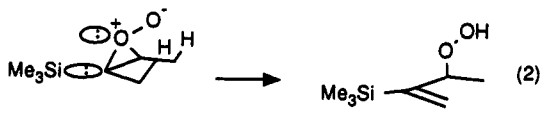
Introduction

The mechanism of the ene reaction of singlet oxygen ($^1O_2$) with alkenes is still a matter of debate.[1] Especially the factors that determine the regioselectivity of the hydrogen abstraction have been subject to intensive investigation in the last few years.[2] It has been found that alkenes like α,β-unsaturated aldehydes,[3] carboxylic acids[4] and derivatives,[3,5] ketones,[6] and sulfoxides[7] display a remarkable regioselectivity in the ene reaction with $^1O_2$ (eq 1),



in which hydrogen abstraction is preferred at the alkyl group *geminal* to the anion-stabilizing substituent. The origin of this selectivity is, however, not completely understood. Rotational barriers[2b,8] have been proposed to account for the regioselectivity found with olefins which contain functional groups or sterically demanding substituents. Subsequently, it has been shown that this explanation is not generally valid and nonbonding interactions of the intermediary perepoxide with the large groups have been invoked.[9]

High regioselectivity of the $^1O_2$ ene reaction was also observed for vinylsilanes[10] and -stannanes.[11] Instead of steric effects, a stereoelectronic model was proposed[10a] in which for the silyl-substituted perepoxide the C–O bond adjacent to the silicon atom is weakened by an antibonding interaction of the C–Si σ bond and the lone pair at the epoxide oxygen (eq 2).



Consequently, this bond is broken preferrentially to lead to the major regioisomer. Since the energy of the C–Si bond is high enough to interact efficiently, this regioselectivity appears to be unique for vinylsilanes.

In order to gain further mechanistic insight into the directing effect of silicon on the regioselectivity of $^1O_2$, the photooxygenation of vinylsilanes with different substitution patterns and double-bond geometry was conducted since in the previous work[10] only *E*-disubstituted derivatives were investigated. Analysis at the stage of the crude hydroperoxide products was especially desirable in order to obtain direct regioselectivity data without prior chemical intervention. Moreover, silyl allylic hydroperoxides should be of interest in organic synthesis since useful transformations can be performed with these substrates.[10,12b,c] Thus, a general regioselective preparation of such hydroperoxides through the convenient photooxygenation of vinylsilanes would be highly desirable.

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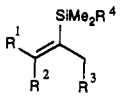
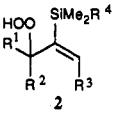
Table 1. Product Studies and Regioselectivities of the Photooxygenation of Vinylsilanes 1[a]



1



2

	R^1	R^2	R^3	R^4	photooxygntn time (h)	regioselectivity[b] 2:3	yield of 2[c] (%)
(*E*)-1a	H	Me	H	Me	1.0	97:3[d]	62[e]
(*Z*)-1a	Me	H	H	Me	1.0	74:26[d]	
(*E*)-1c	H	Me	Me	Ph	1.0	85:15[d,f]	45[g]
(*Z*)-1c	Me	H	Me	Ph	1.0	54:46[d,h]	
(*E*)-1d	H	*n*-Bu	H	Me	1.0	95:5	65
(*Z*)-1d	*n*-Bu	H	H	Me	1.0	81:19	
(*E*)-1e	H	*n*-Bu	Me	Me	0.75	64:36[i]	50
(*Z*)-1e	*n*-Bu	H	Me	Me	3.25[j]	54:46[k]	
1f	Me	Me	H	Ph	0.5	95:5	79
1g	H	$(CH_2)_2$		Me	1.0	93:7	72
1h	H	$(CH_2)_3$		Me	0.5[l]	93:7	45
1i	Me	$(CH_2)_3$		Me	1.3	72:28	43
1j	*n*-C_5H_{11}	$(CH_2)_3$		Me	0.25	88:12[m]	

[a] Photoxygenations were carried out in $CDCl_3$ at −5 to −10 °C with TPP as sensitizer. [b] Determined by ^1H NMR (200 MHz), error ±5%. [c] Isolated, product 2. [d] Extrapolated value (see text). [e] From a 65:35 *E*/*Z* mixture of 1a. [f] 2c: dr 56:44 (*E*/*Z*). [g] From a 28:72 *E*/*Z* mixture of 1c. [h] 2c: dr ≥ 90:10 (*E*/*Z*). [i] 2e: dr 54:46 (*E*/*Z*). [j] 75% conversion. [k] 2e: dr ≥ 90:10 (*E*/*Z*). [l] 63% conversion. [m] Consists of 5% 3j and 7% unidentified product.

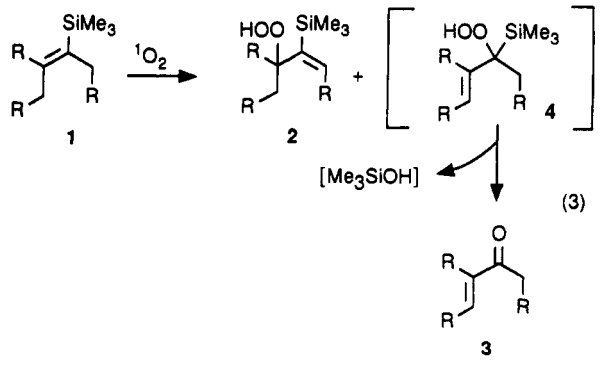
Results

E,*Z* mixtures of the vinylsilanes **1a,b** of different compositions were prepared from the respective vinyllithium precusors as previously reported.[12] Catalytic reductive lithiation[13] of the corresponding vinyl phenyl sulfide provided an *E*,*Z* mixture of vinylsilane **1c**.[14] Stereochemically pure *Z* vinylsilanes **1d,e** were prepared by hydroalumination/bromination of 1-(trimethylsilyl)-hexyne,[15] followed by copper-catalyzed coupling with MeLi for **1d** or lithiation and alkylation with ethyl iodide for **1e** according to the published procedure.[16] The more direct pathway, hydromagnesation of the alkyne followed by alkylation,[17] proved to be less suitable since the final product was always contaminated with the impurity from protonation of the intermediary Grignard reagent, which rendered the purification considerably more difficult.

The corresponding *E* isomers of **1d,e** were synthesized by addition of *n*-butylcopper reagents to (trimethylsilyl)-acetylene and subsequent coupling with methyl or ethyl iodide. The reagent prepared from *n*-BuMgBr, CuBr, and LiBr[18] was used for the preparation of (*Z*)-**1d**;[12b] however, complete alkylation of the intermediary vinylcopper with EtI could not be achieved since the protonated product was formed in comparable amounts. The alternative procedure, employing *n*-BuCu in the presence of $P(OEt)_3$ for carbocupration,[19] requires the carcinogenic HMPA to facilitate alkylation. We found that 1,3-dimethylimidazolinone (DMI)[20] may be used instead; the yield for **1e** was only slightly lower (51%) than those obtained with HMPA (56–70%).[19] While DMI has been used as substitute for HMPA in several other reactions,[20,21] we are not aware of its utilization in organocopper chemistry.

The cyclic vinylsilanes **1g–i** were prepared according to published procedures.[12b,22] Derivative **1j** was obtained by coupling of Bu_2CuLi with the corresponding (chloromethyl)vinylsilane **1k**.[12c]

The photooxygenations of the vinylsilanes **1** were performed in $CDCl_3$ with tetraphenylporphine (TPP) as sensitizer and directly monitored by NMR spectroscopy in order to prevent loss of volatile products during solvent evaporation. The results of the $^1O_2$ ene reaction with the vinylsilanes are summarized in Table 1. In all cases, except **1j**, the reaction proceeded smoothly, and the silyl allylic hydroperoxides **2** were the major products accompanied by smaller amounts of the α,β-unsaturated ketones **3**. These enones result from the regioisomeric α-silyl hydroperoxides **4** by elimination of silanol (eq 3). None of the α-silyl hydroperoxides **4** could be detected by NMR analysis.



(3)

E,*Z* mixtures of different composition were employed for the silanes **1a,b** and the regioselectivities of the pure isomers were obtained by extrapolation. Photooxygenation of vinylsilane **1c** was interrupted at different stages of conversion and analyzed by NMR spectroscopy. Since the *E* isomer reacted considerably faster than the *Z* isomer, again extrapolation to the pure isomers was possible. The hydroperoxides **2c,e** were obtained as mixtures of *E*/*Z*

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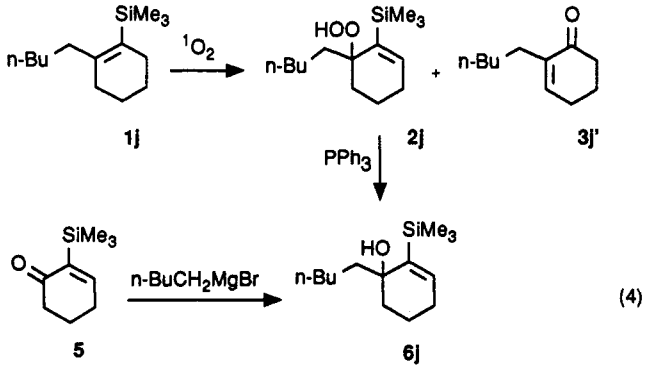
isomers in the case of the *E* diastereomers **1c,e**. The *Z* vinylsilanes produced only the corresponding *E* hydroperoxides **2c,e**. Although exact kinetic measurements were not carried out, simple competition experiments of vinylsilane **1f** with 2-methyl-2-butene revealed that **1f** was about twice as reactive. This result indicates that the silyl group modestly activates the double bond.

The less reactive vinylsilanes (*Z*)-**1e** and **1h** were not photooxygenated completely in order to avoid decomposition of the hydroperoxides. Silane **1h** was also photooxygenated in methanol by using Rose Bengal (RB) as sensitizer. The regioselectivity was identical to the one obtained in $CDCl_3$; however, 4% of enone **5**[23] was formed by dehydration of the hydroperoxide **2h**.

Photooxygenation of vinylsilane **1i** yielded, besides the hydroperoxide **2i**, only 2-methylenecyclohexanone (**3i**). Comparison with an authentic sample showed that 2-methyl-2-cyclohexenone was not formed.

Analyses of the products from the cyclic vinylsilane **1j** was less straightforward (eq 4).



(4)

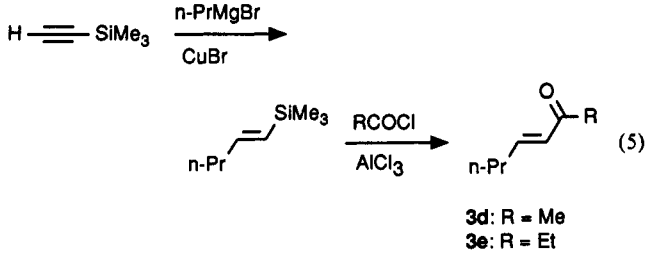
Hydroperoxide **2j** was the major product (88%) in the reaction mixture, as established by NMR analysis relative to the trimethylsilyl groups and normalized to 100%. Enone **3j'**[29] was detected (5%), but the regioisomeric enone **3j**[29] was not observed. One other minor product, probably derived from the labile[5] enone **3j**, could not be identified until now.

As a control experiment, photooxygenation of an *E*/*Z* mixture of vinylsilane **1b** gave within experimental error the same regioselectivity as a mixture of **1a** of identical *E*/*Z* composition, which indicates that the Me_2PhSi compared to the Me_3Si group exercises no influence.

For the characterization of the hydroperoxides **2**, the photooxygenation was performed on preparative scale in dichloromethane as solvent. The hydroperoxides were separated from the enones **3** by low-temperature column chromatography. While under prolonged irradiation some decomposition was observed, after isolation the hydroperoxides were quite stable at room temperature. For example, the ^1H NMR spectrum of a solution of hydroperoxide **2a** in $CDCl_3$ did not change during storage for 3 weeks at room temperature. This persistence allowed their rigorous characterization by NMR and IR spectroscopy and elemental analysis. Only the tertiary hydroperoxide **2j** could not be obtained in pure form due to decomposition during column chromatography. For additional chemical characterization, reduction with triphenylphosphine to the alcohol **6j** was performed, which was identical with an authentic sample prepared by reaction of *n*-pentylmagnesium bromide with enone **5**[12b,23] (eq 4). The low yield (27%) can be attributed to the high propensity for 1,4 addition, which is generally observed with 2-silyl enones.[24]

The stereochemical assignment of the *E* and *Z* hydroperoxides **2e** is based on NOE experiments conducted on the (*Z*)-**2e** diastereomer. The isomers of **2c** were assigned by using ^1H NMR chemical shift arguments. Thus, for the *E* isomer of both **2c** and **2e**, absorption of the hydrogen α to the hydroperoxy group occurred at lower field than for the Z isomer, while the signal of the vinylic proton appeared at higher field for the *E* than for the *Z* isomer. These trends in the chemical shifts coincide with those oberved for the analogous silyl allylic alcohols.[10b] Additionally, diastereomer (*E*)-**2c** displays a larger allylic coupling constant, in agreement with the *E* geometry.

The identity of the enones **3** was established by comparison with authentic samples. These were either commercially available or prepared by literature method (cf. Experimental Section). Enones **3d,e**[26,27] were prepared by acylation[25] of the vinylsilane **1l** (eq 5),[32] a method which is much more convenient than existing ones.[26,27]



(5)

Discussion

Inspection of the data in Table 1 shows that the trimethylsilyl group induces a high geminal selectivity in the ene reaction of alkenes with $^1O_2$. Generally, the *E* isomers were more reactive and more selective than the *Z* isomers. Branching at the *geminal* position decreases the selectivity for the acyclic substrates **1c,e**, while the cyclic vinylsilanes **1g,h** react about as selectively as the simple, unbranched *E* isomer of **1a**. These trends in reactivity and regioselectivity coincide with those found for α,β-unsaturated esters[4] and vinylstannanes.[11] Analogous to the behavior of the latter, the regioisomeric α-hydroperoxy silanes **4** could not be detected, because they readily decomposed *in situ* to the enones **3** and siloxanes (eq 3). This seems to be a general phenomenon, since in all cases in which α-peroxo silanes were expected, only the corresponding carbonyl compounds were observed.[30]

In general, the regioselectivity in the ene reaction of $^1O_2$ with a variety of functionalized olefins can be rationalized

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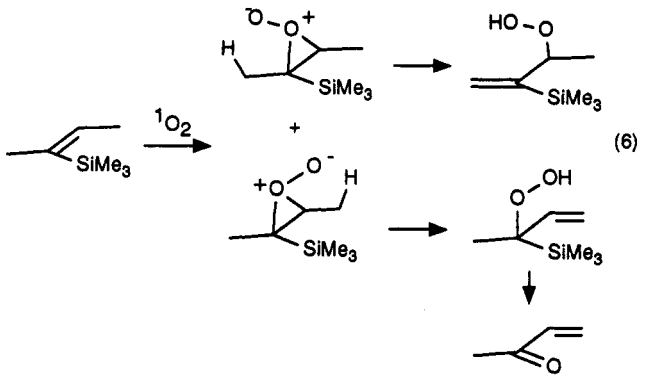
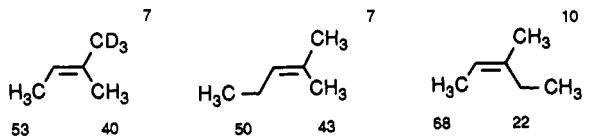
by invoking both electronic and steric factors. In the present case of the vinylsilanes, the previously mentioned theoretical model (eq 2) predicts the preferential opening of the perepoxide intermediate due to electronic interactions. Indeed, in those cases in which predominantly one perepoxide is formed, i.e. *E*-configurated and cyclic vinylsilanes, the regioselectivity is only dictated by cleavage of the C–O bond adjacent to the silyl group and, consequently, a high selectivity results. In contrast, for the *Z* isomers the two regioisomeric products derive from two different perepoxides (eq 6).



It is difficult to predict *a priori* which of the perepoxide regioisomers is preferentially formed, especially since reversible formation of exiplexes is an integral feature in the reaction of the electronically excited $^1O_2$ with organic substrates.[31] The experimental results show, however, that the differences in energy involved are quite small, since the regioselectivities for the *Z* vinylsilanes are modest (Table 1).

A general pattern has also emerged for the effect of branching on the regioselectivity. Analogous to the ester and stannyl groups,[4,11] *geminal* alkyl groups other than methyl also decrease the *geminal* regioselectivity in the case of vinylsilanes 1. Thus, the regioselectivity dropped from 95:5 for vinylsilane (*E*)-**1d** to 64:36 for (*E*)-**1e**.



However, nonfunctionalized, branched alkenes also display this effect,[1] as long as the branching occurs *geminal* to an alkyl group. For example, as for the vinylsilanes (*E*)-**1a** *versus* (*E*)-**1d**, elongation of the alkyl chain at the *non-geminal* position, i.e. 2-methyl-2-butene *versus* 2-methyl-2-pentene, has no effect on the regioselectivity. Presumably the required rotation of the alkyl group to align the allylic hydrogen atom in the proper position for hydrogen abstraction (perpendicular to the double-bond plane[1]) is restricted by the *geminal* substituent.

The considerably lower regioselectivity for the cyclic vinylsilane **1i** (Table 1) can be attributed to the well-established fact that due to conformational restrictions, hydrogen abstraction occurs preferrentially at the exocyclic methyl group in substituted cyclohexenes.[32] This agrees with the fact that the low selectivity for the cyclic derivative **1i** is only a result of abstraction at the methyl group, since the other possible enone was not observed. In analogy to the above arguments, the high *geminal* selectivity found for **1j** can be rationalized by assuming that hydrogen abstraction at the pentyl group is diminished due to the presence of a *geminal* substituent, in this case the cyclohexene ring.

In conclusion, the regioselectivity of $^1O_2$ in the ene reaction with vinylsilanes, which is high for derivatives with a methyl group *geminal* to the silicon functionality and for cyclic substrates, is controlled by a combination of electronic and steric effects. This high selectivity, combined with the ready availability of the vinylsilanes **1**, offers the opportunity for useful applications in organic synthesis.

Experimental Section

General Methods. For instrumentation and materials used in this work see refs 10 and 11. Triethyl phosphite (bp 78–79 °C/60 Torr) and *N,N*-dimethylimidazolinone[20] (DMI, bp 128–129 °C) were distilled over CaH_2 under argon gas immediately prior to use.

Vinylsilanes. Vinylsilanes **1a,b**,[12] (*E*)-**1d**,[12b] (*Z*)-**1d**,[16] (*Z*)-**1e**,[16], **1f**,[28] **1g,h**,[22] and **1i**[12c] were prepared according to literature procedures.

(*E*/*Z*)-(1-Ethyl-1-propenyl)dimethylphenylsilane (1c).[14] A sample of 166 mg (24.0 mmol) of lithium wire was cut in ca. 1-mm pieces directly into 30 mL of THF under an argon atmosphere. To this mixture were added 171 mg (1.00 mmol) of 1-(dimethylamino)naphthalene and 1.78 g (10.0 mmol) 1-ethyl-1-propenylthiobenzene[34], and the solution was cooled to −70 °C. A deep red color developed, and 2.5 h of stirring at −70 °C, 2.00 mL (12.5 mmol) of chlorodimethylphenylsilane was introduced, which was accompanied by immediate decolorization. After an additional 30 min at −70 °C, 10 mL of 2 N aqueous NaOH was added and the cooling bath was removed. The reaction mixture was allowed to reach room temperature, 50 mL of methyl *tert*-butyl ether was added, the layers were separated, the aqueous layer was extracted with 20 mL of methyl *tert*-butyl ether, and the combined organic layers were washed with 2 N NaOH (3 × 30 mL), water (1 × 30 mL), 2 N HCl (3 × 30 mL), a saturated, aqueous $NaHCO_3$ solution (1 × 30 mL), and brine (1 × 30 mL), dried ($MgSO_4$), and finally concentrated (20 °C/20 Torr). Of 2.43 g of crude product, 1.00 g was purified by column chromatography [70 g of neutral aluminum oxide, activity 2–3, petroleum ether (bp 50–60 °C) as eluant] to afford 503 mg (60%) of **1c** as a colorless liquid, *E*/*Z* = 28:72. (*Z*)-**1c**: ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.45 (s, 6H), 1.03 (d, *J* = 7.4 Hz, 3 H), 1.65 (dt, *J* = 6.9, 1.1 Hz, 3 H), 2.10–2.30 (m, 2H), 6.24 (qt, *J* = 6.9, 1.3 Hz, 1H), 7.30–7.40 (m, 3H), 7.50–7.65 (m, 2H). (*E*)-**1c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.39 (s, 6H), 0.90 (d, *J* = 7.6 Hz, 3H), 1.76 (d, *J* = 6.6 Hz, 3H), 2.10–2.30 (m, 2H), 5.95 (q, *J* = 6.6 1H), 7.30–7.40 (m, 3H), 7.50–7.65 (m, 2H). (*E*/*Z*)-**1c**: ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.7 (q), −1.0 (q), 14.2 (q), 14.2 (q), 15.4 (q), 18.2 (q), 22.3 (t), 31.1 (t), 127.6 (d), 127.7 (d), 128.6 (d), 128.7 (d), 133.7 (d), 134.0 (d), 136.0 (d), 137.2 (s), 139.2 (s), 139.7 (s), 139.9 (s), 141.7 (s); IR (neat) ν 1610 cm^{-1}.

(*E*)-(1-Ethyl-1-hexenyl)trimethylsilane (1e).[16] To 3.16 g (22.0 mmol) of CuBr was added 18.7 mL (20.0 mmol) of a 1.07 M solution of *n*-butylmagnesium bromide in diethyl ether at −40 °C, and the solution was stirred for 15 min at −40 to −20 °C. After addition of 4.00 mL (28.0 mmol) of (trimethylsilyl)acetylene and 3.78 mL (22.0 mmol) of triethyl phosphite, the black solution was stirred for 2 h at 0 °C and cooled to −60 °C, and 2.44 mL (30.0 mmol) of ethyl iodide, 4.82 mL (44.0 mmol) of DMI, and 7.55 mL (44.0 mmol) of triethyl phosphite were added. The mixture was allowed to warm up slowly overnight to room temperature, 10 mL of a saturated, aqueous NH_4Cl solution, 10 mL of water, and

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10 mL of pentane were introduced, and the mixture was stirred for an additional 10 min. The layers were separated, washed with 10 mL of a saturated, aqueous NH_4Cl solution and 10 mL of brine, dried ($MgSO_4$), and concentrated (20 °C/20 Torr). The residue was filtered over 30 g of silica gel with petroleum ether (bp 30–50 °C) as eluant, and the filtrate was concentrated and purified by column chromatography [140 g of silica gel, 63–200 μm, petroleum ether (bp 30–50 °C) as eluant] to afford 1.89 g (51%) of (*E*)-**1e** as a colorless liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.06 (s, 9H), 0.84–1.00 (m, 6H), 1.20–1.45 (m, 4H), 2.05–2.20 (m, 4H), 5.69 (t, *J* = 6.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.2 (q), 14.1 (q), 14.8 (q), 22.4 (t), 22.5 (t), 27.9 (t), 31.9 (t) 139.9 (d), 142.3 (s); IR (neat) δ 1600 cm^{-1}.

Trimethyl(2-pentyl-1-cyclohexenyl)silane (1j). A suspension of 571 mg (3.00 mmol) of CuI in 20 mL of diethyl ether was cooled to 0 °C and 4.3 mL (6.00 mmol) of a 1.39 M *n*-BuLi solution in hexane was added within 2 min. After stirring at 0 °C for 5 min, the mixture was cooled to −78 °C and stirred for additional 15 min. A solution of 406 mg (2.00 mmol) of (2-(chloromethyl)-1-cyclohexenyl)trimethylsilane[12c] in 5 mL of diethyl ether was added and stirring was continued at −65 to −30 °C for 5 h. The mixture was allowed to warm up overnight to room temperature, 10 mL of a saturated, aqueous NH_4Cl solution and 10 mL of water were added, the layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with 10 mL of a 10% aqueous $Na_2S_2O_3$ solution, 10 mL of a saturated, aqueous NH_4Cl solution, and 10 mL of brine, dried ($MgSO_4$), and concentrated (20 °C/20 Torr). Kugelrohr distillation of the residue afforded 362 mg (81%) of **1k** as a colorless liquid: oven temperature 80 °C/0.1 Torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.10 (s, 9H), 0.89 (t, *J* = 6.6 Hz, 3H), 1.20–1.60 (m, 10 H), 1.90–2.10 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.4 (q), 14.1 (q) 22.7 (t), 22.9 (t), 23.3 (t), 28.9 (t), 29.2 (t), 30.4 (t), 32.2 (t), 38.5 (t), 128.8 (s), 148.2 (s); (IR) ν 1635 cm^{-1}. Anal. Calcd for $C_{14}H_{28}Si$ (224.5): C, 74.90, H, 12.57. Found: C, 74.55; H, 12.99.

General Procedure for the Photooxygenation of Vinylsilanes 1 (NMR Scale). A solution of ca. 0.1 mmol of the appropriate vinylsilanes and ca. 0.3 mg of tetraphenylporphyrin (TPP) in 1.0 mL of $CDCl_3$ was photooxygenated in a test tube of 1-cm diameter at −5 to −10 °C by passing a slow stream of dry oxygen gas through the solution with a disposable pipette under continuous irradiation with two 150-W sodium lamps. The product ratio of the allylic hydroperoxide **2** and the enones **3** (see Table 1) was determined by ^{1}H NMR spectroscopy.

2-(Trimethylsilyl)-1-pentyl-2-cyclohexenyl Hydroperoxide (2j)). By following the above general procedure, 24.0 mg (0.107 mmol) of **1j** was photooxygenated for 15 min. ^{1}H NMR analysis showed 88% of **2j** (relative to $SiMe_3$ groups and normalized to 100%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 9H), 0.87 (t, *J* = 6.5 Hz, 3H), 1.00–2.20 (m, 14H), 6.32 (t, *J* = 3.8 Hz, 1H), 7.05 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.9 (q), 14.0 (q), 19.5 (t), 22.6 (t), 23.9 (t), 26.8 (t) 29.7 (t), 32.4 (t), 37.1 (t), 86.7 (s), 141.5 (s), 143.8 (d). To the photooxygenate was added 28.0 mg (0.110 mmol) of PPh_3 and ^{1}H and ^{13}C NMR analyses showed that alcohol **5** (see below) was formed quantitatively.

General Procedure for Photooxygenation of Vinylsilanes 1 (Preparative Scale). A solution of 100 to 500 mg of the appropriate vinylsilane **1** and ca. 1 mg of TPP in 5 mL of CH_2Cl_2 was photooxygenated as described above. The solvent was removed by roto-evaporation (0 °C/20 Torr) and the oily residue was purified by column chromatography on silica gel (63-200 μm) at −10 °C.

1-Methyl-2-(trimethylsilyl)-2-propenyl Hydroperoxide (2a). By following the above general procedure, 420 mg (3.27 mmol) of vinylsilane **1a** (*E*/*Z* = 65:35) was photooxygenated for 1 h to yield 326 mg (62%) of **2a** as colorless oil after column chromatography [30 g of silica gel, 10:1 petroleum ether (bp 30–50 °C)/diethyl ether as eluant]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.28 (d, *J* = 6.4 Hz, 3H), 4.69 (q, *J* = 6.4 Hz, 1H), 5.53 (dd, *J* = 2.5, 0.5 Hz, 1H), 5.86 (dd, *J* = 2.5, 1.1 Hz, 1H), 8.00 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.9 (q), 19.3 (q), 85.1 (d), 125.8 (t), 152.4 (s); IR (neat) ν 3650–3060 cm^{-1}. Anal. Calcd for $C_7H_{16}O_2Si$ (160.3): C, 52.45; H, 10.06. Found: C, 52.73; H, 10.25.

1-Methyl-2-(dimethylphenylsilyl)-2-propenyl Hydroperoxide (2b). By following the above general procedure, 126 mg (0.662 mmol) of vinylsilane **1a** (*E*/*Z* = 65:35) was photooxygenated for 2 h to yield 110 mg (75%) of **2a** as a colorless oil after column chromatography [25 g of silica gel, 10:1 petroleum ether (bp 30–50 °C)/diethyl ether as eluant]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.46 (s, 3H), 0.49 (s, 3H), (1.23 (d, *J* = 6.6 Hz, 3H), 4.67 (br q, *J* = 6.6 Hz, 1H), 5.63 (dd, *J* = 2.3, 0.8 Hz, 1H), 5.96 (dd, *J* = 2.3, 1.2 Hz, 1H), 7.32–7.46 (m, 3H), 7.53 (s, 1H), 7.56–7.68 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.5 (q), 19.3 (q), 85.5 (d), 127.7 (t), 128.0 (d), 129.3 (d), 133.9 (d), 137.8 (s), 151.1 (s); IR (CCl_4) δ 3440 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_2Si$ (222.4): C, 64.82; H, 8.16. Found: C, 65.02; H, 8.48.

(*E*/*Z*)-1-Methyl-2-(dimethylphenylsilyl)-2-butenyl Hydroperoxide (2c). By following the above general procedure, 200 mg (0.980 mmol) of vinylsilane **1c** (*E*/*Z* = 72:28) was photooxygenated for 2.5 h to yield 48.0 mg of pure (*E*)-**2c** and 57.0 mg of an *E*/*Z* mixture (combined yield 45%) as a colorless oil after column chromatography [40 g of silica gel, 5:1 petroleum ether (bp 30–50 °C)/diethyl ether as eluant]. (*E*)-**2c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.40 (s, 3H), 0.51 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.78 (d, *J* = 6.8 Hz, 3H), 5.09 (qd, *J* = 6.9, 1.1 Hz, 1H), 6.10 (qd, *J* = 6.8, 1.2 Hz, 1H), 7.30 (br s, 1H), 7.34–7.44 (m, 3H), 7.56–7.68 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.0 (q), −1.6 (d), 15.0 (q), 19.0 (q), 82.5 (d), 128.1 (d), 129.2 (d), 133.9 (d), 138.5 (d), 139.0 (s), 142.5 (s). (*Z*)-**2c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.47 (s, 6H), 1.30 (d, *J* = Hz, 3H), 1.69 (dd, *J* = 7.0, 0.6 Hz, 3H), 4.63 (br q, *J* = 6.4 Hz, 1H), 6.52 (qd, *J* = 7.1, 0.9 Hz, 1H), 7.34–7.44 (m, 3H), 7.56–7.68 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.8 (q), 18.0 (q), 19.1 (q), 85.7 (d), 127.9 (d), 129.9 (d), 133.7 (d), 138.5 (s), 139.2 (d), 140.2 (s). (*E*,*Z*)-**2c**: IR (neat) ν 3520–3100 cm^{-1}, 1590. Anal. Calcd for $C_{13}H_{20}O_2Si$ (236.4): C, 66.05; H, 8.53. Found: C, 66.32; H, 8.80.

1-Butyl-2-(trimethylsilyl)-2-propenyl Hydroperoxide (2d). By following the above general procedure, 300 mg (1.76 mmol) of vinylsilane (*E*)-**1d** was photooxygenated for 1 h to yield 230 mg (65%) of **2d** as a pale red oil after column chromatography [50 g of silica gel, 5:1 petroleum ether (bp 30–50 °C)/diethyl ether as eluant): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 9H), 0.89 (t, *J* = 7.2 Hz, 3H), 1.20–1.70 (m, 6H), 4.51 (br t, *J* = 6.2 Hz, 1H), 5.56 (dd, *J* = 2.7, 0.4 Hz, 1H), 5.83 (dd, *J* = 2.7, 1.0 Hz, 1H), 7.95 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.8 (q), 13.9 (q), 22.6 (t), 28.0 (t), 32.9 (t) 90.3 (d), 126.8 (t), 151.6 (s); IR (neat) ν 3510–3050 cm^{-1}. Anal. Calcd for $C_{10}H_{22}O_2Si$ (202.4): C, 59.35; H, 10.96. Found: C, 59.73, H, 11.07.

(*E*/*Z*)-1-Butyl-2-(trimethylsilyl)-2-butenyl Hydroperoxide (2e). By following the above general procedure, 350 mg (1.90 mmol) of vinylsilane (*E*)-**1e** was photooxygenated for 1 h to yield 369 mg of a red oil. After column chromatography [30 g of silica gel, 15:1 petroleum ether (bp 30–50 °C)/methyl acetate as eluant] of 205 mg of the crude product, there were obtained 51.0 mg of pure (*E*)-**2e** and 64.0 mg of an *E*/*Z* mixture (combined yield 50%) as colorless oils. (*E*)-**2e**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.82–0.94 (m, 3H), 1.20–1.75 (m, 6H), 1.78 (d, *J* = 6.8 Hz, 3H), 4.94–5.02 (m, 1H), 6.09 (qd, *J* = 6.8, 0.9 Hz, 1H), 7.72 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.5 (q), 13.5 (q), 15.2 (q), 22.7 (t), 28.2 (t), 32.9 (t), 86.3 (d), 138.6 (t), 142.3 (s). (*Z*)-**2e**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.20 (s, 9H), 0.82–0.96 (m, 3H), 1.20–1.75 (m, 6H), 1.85 (d, *J* = 6.7 Hz, 3H), 4.42 (br t, *J* = 6.2 Hz, 1H), 6.37 (qd, *J* = 7.0, 0.8 Hz, 1H), 7.64 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.3 (q), 13.7 (q), 17.5 (q), 22.6 (t), 28.2 (t), 33.4 (t), 91.0 (d), 139.0 (d), 139.9 (s); IR (neat) ν 3520–3100, 1595 cm^{-1}. Anal. Calcd for $C_{11}H_{24}O_2Si$ (202.4): C, 61.06; H, 11.18. Found: C, 61.41, H, 10.93.

1,1-Dimethyl-2-(dimethylphenylsilyl)-2-butenyl Hydroperoxide (2f). By following the above general procedure, 150 mg (0.734 mmol) of vinylsilane **1f** was photooxygenated for 0.5 h to yield 137 mg (79%) of **2f** as a colorless oil after column chromatography [30 g of silica gel, 6:1 petroleum ether (bp 30–50 °C)/diethyl ether as eluant]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.49 (s, 6H), 1.33 (s, 6H), 5.60 (d, *J* = 1.7 Hz, 1H), 5.91 (d, *J* = 1.7 Hz, 1H), 6.96 (br s, 1H), 7.30–7.40 (m, 3H), 7.50–7.60 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.1 (q), 25.9 (q), 87.0 (s), 127.0 (t), 128.0 (d), 129.2 (d), 133.9 (d), 138.6 (s), 155.3 (s); IR (neat) ν 3500–3200 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2Si$ (236.4): C, 66.05; H, 8.53. Found: C, 66.06; H, 8.37.

2-(Trimethylsilyl)-2-cyclopentenyl Hydroperoxide (2g).

By following the above general procedure, 500 mg (3.56 mmol) of vinylsilane **1g** was photooxygenated for 2.5 h to yield 444 mg (72%) of **2g** as a colorless oil after column chromatography [50 g of silica gel, 30:1 petroleum ether (bp 30–50 °C)/methyl *tert*-butyl ether as eluant]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.92–2.20 (m, 2H), 2.25–2.40 (m, 1H), 2.48–2.68 (m, 1H), 5.24 (m, 1H), 6.37 (td, J = 2.3, 1.0 Hz, 1H), 7.63 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.3 (q), 29.2 (t), 33.5 (t), 94.7 (d), 141.6 (s), 149.0 (d); IR (CCl_4) ν 3520, 1575 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2Si$ (172.4): C, 55.77; H, 9.36. Found: C, 56.06; H, 9.69.

2-(Trimethylsilyl)-2-cyclohexenyl Hydroperoxide (2h).[10c] By following the above general procedure, 752 mg (4.87 mmol) of vinylsilane **1h** was photooxygenated for 25 h in 100 mL of methanol using 50 mg of Rose Bengal, 30 mg of 2,6-di-*tert*-butyl-4-methylphenol, and an immersion lamp apparatus[10c] to yield 411 mg (45%) of **2h** as a colorless oil after column chromatography [40 g of silica gel, 4:1 petroleum ether (bp 30–50 °C)/diethyl ether as eluant]: ^{1}H NNR (200 MHz, $CDCl_3$) δ 0.10 (s, 9H), 1.50–2.20 (m, 6H), 4.57 (m, 1H), 6.29 (m, 1H), 7.73 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.3 (q), 17.4 (t), 26.4 (t), 27.1 (t), 80.2 (d), 135.5 (s), 143.9 (d); IR (CCl_4) ν 3610 cm^{-1}. Anal. Calcd for $C_9H_{18}O_2Si$ (186.3): C, 58.04; H, 9.74. Found: C, 58.03, H, 9.84.

1-Methyl-2-(trimethylsilyl)-2-cyclohexenyl Hydroperoxide (2i). By following the above general procedure, 300 mg (1.78 mmol) of vinylsilane **1i** was photooxygenated for 1.5 h to yield 153 mg (43%) of **2i** as a colorless oil after column chromatography (30 g of silica gel, CH_2Cl_2 as eluant): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.36 (s, 3H), 1.50–2.20 (m, 6H), 6.19 (t, J = 4.6 Hz, 1H), 7.10 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.7 (q), 19.3 (q), 24.8 (t), 26.9 (t), 33.2 (t), 84.4 (s), 141.1 (s), 142.5 (d); IR (neat) ν 3540–3080, 1590 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O_2Si$ (200.4): C, 59.95; H, 10.06. Found: C, 60.38; H, 10.28.

Preparation of Authentic Samples. 1-Pentyl-2-(trimethylsilyl)cyclohex-2-en-1-ol (6j). To a solution of *n*-phenylmagnesium bromide, prepared from 121 mg (5.00 mmol) of magnesium and 755 mg (5.00 mmol) of 1-bromopentane in 10 mL of diethyl ether, was added as solution of 504 mg (3.00 mmol) of enone **5**[12c] in 5 mL of diethyl ether within 15 min. After 2 h of stirring at room temperature, 5 mL of a saturated, aqueous NH_4Cl solution and 5 mL of water were added and the layers separated. The aqueous layer was extracted with pentane (2 × 5 mL), and the combined organic layers were washed with 5 mL of a saturated, aqueous NH_4Cl solution and 5 mL of brine, dried ($MgSO_4$), and concentrated (20 °C/20 Torr). A 390-mg sample of the 608-mg brown, oily residue was purified by column chromatography [40 g of silica gel, 6:1 petroleum ether (bp 30–50 °C)/diethyl ether as eluant] to yield 124 mg (27%) of **6j** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H), 1.20–1.82 (m, 12H), 1.96–2.15 (m, 3H), 6.04 (t, J = 3.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 1.0 (q), 14.0 (q), 19.1 (t), 22.7 (t), 23.2 (t), 26.6 (t), 32.4 (t), 35.3 (t), 40.7 (t), 74.2 (s), 138.8 (d), 145.9 (s); IR (neat) ν 3620–3200, 1585 cm^{-1}. Anal. Calcd for $C_{14}H_{28}OSi$ (204.5): C, 69.93; H, 11.74. Found: C, 70.01, H, 11.68.

(*E*)-3-Hepten-2-one (3d).[26] To 2.58 g (18.0 mmol) of CuBr was added 15.0 mL (16.5 mmol) of a 1.1 M solution of *n*-propylmagnesium bromide in diethyl ether at −35 °C. The resulting suspension was stirred at −30 to −20 °C for 15 min, 3.00 mL (21.0 mmol) of (trimethylsilyl)acetylene and 3.10 mL of triethyl phosphite were added, and stirring was continued at 0 °C for 2 h. A saturated, aqueous NH_4Cl solution (20 mL) was added dropwise, followed by 10 mL of a 10% aqueous $Na_2S_2O_3$ solution. After all solids had dissolved, the layers were separated, the aqueous layer was extracted with pentane (3 × 10 mL), and the combined organic layers were washed with a 10% aqueous $Na_2S_2O_3$ solution (1 × 10 mL), a saturated, aqueous NH_4Cl solution (1 × 10 mL), and brine (1 × 10 mL), and dried ($MgSO_4$). The solvent was removed by distillation over a 10-cm Vigreux column. Distillation of the residue afforded (*E*)-1-pentenyltrimethylsilane (**11**) as colorless liquid: bp 125–135 °C/760 Torr (lit.[33] bp 135 °C/760 Torr): ^{1}H NMR and IR data matched those reported;[33] ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.2 (q), 13.7 (q), 21.8 (t), 38.3 (t), 129.7 (d), 147.1 (d).

A suspension of 266 mg (2.00 mmol) of $AlCl_3$ in 10 mL of dichloromethane was cooled to 0 °C and treated with 0.14 mL (2.00 mmol) of acetyl chloride and a solution of 142 mg (1.00 mmol) of the silane **11** in 3 mL of dichloromethane. After 2.5 h of stirring at room temperature, 5 mL of a saturated, aqueous $NaHCO_3$ solution was added dropwise and the mixture was stirred vigorously for 10 min. The layers were separated, and the organic layer was washed with a saturated, aqueous $NaHCO_3$ solution (3 × 5 mL) and brine (1 × 5 mL), dried ($MgSO_4$), and concentrated (20 °C/20 Torr). The residue was purified by column chromatography [20 g of silica gel, 2:1 petroleum ether (bp 30–50 °C)/methyl *tert*-butyl ether as eluant] to yield 76.0 mg (68%) of **3d** as a colorless liquid: ^{1}H NMR and IR data matched those reported;[26] ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.5 (q), 21.2 (t), 26.7 (t), 34.5 (t), 131.3 (d), 148.2 (d), 198.6 (s).

(*E*)-4-Octen-3-one (3e). Analogous to the above procedure, 173 mg (68%) of **3e** was obtained by starting from 284 mg (2.00 mmol) of silane **11**, 392 mg (5.00 mmol) of $AlCl_3$, and 0.44 mL (5.00 mmol) of propionyl chloride. ^{1}H and ^{13}C NMR and IR spectral data matched those reported.[27]

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