Photooxygenation of Vinylstannanes: Tin-Substituted Allylic Hydroperoxides through the Regio- and Diastereoselective Ene Reaction with Singlet Oxygen

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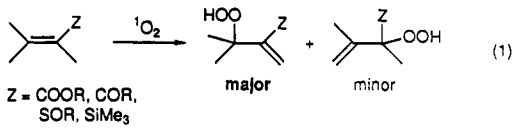
For the first time the photooxygenation of vinylstannanes 1 was investigated. Thus, dye-sensitized oxygenation of acylic and cyclic tri- and tetrasubstituted vinylstannanes yielded regioselectively β-stannylallylic hydroperoxides 2 in all cases. As byproducts were formed the α,β-enones 3′, which derive from the regioisomeric ene product 3 through elimination of trialkyltin hydroxide. The degree of regioselectivity depended on the configuration of the precursor olefin as well as on the substitution pattern at the tin atom. Comparison with the analogous olefinic carbon and silicon compounds reveals that the high degree of *gem* selectivity in the ene reaction of vinylstannanes is the result of composite steric and electronic factors reflected in the perepoxide intermediate. The regioselectively produced hydroperoxides represent hitherto unknown oxy-functionalized organotin compounds which should serve as novel synthetic building blocks in organic synthesis.

Introduction

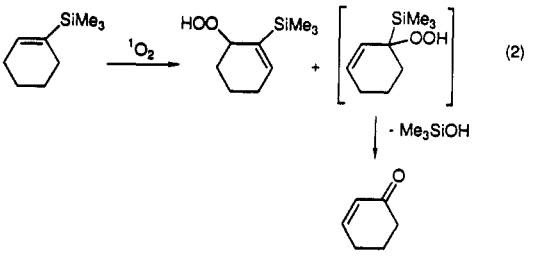
The regio- and stereochemistry of the ene reaction of singlet oxygen with olefins has received considerable attention in the last few years. Whereas simple alkyl-substituted olefins react with singlet oxygen in a rather unselective manner since often all possible isomers are formed in comparable amounts,[1] remarkable regioselectivity is observed for substrates with either sterically demanding groups[2] or carbanion-stabilizing functionalities at the double bond such as α,β-unsaturated esters,[3] ketones,[4] sulfoxides,[5] and vinylsilanes[6] (eq 1). The high



(1)

gem selectivity of the former substrates, which results in the abstraction of hydrogen from the more crowded side of the double bond, is explained by steric[2] interactions of the large group with the attacking singlet oxygen through a zwitterionic perepoxide intermediate.

In the photooxygenation of vinyl silanes, however,[6] which yields β-trimethylsilyl allylic alcohols as the only products after subsequent reduction of the hydroperoxides with sodium borohydride, electronic effects have also been invoked. Antibonding interactions of the occupied σ orbital of the C–Si bond with the lone pair of the nonterminal oxygen of a perepoxide intermediate are held responsible for the high degree of selectivity. Nevertheless, the regioselectivity is not always as high as claimed because α,β-enones are formed as byproducts from the decomposition of the labile α-hydroperoxy allylic silanes[7] (eq 2).



(2)

These results prompted us to investigate whether the photooxygenation of the analogous vinylstannanes also shows comparable *gem* selectivity. Photooxygenation of the readily available vinylstannanes could serve as an attractive entry into regioselectively oxyfunctionalized organotin compounds, which are of wide interest for organic synthesis in view of their facile functionalization by metal exchange and palladium-catalyzed coupling reactions.[8] Presently, we report the results of our investigation, which demonstrate that the regioselective ene reaction of vinylstannanes with singlet oxygen can afford valuable building blocks for preparative purposes.

Results

Z,E mixtures of vinylstannanes **1a–d** and **1i** (Table I) were prepared either from the readily available corresponding vinylmagnesium or -lithium precursors. From these mixtures the pure *Z* isomeric vinylstannanes **1a,b** were obtained by photooxygenation and recovery of the less reactive *Z* isomers at half conversion. The pure *E* isomers were synthesized by molybdenum-catalyzed hydrostannation of 2-butyne.[9] The synthesis of vinylstannanes **1e–h** was accomplished by starting from the

(1) Frimer, A. A.; Stephenson, L. M. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press Inc.: Boca Raton, 1985; Vol. II, p 67.
(2) Orfanopoulos, M.; Stratakis, M.; Elemes, Y. *J. Am. Chem. Soc.* **1990**, *112*, 6417.
(3) (a) Ensley, H. E. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, 1990; Vol. 2, p 181. (b) Adam, W.; Griesbeck, A. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1070. (c) Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1985**, *26*, 5991.
(4) Ensley, H. E.; Carr, R. V. C.; Martin, R. S.; Pierce, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2836.
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(7) Adam, W.; Richter, M. *Tetrahedron Lett.* **1992**, *33*, 3461.
(8) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(9) Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.

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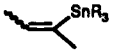
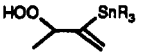
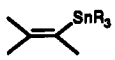
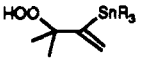
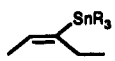
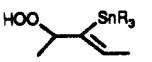
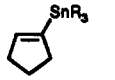
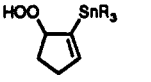
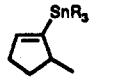
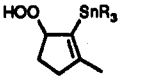
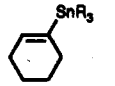
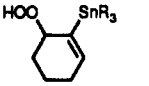
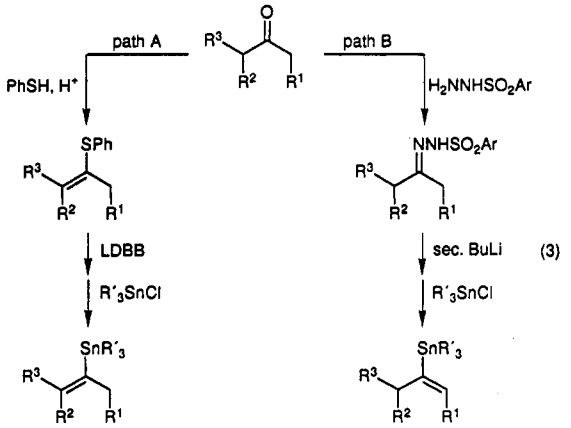
Table I. Product Studies of the Photooxygenation of Vinylstannanes 1

	substrate 1						hydroperoxide 2	
entry	structure		R	E:Z	solvent[a]	time[b] (h)	regioselectivity 2:3[c]	structure	yield[d] (%)
1		1a	Me	100:0	CD_3OD	0.5	89:11		35[e]
2		1a	Me	100:0	$CDCl_3$	0.5	87:13		
3		1a	Me	0:100	CD_3OD	2	58:42		
4		1b	*n*-Bu	100:0	$CDCl_3$	0.5	92:8		
5		1b	*n*-Bu	5:95	$CDCl_3$	2	74:26		59[f]
6		1c	Ph	50:50	$CDCl_3$	4.5	88:12		71
7		1d	*i*-Pr	32:68	$(CD_3)_2CDOD$	2.3	90:10		31
8		1e	*n*-Bu		$CDCl_3$	0.5	93:7		78
9		1f	*n*-Bu	100:0	$CDCl_3$	4	66:34		64[g]
10		1g	*n*-Bu		$CDCl_3$	1	93:7		79
11		1h	*n*-Bu		$CDCl_3$	1	92:8		74
12		1i	*n*-Bu		CH_3OH/C_6H_6	19.5	88:12[h]		52

[a] At −20 °C, Rose Bengal or TPP (in $CDCl_3$) as sensitizer. [b] Conversion >90%, error limits ±5% of stated values. [c] Error limits ±3% of stated values, mass balance >90%. [d] Isolated yield; preparative work in MeOH for **1a**, in $MeOH/C_6H_6$ for **1b,i**, in EtOH for **1d**, and in CH_2Cl_2 for **1c,e,f,g,h**. [e] By starting from (*Z,E*)-**1a** = 82:18. [f] By starting from (*Z,E*)-**1b** = 77:23. [g] (*Z,E*)-**2f** = 95:5. [h] Determined by ^1H NMR spectroscopy of the crude reaction mixture.

corresponding ketones through reductive lithiation of the corresponding vinyl thioethers[10] (path A, eq 3) or the

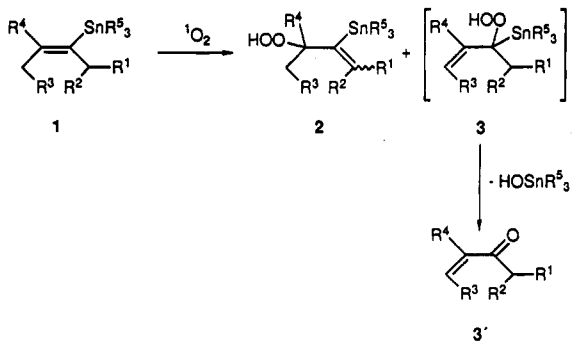


(3)

Shapiro reaction[11] (path B, eq 3). These two reaction pathways allow the introduction of the double bond in a regioselective manner, in which the Shapiro procedure yields the lower substituted and the reductive lithiation the higher substituted vinylstannanes.

Photooxygenation of the vinylstannanes **1** with Rose Bengal or tetraphenylporphine as sensitizers yielded in all cases the β-stannylallylic hydroperoxides **2** as main products, besides smaller amounts of the α,β-unsaturated ketones **3′** (eq 4). These enones derive from the regioisomeric ene products **3**, which could not be detected even at low temperature because they readily eliminate trialkyltin hydroxide to form enones **3′**.

To determine the regioselectivity, the vinylstannanes **1** were photooxygenated on the NMR scale in deuterated solvents at low temperature to prevent decomposition of



(4)

1 **2** **3** **3′**

the sensitive hydroperoxides and loss of the volatile enones on solvent removal. For the full characterization of the novel β-stannylallylic hydroperoxides **2**, preparative-scale photooxygenations were performed at low temperatures to permit isolation of sufficient amounts of product for purification. Chlorinated as well as nonchlorinated solvents can be used, but the latter are preferred in reactions which demand prolonged irradiation times (especially vinylstannane **1i**) to avoid decomposition of the labile ene products. Hydroperoxides **2** could readily be separated in moderate to good yields (31–79%) from the byproducts by flash chromatography on silica gel at 0 °C and were obtained as colorless, unstable oils (except the crystalline **2c**), which slowly decomposed on standing at room temperature to give colorless high-molecular-weight materials.

The results of the ene reaction of singlet oxygen with vinylstannanes are given in Table I. The reaction exhibited no significant solvent effect as shown by the results for $CDCl_3$ versus CD_3OD (entries 2 and 1). The regioselectivity of the ene reaction, however, strongly depended on the configuration of the double bond in substrate **1** as well as on the substitution pattern at the tin atom, as displayed by the 2-butenyl-substituted stannanes **1a–d**. The *E*-configurated stannanes, which are much more reactive toward singlet oxygen than the

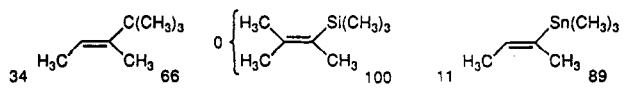
(10) (a) Cohen, T.; Doubleday, M. D. *J. Org. Chem.* **1990**, *55*, 4784. (b) Adam, W.; Richter, M. *Chem. Ber.* **1992**, *125*, 243.
(11) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147.

corresponding *Z* precursors, showed high *gem* selectivity (in all cases ≥88%; entries 1, 4, 6, 7). The regioselectivity in the ene reaction of the *Z* isomers was significantly lower (from 58 to about 85% geminal abstraction; entries 3, 5, 6, 7). In both cases the regioselectivity increased with steric bulk at the tin center, as evidenced by the series $SnMe_3$, $Sn(n\text{-}Bu)_3$, $SnPh_3$, and $Sn(i\text{-}Pr)_3$ (entries 1, 3–7). This trend was more pronounced for the *Z* olefins (entries 3, 5). The trisubstituted vinylstannane **1e** (entry 8) gave essentially the same regioselectivity as the *E*-configurated substrate **1b** (entry 4), so that the additional methyl group at the double bond exercises only a nominal effect. Moreover, increasing substitution at the β-carbon in the open-chain substrate (*E*)-**1f** (entry 9) resulted in lower regioselectivity, although the reaction is highly stereoselective and yields (*Z*,*E*)-**2f** in a 95:5 ratio. Contrary to this, for the cyclic derivatives **1g–i** (entries 10–12) the photooxygenation proceeded with high regioselectivity (geminal abstraction ≥88%), and substitution at the geminal site caused insignificant changes, as becomes evident for substrates **1g** (entry 10) versus **1h** (entry 11).

Discussion

As shown in Table I, the *E*-configurated vinylstannanes, which can be readily prepared in a stereoselective manner by the Shapiro reaction[11] or by catalytic hydrostannation,[9] exhibit in all cases high *gem* selectivity to give regioselectively the β-stannylallylic hydroperoxides **2** (eq 4). This regioselectivity coincides also with their higher reactivity; both facts can be rationlized in terms of the cis effect.[12] Branching at the geminal site does not influence the reactivity of the cyclic stannanes **1g,h**, which in view of their less flexible geometry can be attacked preferentially by singlet oxygen from that side of the molecular plane which allows stabilization of the perepoxide intermediate by the cis effect.[12] In the case of vinylstannane **1f**, however, the reaction is less regioselective, although completely stereoselective, to yield the hydroperoxide (*Z*)-**2f** in high preference. This lack of regioselectivity is presumably caused by 1,3-allylic strain between the substituent at the geminal position and the allylic methyl group for this conformationally more flexible system, which forces the allylic hydrogens at the geminal site out of the required perpendicular position to the double bond. The same conformational interactions are also responsible for the observed stereoselectivity because (*Z*)-**2f** results from the intermediate in which the methyl group at the geminal site occupies the less strained position.

The comparison of analogous carbon and silicon derivatives of vinylstannane (*Z*)-**1a** is informative. The *tert*-butyl-substituted olefin **4**[2] exhibits only a moderate

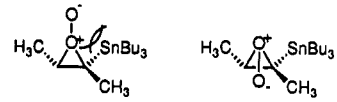


4 5 *E*-**1a**

gem selectivity, i.e., a product ratio of 66:34 in favor of geminal abstraction. This moderate regioselectivity presumably results from steric interactions of the large *tert*-butyl group with the nonterminal oxygen in the perepoxide intermediate ("nonbonding large group effect").[2] In contrast, vinylsilane **5** shows abstraction at the geminal site completely (100%) regioselectively.[2] This high regiocontrol is explained in terms of repulsive electronic interactions between the occupied σ orbital of the C–Si bond and the lone pair of the nonterminal perepoxide oxygen.[6a]

In the corresponding vinylstannane (*E*)-**1a**, however, the regioselectivity decreases somewhat, namely to 89:11. From the above-mentioned theoretical work[6a] one would have expected higher electronic repulsion for this substrate because of the higher energy of the σ orbital of the C–Sn bond and thus even stronger interaction with the lone pair orbital in view of the smaller energy gap. Apparently, the regioselectivity of the $^1O_2$ ene reaction of vinyl compounds is influenced by electronic as well as steric factors. For steric interactions, the selectivity should decrease in the order $(CH_3)_3C > (CH_3)_3Si > (CH_3)_3Sn$ because of increasing length of the carbon–metal bond and thus decreasing effective size[13] of the substituents. This steric influence is clearly exhibited by the *E*- and *Z*-configurated vinylstannanes investigated here for the stannyl groups of different steric bulk (entries 2–7 in Table I). On the other hand, the eletronic interactions should increase in the order $(CH_3)_3C < (CH_3)_3Si < (CH_3)_3Sn$ and the regioselectivity in the same direction. In the *E*-configurated vinylstannanes these electronic interactions seem to dominate, and the net result of the two counteracting effects is a maximum in regioselectivity for vinylsilanes and a minimum for the carbon analog, and the vinylstannanes fall in between.

For the *Z*-configurated vinylstannanes, which generally exhibit a lower regioselectivity, the steric interactions become indeed dominating. This is clearly reflected by the increasing size of the R_3Sn moiety in the series **1a** < **1b** < **1d** and the corresponding increasing regioselectivity (cf. entries 3, 5, 7 in Table I). In these substrates two perepoxide intermediates **A** and **B** can be formed. With



A B

growing steric bulk at the tin moiety, the perepoxide **A** is disfavored because of severe steric hindrance and formation of hydroperoxides **2** is preferred.

In summary, for the first time the photooxygenation of vinylstannanes **1** was investigated and shown to yield the novel β-stannylallylic hydroperoxides **2** in good yields and in high regio- and stereoselectivity. Thereby a convenient and effective alternative to the standard methodology for the preparation of oxo-functionalized vinylstannanes through the hydrostannation of the corresponding alkynes has been made available,[9,14] since the latter method is not generally regioselective and cannot be applied to cyclic substrates. The now readily accessible new class of oxy-functionalized vinylstannanes should be of interest in organic synthesis.

(12) (a) Orfanopoulos, M.; Grdina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275. (b) Schulte-Elte, K. H.; Rautenstrauch, V. *J. Am. Chem. Soc.* **1980**, *102*, 1738. (c) Adam, W.; Catalani, L. H.; Griesbeck, A. *J. Org. Chem.* **1986**, *51*, 5494. (d) Adam, W.; Nestler, B. *Liebigs Ann. Chem.* **1990**, 1051.

(13) Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5.

(14) Konoike, T.; Araki, Y. *Tetrahedron Lett.* **1992**, *33*, 5093.

Experimental Section

General Methods. All melting points and boiling points are uncorrected. Solvents were purified according to standard procedures. TLC was performed on Polygram Sil G UV (40 × 80 mm), Macherey & Nagel. Silica gel 63–200 μm was used for column chromatography and silica gel 32–64 μm for flash chromatography, both from Woelm. IR spectra were recorded on a Perkin-Elmer Model 1420 instrument. ^{1}H NMR spectra were obtained at 250 MHz on a Bruker AC 250 or at 200 MHz on a Bruker AC 200 instrument with $CDCl_3$ (δ 7.26) as internal standard. ^{13}C NMR spectra were recorded on a Bruker AC 250 or a Bruker AC 200 instrument at 69.2 or 50.3 MHz with $CDCl_3$ (δ 77.0) as internal standard. ^{1}H NMR resonances of the tributylstannyl groups of the alkenylstannanes **1e–i**, **2b**, and **2e–i** at δ 0.75–1.1 (m, 15H) and 1.2–1.6 (m, 12H) were not listed in the reported ^{1}H NMR data. The separate J (^{117}SnH) and J (^{119}SnH) values were reported when the satellite peaks were clearly distinct; otherwise the indicated J_{HSn} values represent approximate mean values of J (^{117}SnH) and J(^{119}SnH).

Vinylstannanes. *Z,E* mixtures of vinylstannanes **1a,b** were synthesized in 70% and 79% yield in an analogous manner to **1c,d** (see below) by reaction of 2-butenylmagnesium bromide with the appropriate tin halide.[15] The pure *Z* isomers were obtained from these mixtures by photooxygenation and recovery of the less reactive *Z* isomer at half conversion by column chromatography on silica gel. Isomerically pure (*E*)-**1a** and (*E*)-**1b** were obtained in 26% yield by molybdenum-catalyzed hydrostannation of 2-butyne according to the Guibé[9] procedure. (*E*)-**1f**[15] and **1g**[17] were synthesized in 69% and 79% yield through the Shapiro reaction by the procedure described for **1h** (see below). Stannane **1i** was prepared by reaction of 1-lithiocyclohexene[18] with tri-*n*-butyltin chloride at −10 °C in 84% yield.

(*Z,E*)-(1-Methyl-1-propenyl)triphenylstannane (1c). To 1.22 g (50.0 mmol) of magnesium turnings in 10 mL of dry THF was added a solution of 6.75 g (50.0 mmol) of 2-bromo-2-butene in 20 mL of THF at 50 °C within 1.5 h. After complete consumption of the metal, the mixture was cooled to 0 °C, treated with a solution of 9.64 g (25.0 mmol) of triphenyltin chloride in 20 mL of THF, and stirred for 16 h at ambient temperature. After hydrolysis with 20 mL of saturated NH_4Cl solution, the organic layer was separated, washed with 10% KF solution (20 mL), water (20 mL), and brine (20 mL), dried ($MgSO_4$), and evaporated (50 °C, 20 Torr). Recrystallization of the residue from ethanol yielded 8.25 g (82%) of colorless needles, mp 91–98 °C, as a 50:50 mixture of *Z/E* isomers.

(*E*)-**1c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.80 (dq, J = 6.5, 1.1 Hz, 3H), 2.05 (m, 3H), 5.93 (qq, J = 6.5, 1.9 Hz, 1H), 7.30–7.80 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3 (q), 18.8 (q), 128.4 (d), 128.8 (d), 135.6 (s), 137.1 (d), 139.1 (s), 139.2 (d). (*Z*)-**1c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.74 (dq, J = 6.6, 1.6 Hz, 3H), 2.05 (m, 3H), 6.47 (qq, J = 6.6, 1.7 Hz, 1H), 7.30–7.80 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.9 (q), 27.1 (q), 128.5 (d), 128.8 (d), 135.4 (s), 137.2 (d), 137.9 (d), 138.7 (s); IR (CCl_4) ν 1630 cm^{-1}. Anal. Calcd for $C_{22}H_{22}Sn$ (405.1): C, 65.22; H, 5.47. Found: C, 65.44; H, 5.42.

(*Z,E*)-Tris(2-methylethyl)(1-methyl-1-propenyl)stannane (1d). Stannane **1d** was obtained in an analogous manner to **1c** from 50 mmol of 2-butenylmagnesium bromide and 8.50 g (30.0 mmol) of *i*-Pr_3SnCl[19] to yield 7.56 g (83%) of a colorless oil, bp 120 °C (15 Torr).

(*E*)-**1d**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.29 (d, J = 6.9 Hz, 18H), 1.45–1.64 (m, 3 H), 1.70 (m, 3 H), 1.85 (m, J_{HSn} = 45 Hz, 3H), 5.64 (qq, J = 6.5, 1.9 Hz, J_{HSn} = 58.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8 (q), 14.4 (q), 15.3 (q), 22.2 (d), 135.6 (d), 137.9 (s). (*Z*)-**1d**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31 (d, J = 7.2 Hz, 18H), 1.45–1.64 (m, 3 H), 1.93 (m, J_{HSn} = 40 Hz, 3H), 6.20 (qq, J = 6.6, 1.6 Hz, J_{HSn} = 40 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.2 (q), 20.3 (q), 22.2 (d), 27.7 (q), 135.0 (d), 138.7 (s); IR (neat) ν 1623, 1611 cm^{-1}. Anal. Calcd for $C_{13}H_{28}Sn$ (303.1): C, 51.52; H, 9.31. Found: C, 51.33; H, 9.58.

Tri-*n*-butyl(1,2-dimethyl-1-propenyl)stannane (1e). To a solution of 21.0 mmol of lithio-4,4′-di-*tert*-butylbiphenylide (LDBB)[10] in 50 mL of dry THF was added a solution of 1.78 g (10.0 mmol) of [(1,2-dimethyl-1-propenyl)thio]benzene[20] in 40 mL of THF within 30 min at −78 °C. When the color of the solution had turned from dark purple to red, a solution of 3.42 g (10.5 mmol) of *n*-Bu_3SnCl in 10 mL of THF was added, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was washed with 1 N NaOH (4 × 50 mL) to remove thiophenol and then with water (50 mL) and brine (50 mL) and dried ($MgSO_4$). After removal of the solvent (50 °C at 20 Torr), 10 mL of EtOH was added, and the precipitated excess 4,4′-di-*tert*-butylbiphenyl (DBB) was removed by filtration. Evaporation of the solvent (50 °C at 20 Torr) and column chromatography on silica gel [absorbant/substrate ratio 100:1, petroleum ether (50–60) as eluant] yielded 1.68 g (45%) of a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.74 (m, 3H), 1.76 (m, 3H), 1.79 (m, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 10.3 (t), 13.7 (q), 19.1 (q), 20.9 (q), 27.5 (t), 29.3 (t), 28.2 (q), 135.5 (s), 140.5 (s); IR (neat) ν 1620 cm^{-1}. Anal. Calcd for $C_{17}H_{36}Sn$ (359.2): C, 56.85; H, 10.10. Found: C, 57.13; H, 10.24.

Tri-*n*-butyl(5-methyl-1-cyclopenten-1-yl)stannane (1h). To a solution of 15.0 g (39.7 mmol) of (2-methyl-1-oxocyclopentyl)-triisopropylbenzenesulfonylhydrazone[21] in 150 mL of petroleum ether (50–70 °C)/TMEDA (1:1) was added 42.4 mL (83.4 mmol) of a 2.0 M *sec*-butyllithium solution (in petroleum ether) at −78 °C and the resulting solution stirred at this temperature for 2 h. The reaction mixture was allowed to warm to 0 °C until evolution of nitrogen had ceased and immediately recooled to −78 °C. After the addition of 12.9 g (39.7 mmol) of *n*-Bu_3SnCl, the reaction mixture was allowed to warm to room temperature within 1 h, and 40 mL of saturated NH_4Cl solution was added. The organic layer was separated, washed with water (4 × 50 mL), 10% KF solution (50 mL), and brine (50 mL), and dried ($MgSO_4$). Evaporation of the solvent (60 °C/20 Torr) and distillation of the residual liquid yielded 11.6 g (78%) of a yellow oil: bp 93–96 °C/0.05 Torr; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.05 (d, J = 7.0 Hz, 3H), 1.50 (m, 1H), 1.97–2.10 (m, 1H), 2.24–2.50 (m, 2H), 2.78 (m, 1H), 5.81 (q, J = 2.1 Hz, J_{HSn} = 36 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.5 (t), 13.7 (q), 21.8 (q) 28.0 (t), 29.2 (t), 32.5 (t), 34.0 (t), 41.6 (d), 140.3 (d), 150.2 (s); IR (neat) ν 3025, 1579 cm^{-1}. Anal. Calcd for $C_{18}H_{36}Sn$ (371.2): C, 58.24; H, 9.78. Found: C, 57.91; H, 10.03.

General Procedure for the NMR-Scale Photooxygenation of Vinylstannanes 1. A solution of ca. 0.1 mmol of the corresponding vinylstannane and ca. 1 mg of sensitizer (Rose Bengal or TPP) in 0.5 mL of the appropriate deuterated solvent (the exact conditions are given in Table I) was photooxygenated directly in an NMR tube at −20 °C by passing a slow stream of dry oxygen gas through the solution by means of a capillary while externally irradiating with two 150-W sodium lamps until complete conversion of the vinylstannane (TLC). Product ratio 2:3 was determined by ^{1}H NMR.

General Procedure for the Preparative Photooxygenation of Vinylstannanes 1. A solution of 1–8 mmol of the corresponding vinylstannane **1** in 50 mL of the appropriate solvent (the exact conditions are given in Table I) was photooxygenated by passing a slow stream of dry oxygen gas at −25 °C while external irradiating with two 150-W sodium lamps in the presence of TPP (in CH_2Cl_2) or Rose Bengal (in MeOH, MeOH/benzene, or ethanol) as sensitizer (ca. 5 × 10^{-4} M) until complete conversion of the vinylstannane (TLC). Solvent was removed by rotoevaporation (0 °C at 20 Torr), and the remaining oily residue was purified by flash chromatography at 0 °C on silica gel [ratio of 50:1 absorbant to substrate, petroleum ether (30–50 °C)/ether mixtures (3:1 to 8:1) as eluant].

1-Methyl-2-(trimethylstannyl)-2-propenyl Hydroperoxide (2a). Photooxygenation of 1.54 g (7.04 mmol) of vinylstannane (*Z,E*)-**1a** (82:18) in methanol for 3 h yielded 626 mg (35%) of colorless oil after silica gel flash chromatography: ^{1}H NMR

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(200 MHz, $CDCl_3$) δ 0.21 (s, J_{HSn} = 53/55 Hz, 9H), 1.24 (d, J = 6.5 Hz, 3H), 4.65 (qt, J = 6.5, 1.1 Hz, J_{HSn} = 55 Hz, 1H), 5.36 (dd, J = 2.1, 1.1 Hz, J_{HSn} = 69 Hz, 1H), 5.86 (dd, J = 2.1, 1.1 Hz, J_{HSn} = 141 Hz, 1H), 7.74 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ -8.7 (q), 19.4 (q), 88.7 (d), 126.1 (t), 156.4 (s); IR (neat) ν 3600–3100, 3050, 1629 cm^{-1}. Anal. Calcd for $C_7H_{16}O_2Sn$ (250.9): C, 33.51; H, 6.43. Found: C, 33.49; H, 6.68.

2-(Tri-*n*-butylstannyl)-1-methyl-2-propenyl Hydroperoxide (2b). The photooxygenation of 509 mg (1.47 mmol) vinylstannane (*Z*,*E*)-**1b** (77:23) in 5:1 methanol/benzene as solvent for 6 h afforded 329 mg (59%) of colorless oil after silica gel flash chromatography: ^1H NMR (250 MHz, $CDCl_3$) δ 1.27 (d, J = 6.5 Hz, 3H), 4.65 (qt, J = 6.5, 1.1 Hz, J_{HSn} = 49 Hz, 1H), 5.37 (dd, J = 2.2, 1.1 Hz, J_{HSn} = 61/59 Hz, 1H), 5.93 (dd, J = 2.2, 1.1 Hz, J_{HSn} = 130/124 Hz, 1H), 7.73 (s, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 10.1 (t), 13.7 (q), 19.3 (q), 27.4 (t), 29.0 (t), 88.5 (d), 126.4 (t), 155.9 (s); IR (neat) ν 3600–3100, 3030 cm^{-1}. Anal. Calcd for $C_{16}H_{34}O_2Sn$ (377.2): C, 50.95; H, 9.09. Found: C, 51.40; H, 9.46.

1-Methyl-2-(triphenylstannyl)-2-propenyl Hydroperoxide (2c). In the photooxygenation of 1.02 g (2.52 mmol) of vinylstannane (*Z*,*E*)-**1c** (50:50) in CH_2Cl_2 for 14 h was obtained 794 mg (71%) of colorless cubes, mp 78–79 °C, after silica gel flash chromatography: ^1H NMR (200 MHz, $CDCl_3$) δ 1.29 (d, J = 6.5 Hz, 3H), 4.83 (qt, J = 6.5, 1.1 Hz, J_{HSn} = 62 Hz, 1H), 5.62 (t, J = 1.3 Hz, J_{HSn} = 77/80 Hz, 1H), 6.15 (t, J = 1.3 Hz, J_{HSn} = 162/170 Hz, 1H), 7.30–7.85 (m, 15H), 7.51 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.4 (q), 87.5 (d), 128.7 (d), 129.2 (d), 129.3 (t), 137.2 (d), 137.7 (s), 154.3 (s); IR (CCl_4) ν 3530–3400, 1640 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_2Sn$ (437.1): C, 60.45; H, 5.07. Found: C, 60.45; H, 5.08.

1-Methyl-2-[tris(2-methylethyl)stannyl]-2-propenyl Hydroperoxide (2d). In the photooxygenation of 1.00 g (3.30 mmol) of vinylstannane **1d** in ethanol for 7.5 h was obtained 345 mg (31%) of a colorless oil after silica gel flash chromatography. ^1H NMR (200 MHz, $CDCl_3$) δ 1.27 (d, J = 6.4 Hz, 3H), 1.32 (d, J = 6.8 Hz, J_{HSn} = 64 Hz, 18H), 1.40–1.80 (m, 3H). 4.63 (qt, J = 6.4, 1.2 Hz, J_{HSn} = 41/43 Hz, 1H), 5.33 (dd, J = 2.2, 1.1 Hz, J_{HSn} = 54 Hz, 1H), 5.97 (dd, J = 2.2, 1.3 Hz, J_{HSn} = 118 Hz, 1H), 7.69 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.3 (d), 19.1 (q), 22.1 (q), 88.0 (d), 126.8 (t), 154.7 (s); IR (neat) ν 3600–3100, 3055 cm^{-1}. Anal. Calcd for $C_{13}H_{28}O_2Sn$ (335.1): C, 46.60; H, 8.42. Found: C, 46.44; H, 8.20.

2-(Tri-*n*-butylstannyl)-1,1-dimethyl-2-propenyl Hydroperoxide (2e). The photooxygenation of 505 mg (1.41 mmol) of vinylstannane **1e** in CH_2Cl_2 for 2 h yielded 432 mg (78%) of a colorless oil after silica gel flash chromatography: ^1H NMR (250 MHz, $CDCl_3$) δ 1.33 (s, 6H), 5.26 (d, J = 1.6 Hz, J_{HSn} = 65/68 Hz, 1H), 5.81 (d, J = 1.6 Hz, J_{HSn} = 130/137 Hz, 1H), 7.34 (s, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 10.7 (t), 13.7 (q), 25.0 (q), 27.4 (t), 29.0 (t), 87.3 (s), 123.4 (t), 160.2 (s); IR (neat) ν 3600–3100, 1630 cm^{-1}. Anal. Calcd for $C_{17}H_{36}O_2Sn$ (391.2): C, 52.20; H, 9.28. Found: C, 52.62; H, 9.47.

(*Z*)-2-(Tri-*n*-butylstannyl)-1-methyl-2-butenyl Hydroperoxide (2f). The photooxygenation of 544 mg (1.51 mmol) of vinylstannane **1f** in CH_2Cl_2 for 2 h yielded 380 mg (64%) of a colorless oil after silica gel flash chromatography: ^1H NMR (200 MHz, $CDCl_3$) δ 1.19 (d, J = 6.5 Hz, 3H), 1.77 (d, J = 6.5 Hz, 3H), 4.56 (br q, J = 6.4 Hz, J_{HSn} = 56 Hz, 1H), 6.37 (qd, J = 6.6, 0.9 Hz, J_{HSn} = 119/124 Hz, 1H), 7.62 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.7 (t), 13.6 (q), 19.4 (q), 19.5 (q), 27.4 (t), 29.0 (t), 89.2 (d), 137.5 (d), 145.7 (s); IR (neat) ν 3600–3100, 1617 cm^{-1}. Anal. Calcd for $C_{17}H_{36}O_2Sn$ (391.2): C, 52.20; H, 9.28. Found: C, 52.61; H, 9.55.

2-(Tri-*n*-butylstannyl)-2-cyclopenten-1-yl Hydroperoxide (2g). In the photooxygenation of 510 mg (1.43 mmol) of vinylstannane **1g** in CH_2Cl_2 for 1.5 h was obtained 441 mg (79%) of a colorless oil after silica gel flash chromatography: ^1H NMR (200 MHz, $CDCl_3$) δ 1.90–2.20 (m, 2H), 2.25–2.70 (m, 2H), 5.20 (m, 1H), 6.24 (m, J_{HSn} = 32 Hz, 1H), 7.54 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.4 (t), 13.6 (q), 27.2 (t), 28.3 (t), 29.0 (t), 33.6 (t), 96.6 (d), 141.2 (s), 148.6 (d); IR (neat) ν 3620–3120, 3025, 1580 cm^{-1}. Anal. Calcd for $C_{17}H_{34}O_2Sn$ (389.2): C, 52.47; H, 8.81. Found: C, 52.56; H, 8.52.

2-(Tri-*n*-butylstannyl)-5-methyl-2-cyclopenten-1-yl Hydroperoxide (2h). From the photooxygenation of 510 mg (1.37 mmol) of vinylstannane **1h** in CH_2Cl_2 for 70 min was obtained 412 mg (74%) of a reddish oil after silica gel flash chromatography: ^1H NMR (200 MHz, $CDCl_3$) δ 1.84 (br s, 3H), 1.97–2.68 (m, 4H), 5.11 (m, 1H), 7.50 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.7 (t), 13.7 (q), 19.1 (q), 27.4 (t), 29.2 (t), 29.6 (t), 37.9 (t), 97.5 (d), 133.3 (s), 159.3 (s); IR (neat) ν 3600–3100, 1616 cm^{-1}. Anal. Calcd for $C_{18}H_{36}O_2Sn$ (403.2): C, 53.62; H, 9.00. Found: C, 53.90; H, 9.03.

2-(Tri-*n*-butylstannyl)-2-cyclohexen-1-yl Hydroperoxide (2i). The photooxygenation of 750 mg (2.02 mmol) of vinylstannane **1i** in 10:1 methanol/benzene for 19.5 h yielded 394 mg (53%) of a colorless oil after silica gel flash chromatography: ^1H NMR (250 MHz, $CDCl_3$) δ 1.55–2.20 (m, 6H), 4.50 (m, 1H), 6.03 (dt, J = 3.6, 2.0 Hz, J_{HSn} = 63 Hz, 1 H), 7.68 (s, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 9.7 (t), 13.7 (q), 18.9 (t), 27.4 (t), 27.5 (t), 27.6 (t), 29.3 (t), 29.3 (t), 83.8 (d), 138.7 (s), 142.7 (d); IR (neat) ν 3600–3100, 1605 cm^{-1}. Anal. Calcd for $C_{18}H_{36}O_2Sn$ (403.2): C, 53.62; H, 9.00. Found: C, 53.86; H, 8.98.

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