Photosensitized Oxygenation of Twisted 1,3-Dienes: Abnormally Higher Reactivity of Vinyl Hydrogen Rather than Allyl Hydrogen toward Singlet Oxygen

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As one of the novel examples to investigate the characteristic reactivity of significantly twisted 1,3-dienes, the photosensitized oxygenation of two types of significantly twisted 1,3-dienes, *cis*-β-ionol derivative **2** and acyclic derivative **11**, is investigated. Photosensitized oxygenation of **2a**−**f** and **11a**−**e** revealed that the vinyl hydrogen Ha was more reactive than the allyl hydrogen Hb. Thus, phenyl derivative **2e** and *tert*-butyl-substituted compound **11d** selectively produced allenes **3e** and **13d** in 67% and 75% yield resulting from the ene reaction of the vinyl hydrogen Ha rather than allyl alcohols **4e** and **14d** resulting from the allyl hydrogen abstraction in 24% and 8% yield, respectively. Furthermore, in the case of methyl-substituted compound **11b**, the extent of the inherent reactivity of the vinyl hydrogen Ha was similar to that of the allyl hydrogen Hc. On the basis of X-ray analysis and MM and MO calculations, the discovered abnormally higher reactivity of the vinyl hydrogen would be rationalized by considering mainly the large $\sigma^*-\pi$ orbital interaction between the vinyl C−H bond and another double bond in significantly twisted 1,3-dienes resulting from calculations of HOMO electron densities.

Introduction

Conjugated 1,3-dienes are some of the most common systems in organic synthesis, and their derivatives are widely used for the construction of numerous six-membered carbocycles by pericyclic reactions.[1] On the other hand, the chemistry of significantly twisted 1,3-dienes is relatively limited. Thus, the structural characteristics of twisted 1,3-dienes have been observed in cycloalkene derivatives substituted with a vinyl group having bulky substituents,[2] polysubstituted 1,3-butadienes,[3] bis-isopropylidenebornane derivatives,[4] and retinoid compounds.[5] Compared with these examples, little study on the characteristic reactivities of twisted 1,3-dienes can be found in the literature.[6] As a novel example for the characteristic reactivity, Hanack and co-workers reported that the solvolysis of twisted 2-bromo 1,3-diene derivatives was much faster than that of the conjugated ones.[7] However, no study on the reactivity of the vinyl hydrogen in significantly twisted 1,3-dienes has been reported, probably because these compounds are relatively unusual and the method of their synthesis has not been well established.

In 1968, we and another two groups independently reported the first example of allene formation by an ene reaction of vinyl hydrogens in *trans*-β-ionone derivatives with a singlet oxygen.[8] The yields of the allenes, however, were less than 10% for all the reported compounds, and a 1,4-addition product and the product resulting from the ene reaction of the allyl hydrogen were produced as major products. The reported unique allene formation should be attributable to the characteristic nature of the slightly twisted 1,3-diene of β-ionone derivatives because photosensitized oxygenation of normal conjugated 1,3-dienes did not produce allene at all.[9] In our program of

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(1) For example: (a) Kloetzel, M. C. The Diels−Alder Reaction with Maleic Anhydride. In *Organic Reactions*; Adams, R., et al., Eds.; John Wiley & Sons: New York, 1948; Vol. 4, pp 1−59. (b) Holmes, H. L. The Diels−Alder Reaction: Ethylenic and Acetylenic Dienophiles. In *Organic Reactions*; Adams, R., et al., Eds.; John Wiley & Sons: New York, 1948; Vol. 6, pp 60−173. (c) Ciganek, E. The Intramolecular Diels−Alder Reaction. In *Organic Reactions*; Dauben, W. G., et al., Eds.; John Wiley & Sons: New York, 1984; Vol. 32, pp 1−374.

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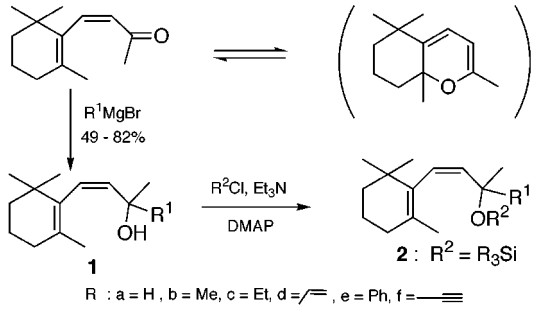
Scheme 1



the synthetic study of peridinin, which is a norcarotenoid possessing an allene moiety in one terminal, our attention had been focused on the novel allene formation with singlet oxygen. We designed *cis*-β-ionol derivatives **1** and **2** as significantly twisted 1,3-dienes and examined their photosensitized oxygenation. We found a regioselective ene reaction of the vinyl hydrogen rather than the allyl hydrogen with the singlet oxygen. Furthermore, in newly designed linear significantly twisted 1,3-dienes, we also observed the high reactivity of the vinyl hydrogen compared to the allyl hydrogen in a manner similar to that previously discussed. These abnormally higher reactivities of the vinyl hydrogen rather than the allyl hydrogen toward the singlet oxygen in significantly twisted 1,3-dienes would be rationalized by considering large $\sigma^*-\pi$ orbital interactions between the vinyl C−H bond and another double bond. In this paper, as one of the novel examples to study the characteristic reactivity of significantly twisted 1,3-dienes, we would like to describe in detail the photosensitized oxygenation of significantly twisted 1,3-dienes and report the first examples that the vinyl C−H bond of significantly twisted 1,3-dienes is remarkably activated due to the large interaction between the σ^* orbital of the vinyl C−H bond and the π orbital of another double bond.[10,11]

Results

Synthesis, Photooxygenation, and Conformational Analysis of *cis*-β-Ionol Derivatives. As a significantly twisted 1,3-diene, we designed *cis*-β-ionol derivatives possessing a tetrasubstituted carbon atom. The requisite substrates **1b**−**f** and **2b**−**f** were prepared by the Grignard reaction of *cis*-β-ionone[12] followed by silylation as shown in Scheme 1. The Grignard reactions required reflux conditions in THF because *cis*-β-ionone is mainly present as α-pyran at room temperature and as an equilibrium mixture at higher temperature.[13] The alkylated products **1b**−**f** were obtained by the reaction with methyl, ethyl, vinyl, phenyl, and ethynyl Grignard reagents in 49−82% yields as a nearly 1:1 mixture of rotational isomers, which were detectable by NMR. Silylation of the resulting alcohols **1b**−**f** along with *cis*-β-ionol (**1a**)[12] with triethylsilyl chloride gave the corresponding silyl ethers **2a**−**f** and that of **1d** with trimethylsilyl chloride gave the trimethylsilyl ether **2d-1** under the usual conditions, while treatment of **1d** with more bulky *tert*-butyldimethylsilyl chloride completely recovered the starting material. The prepared silyl ethers **2b**−**f** were used for the next step without purification because of their instability for column chromatography. The photosensitized oxygenations were carried out in dichloromethane by irradiation using a halogen lamp under an oxygen atmosphere in the presence of a catalytic amount of tetraphenylporphine and 1 molar equiv of triethyl phosphite or triphenylphosphine at 0 °C. Methanol as a solvent or methylene blue as a sensitizer was not suitable for this reaction. In addition, the presence of the phosphine reducing agents gave the oxygenated products **3** and **4** in 67−95% combined yield, while in their absence, the yields of the combined products were less than 50%.[14] Thus, the intermediary peroxides seemed to be unstable. The results of the photosensitized oxygenation are shown in Scheme 2 and listed in Table 1. In entries 8 and 10 of Table 1, the allenes **3d**,**e**, which resulted from the vinyl hydrogen abstraction at C7, were obtained in 63 and 67% yield along with exomethylene **4d**,**e**, which were produced by the allyl hydrogen abstraction at C11, in 32 and 24% yield from **1d**,**e**, respectively. *Surprisingly, in these cases the vinyl hydrogens were clearly more reactive than the allyl hydrogens toward the singlet oxygen.* The obtained products, except for **3b** and **4b**, were a mixture of diastereoisomers of almost 1:1 ratio, and these would result from the rotational isomers. In Table 1, we additionally noticed the following three points relating to the C9 substituents responsible for the selective allene formation: (1) The C9 carbon atom should be quaternary. (2) The sterically bulky group for R^2 is essentially important. (3) Unsaturated substituent for R^1 may be concerned in the selective allene formation. For the first point, in entry 1, compound **2a** having a tertiary carbon at C9 and a triethylsilyl group of R^2 gave the exomethylene **4a** in nearly four times greater amount than the allene **3a**, whereas the compounds **2b**−**f** having a quaternary C9 carbon and a triethylsilyl group of R^2 predominantly gave the allenes **3b**−**f** rather than the exomethylenes **4b**−**f**. Obviously, the fully substituted carbon atom at C9 clearly affected the allene formation. For the second point, in every R^1 substituent, in particular entries 6−8, the triethylsilyl group of R^2 gave the best selectivity for the allene formation. Bulkiness of the R^2 group clearly affected the selective ene reaction of the C7 vinyl hydrogen against that of the C11 allyl methyl hydrogen. For the third point, comparing the results of entries 3, 5, and 8, where R^1 is methyl, ethyl, and vinyl and R^2 is triethylsilyl in **2**, we noticed that the unsaturated substituent at the C9 position might participate in the selective allene formation. The photosensitized oxygenation of ethynyl derivative **2f** was then examined under the same conditions, and allene **3f** was obtained in 55% yield along with exomethylene **4f** in 27% yield as described in entry 11. Thus, the similar ratio of the products, **3** and **4**, from the photooxygenation of methyl,

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Scheme 2

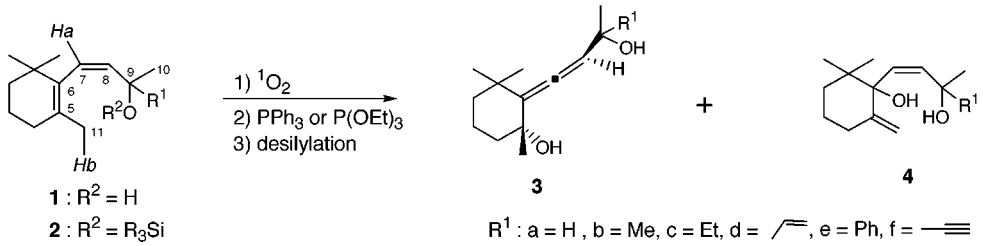


Table 1. Ene Reaction of *β*-Ionol Derivatives with Singlet Oxygen

Entry	Substrates	R^1	R^2	Yield of **3**[a] (%)	Yield of **4**[a] (%)	Products **3** or **4**
1	**2a**	H	$SiEt_3$	17[c]	70[c]	**3a**, **4a**
2	**1b**	Me	H	40	54	**3b**, **4b**
3	**2b**	Me	$SiEt_3$	51[b]	29[b]	**3b**, **4b**
4	**1c**	Et	H	40	44	**3c**, **4c**
5	**2c**	Et	$SiEt_3$	52[b]	15[b]	**3c**, **4c**
6	**1d**		H	37	55	**3d**, **4d**
7	**2d-1**		$SiMe_3$	40[b]	40[b]	**3d**, **4d**
8	**2d-2**		$SiEt_3$	63[b]	32[b]	**3d**, **4d**
9	**1e**	Ph	H	39	51	**3e**, **4e**
10	**2e**	Ph	$SiEt_3$	67[b]	24[b]	**3e**, **4e**
11	**2f**		$SiEt_3$	55[b]	27[b]	**3f**, **4f**

[a] Isolated yield. [b] The yields were for three steps: silylation of the corresponding alcohols followed by photosensitized oxygenation and then desilylation. [c] The yield was for two steps: photosensitized oxygenation and then desilylation.

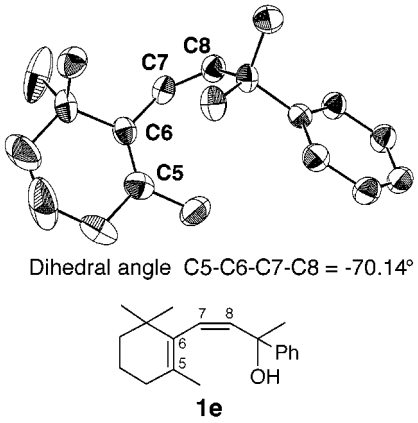


Figure 1. ORTEP drawing of **1e**.

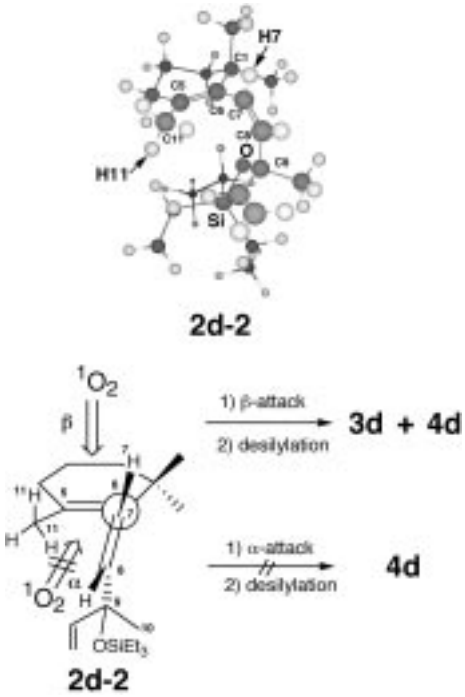


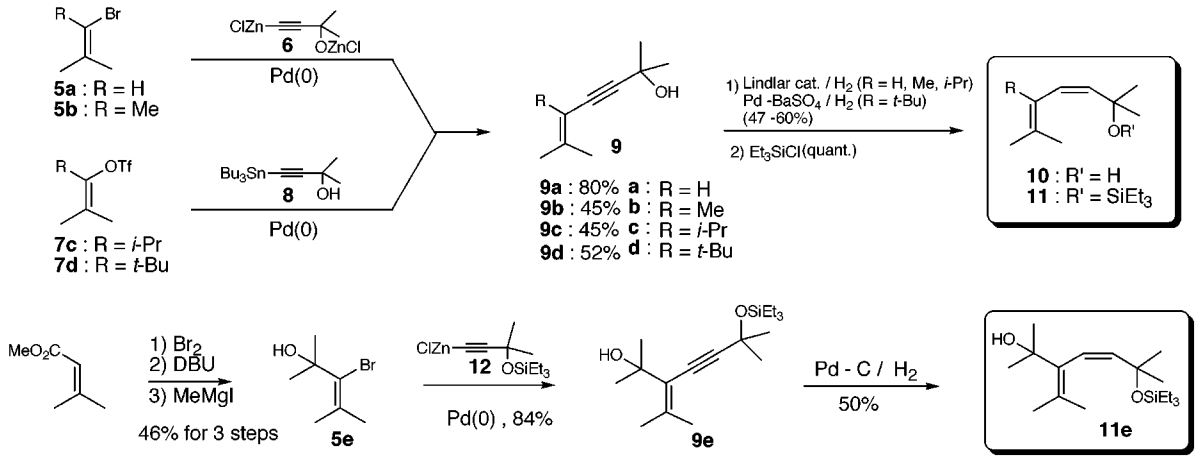
Figure 2. Chem 3D representation of optimized structure of **2d-2** and its pictorial representation.

ethyl, and ethynyl derivatives of R^1 (entries 3, 5, and 11) suggests that some participation of the unsaturated bond at C9 may contribute to the selective allene formation.

To understand the previous observations, we tried to determine the conformation of the *cis*-*β*-ionol derivatives. Fortunately, the conformation of one of the rotational isomers of the phenyl derivative **1e** was successfully determined by X-ray analysis as shown in Figure 1. It was revealed that this molecule entirely exists in an s-cis conformer and that the double bond in the cyclohexene ring makes a torsion angle of about 70° toward the *z*-olefin plane. Thus, this molecule is largely twisted around the C6−C7 single bond. On the basis of the results obtained by X-ray analysis, the most stable conformation of another rotational isomer of **1e** and two rotational isomers of the vinyl derivative **2d-2** were obtained by molecular mechanics and molecular orbital calculations.[15] Their conformations were almost identical and are represented by that of one isomer of **2d-2** as shown in Figure 2. In its pictorial representation, the vinyl hydrogen at C7 is exactly located at the *β*-face, and therefore, the attack of the singlet oxygen from the α-face only abstracts the allyl hydrogen to give the exomethyl-

(15) The geometries were optimized with the CFF91 force field using software packages Insight II 2.1.0 Program. Biosym, Technol., Inc., San Diego, CA, and with semiempirical method (PM3) using the SPARTAN versions 3.1, 4.0 Wavefunction, Inc., Irvine, CA. The conformation of the compounds possessing a full substituent carbon at C9 is represented by that of **2d-2** because their most stable conformations obtained by calculations are almost same as that of **2d-2** except the substituents R^1 and R^2.

Scheme 3



ene compound **4d**. However, the α-face is entirely covered over by the bulky substituents at the C9 position. The results of entries 6−8 in Table 1 clearly demonstrate the remarkable effect of the bulky substituents at the C9 position of compound **2** in comparison with the results of entry 1. Thus, the singlet oxygen attacks **2d-2** selectively from its *β*-face and abstracts the C7 vinyl hydrogen to give the allene **3d** or abstracts the C11 allyl hydrogen to give the exomethylene **4d**, respectively. In the case of free hydroxy compounds **1b**−**e**,[15] the corresponding allene **3** resulting from *β*-face attack of singlet oxygen were produced in moderate yield along with exomethylene **4**. The remarkable hydroxyl group directing effect, which was recently reported by Adam's group in the photosensitized oxygenation of secondary alcohols,[16] was not observed in our tertiary alcohols **1b**−**e**.

The above conformational analysis for **2d-2** made possible the comparison of the relative reactivity between the C7 vinyl hydrogen Ha and the C11 allyl hydrogen Hb toward the singlet oxygen (See Discussion).

Synthesis and Photosensitized Oxygenation of Acyclic Twisted 1,3-Dienes. Next, acyclic substrates **11a**−**e** were designed for the photosensitized oxygenation because the substituent R at the one olefin group could be changed from hydrogen to methyl, isopropyl, and *tert*-butyl, and their 1,3-diene structures would be twisted by the bulky substituent of R. The synthesis of these 1,3-diene derivatives having bulky substituents (R = isopropyl and *tert*-butyl) was somewhat unusual.[17] After several unsuccessful attempts by ionic reactions, we found that their synthesis was achieved by palladium-catalyzed coupling of the appropriate vinyl halides or enol triflates with zinc or stannyl acetylides followed by partial hydrogenation strategy (Scheme 3). Thus, compounds **9a**,**b** were prepared from commercially available vinyl bromides **5a**,**b**, respectively, by reaction with zinc acetylide **6**, which was derived from a lithium derivative of 3-methyl-1-butyn-3-ol and zinc chloride, in the presence of tetrakis(triphenylphosphine)palladium (THF/60 °C: **9a**, 80% yield; **9b**, 45% yield).[18] Compounds **9c**,**d** having bulky substituents were synthesized by the coupling of stannylacetylide **8** with enol triflates **7c**,**d**,[19] which were prepared from the corresponding ketones[20] by reaction with lithium diisopropylamide and *N*-phenyltrifluoroimide, in the presence of the same palladium reagent (THF/rt: **9c**, 45% yield; **9d**, 52% yield).[21] Another eneyne compound **9e** was also synthesized in 84% yield by coupling of vinyl bromide **5e** prepared from methyl 3,3-dimethylacrylate with **12** under the same conditions as those of **5a**,**b**. Partial reduction of the acetylene groups of **9a**−**e** to the corresponding *cis*-olefins by catalytic hydrogenation in hexane reflected the reactivity of their acetylene groups. Thus, **10a**,**b** were obtained with Lindlar catalyst in the presence of a catalytic amount of quinoline (**10a**, 47% yield; **10b**, 49% yield). In the absence of quinoline with Lindlar catalyst, **10c** was obtained (47% yield). The hydrogenation of **9d** with palladium on barium sulfate gave **10d** (60% yield) and of **9e** with palladium charcoal in methanol gave **11e** (90% yield). The *cis*-alcohols obtained were transformed into the corresponding triethylsilyl ethers **11a**−**d** by the usual way in excellent yield, and they were used for photosensitized oxygenation without purification because of their instability for column chromatography. It was noteworthy that the synthesized compounds exhibited characteristic spectroscopic nature. Thus, the maximum absorption values of the electronic spectra of compounds **10b**−**d** were less than 210 nm, whereas that of **10a** was 238 nm.[22] It is evident that 1,3-dienes in the compounds **10b**−**d** are not conjugated, and these molecules are significantly twisted around the central single bond of the 1,3-dienes. The most stable conformations of **11b**−**e** were obtained by molecular mechanics calculations and molecular orbital calculations similar to those of the *cis*-

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(22) It has been well-known that the molar absorptivity in electronic spectra shows the probability of the activation to the excited state of molecules. Therefore, it has been pointed that there is some relationship between the molar absorptivity and the torsion angle of two unsaturated bonds in 1,3-dienes. In the present cases, however, measurement of the exact molar absorptivity of **10b**−**d** was unfortunately very difficult. On the other hand, maximum absorption values of **10a**−**d** show whether the 1,3-dienes in these molecule are conjugated: Hedden, G. D.; Brown, W. G. *J. Am. Chem. Soc.* **1953**, *75*, 3744.

Scheme 4

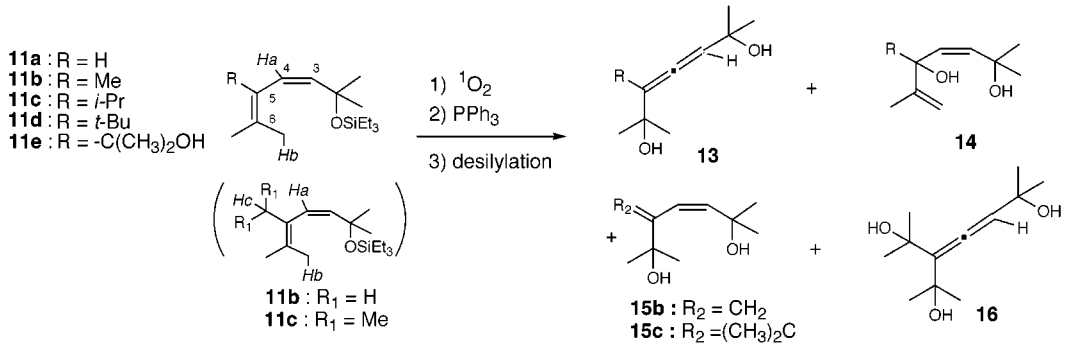

Table 2. Ene Reaction of Acyclic Twisted 1,3-Dienes with Singlet Oxygen

entry	substrates	yield (%) of **13**[a]	yield (%) of **14**[a]	yield (%) of **15**[a,b]	yield (%) of **16**[a,b]
1	**1a**	29[b] (**13a**)	45[b] (**14a**)		
2	**11b**	32[b] (**13b**)	12[b] (**14b**)	42 (**15b**)	
3	**11c**	38[b] (**13c**)	27[b] (**14c**)	8 (**15c**)	17 (**16**)
4	**11d**	75[b] (**13d**)	8[b] (**14d**)		
5	**11e**	74[c] (**13e**)	9[c] (**14e**)		

[a] Isolated yield. [b] The yields were for three steps; silylation of the corresponding alcohols followed by photosensitized oxygenation and then desilylation. [c] The yields were for two steps: photosensitized oxygenation and desilylation.

β-ionol derivatives **2d-2** and **2e**. The results of the calculations also support their significantly twisted structures.

The photosensitized oxygenation of **11a**−**e** was carried out under the same conditions as those of the *cis*-*β*-ionol derivatives. In these compounds, the triethylsilyl group was also essentially important for comparing the relative reactivity between the vinyl hydrogen Ha and the allyl hydrogen Hb of compound **11** in a similar manner as the case of the *cis*-*β*-ionol derivatives. The results are shown in Scheme 4 and Table 2. In the photosensitized oxygenation of compounds **11a**−**e**, the ene reaction of Ha and Hb gave allene **13** and isopropenyl compound **14**, respectively. In the case of **11b**,**c**, the ene reaction of Hc gave compound **15b**,**c**, respectively, and **15c** would produce allene **16** by further oxygenation. Because the silyl ethers of both the 1,3-dienes **11a**−**d** and the oxygenated products were not stable for column chromatography, the yields mentioned were for three steps: silylation, photosensitized oxygenation, and then desilylation. In compounds **11d**,**e** having a bulky quaternary carbon atom in the R group, allenes **13d**,**e** were produced in 75 and 74% yield along with isopropenyl compounds **14d**,**e** in 8 and 9% yield, respectively. In these cases, the abstracted vinyl hydrogen Ha and allyl hydrogen Hb of **11d**,**e** are located at the opposite side on the C5−C6 double bond, and their vinyl hydrogens Ha were abnormally much more reactive than their allyl hydrogens Hb toward the singlet oxygen. On the contrary, compound **11a** produced allene **13a** and isopropenyl compound **14a** in 29 and 45% yield, respectively. These results are well compatible with those of the cyclic *cis*-*β*-ionol derivatives. In addition, photosensitized oxygenation of **11b** (entry 2 in Table 2) gave allene **13b** and allyl alcohol **15b** in 32 and 42% yield, respectively, along with isopropenyl compound **14b** in 12% yield. In this case, the abstracted vinyl hydrogen Ha and allyl hydrogen Hc are located at the same side on the C5−C6 double bond in **11b**, and the allene **13b** and the allyl alcohol **15b** were produced by the ene reaction of the Ha and Hc in **11b**, respectively. Therefore, the relative yields of **13b** and **15b** obviously reflect the relative *inherent reactivity* between the vinyl hydrogen Ha and the allyl hydrogen Hc. *This result was the first example to directly compare the relative inherent reactivity between the vinyl hydrogen and the allyl hydrogen in significantly twisted 1,3-dienes toward a singlet oxygen under the same conditions. It is quite interesting that the vinyl hydrogen Ha shows an extent of inherent reactivity similar to that of the allyl hydrogen Hc toward singlet oxygen in significantly twisted 1,3-dienes.* Next, in the photooxygenation of the compound **11c**, allene **13c**, isopropenyl compound **14c**, diene **15c**, and trihydroxy allene **16** were obtained after desilylation in 38, 27, 8, and 17% yield, respectively. In this case, because compound **16** must be produced from **15c**, the allyl hydrogen Hc was totally abstracted in 25% yield, and hence, the relative reactivity of the vinyl hydrogen Ha and the allyl hydrogen Hc in **11c** is estimated to be 38:25.

Discussion

The ene reaction of a singlet oxygen with alkenes often exhibits a remarkable regio-[23] and stereoselectivity.[24] In particular, the prominent controlling factor for the regioselectivity is classified as the so-called "cis effect",[25] and

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the cis effect selectivity has attracted the mechanistic interest in singlet oxygen oxidation of many organic chemists. Stephenson suggested that the interaction between the LUMO of oxygen and the "pseudobutadiene-like" HOMO of the *cis*-olefin stabilizes the transition state more than that of the *trans*-olefin, leading to the formation of the proper perepoxide intermediate.[26,27] Schulte-Elte and co-workers suggested for cycloalkenes that regioselectivity of the singlet oxygen ene reaction is related to the conformation of the allylic hydrogens with respect to the olefin plane.[28] Recently, other predominant controlling factors for the regioselectivity in the ene reaction have been classified as the "*gem*-directing effect"[23q,29] and "nonbonding large group effect".[30] The former applies to *gem*-substituted olefins with the electron-withdrawing group, and abstraction at the geminal position is predominant. The latter has been recognized in the transition state for the formation of the perepoxide intermediates, and the preferred site of abstraction is geminal to the larger substituent of the double bond. These various mechanistic studies of the ene reaction of singlet oxygen with simple olefins, isotope effect measurements of the tetramethylethylene-d_6 series,[31] 2-butene-d_3 series,[30a] trisubstituted alkene series,[32] and the reaction of *trans*-cyclooctene[14b] have strongly suggested that the reaction proceeds through a polarized intermediate with perepoxide geometry, and the rate-determining step in the ene photooxygenation is the formation of the perepoxide intermediate. Thus, the perepoxide intermediate has been generally accepted now.

All the reported systems, however, in the mechanistic study for ene photooxygenation are relatively simple olefins, and the abstracted hydrogens possess very similar character; they are all allylic hydrogens. The regioselectivity of the singlet oxygen ene reaction has been mainly considered in connection with the substituent effect such as the "cis effect", the "*gem*-directing effect", and the "nonbonding large group effect"; therefore, the consideration on *the inherent reactivity* of each compared hydrogen has not been required. However, in our present system one of the abstracted hydrogens is allyl and the other is vinyl. Generally, the reactivities of these hydrogens are regarded to be quite different. What is the reason why the selective ene reaction of the vinyl hydrogen Ha rather than the allyl hydrogen Hb remarkably proceeds in the significantly twisted 1,3-dienes **2d-2**, **2e**, and **11d**−**e**?

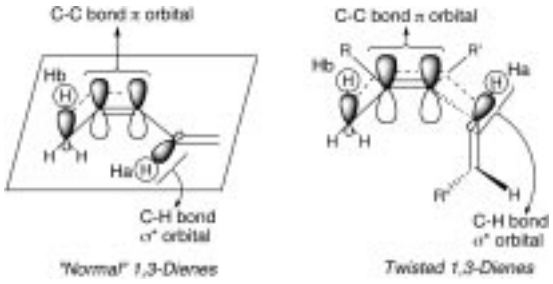

Figure 3. Activation of the vinyl hydrogen in twisted 1,3-dienes by $\sigma^*-\pi$ orbital interaction.

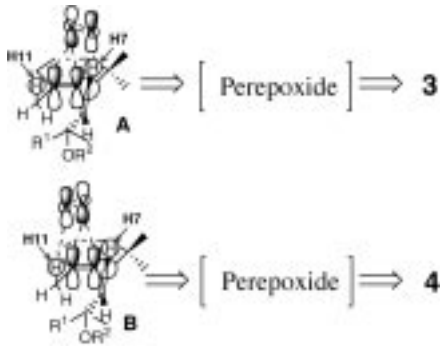

Figure 4. Orbital interaction between singlet oxygen and the twisted 1,3-diene.

Focusing our attention on the conformations of the significantly twisted 1,3-dienes **2d-2**, **2e**, and **11d**−**e**, we can easily notice that the vinyl C−Ha bond is close to perpendicular to another double bond and that its conformation is favorable for the ene reaction with a singlet oxygen. Moreover, such a C−H bond would be parallel to the π orbital of another double bond and may be activated by orbital interaction in a similar manner as an allyl C−H bond as shown in Figure 3. We first considered the relative reactivity between the vinyl hydrogen Ha and the allyl hydrogen Hb in the ground state because of their different reactivities, although the regioselectivity of the singlet oxygen ene reaction should be discussed in the transition states. We planned to compare the relative electron density of the frontier orbitals around the vinyl C−Ha bond and the allyl C−Hb bond in order to investigate the relative inherent reactivity of these hydrogens because it has been well-known that the ene reaction of the singlet oxygen with olefins starts from interactions of the LUMO of the singlet oxygen with the HOMO of olefins as shown in Figure 4.[33] In Figure 4, the structure **A** is a plausible transition state to produce the perepoxide intermediate, which leads to the allene **3**, whereas the transition state **B** is that for the exomethylene **4**.

The relative electron densities of the frontier orbitals of **2d-2** were calculated with HF/6-31G* level by the

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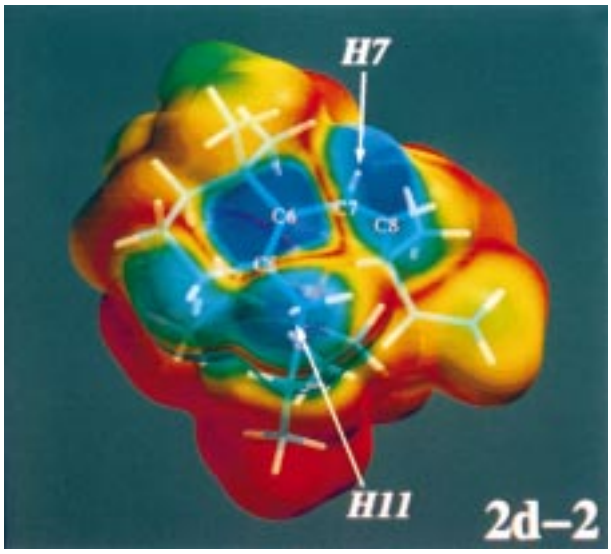

Figure 5. Electron density surface of **2d-2** encoded by the electron density of HOMO, which was calculated at the HF/6-31G* level. Scale: 0.000 e/Å^3 (red) to 0.012 e/Å^3 (blue).

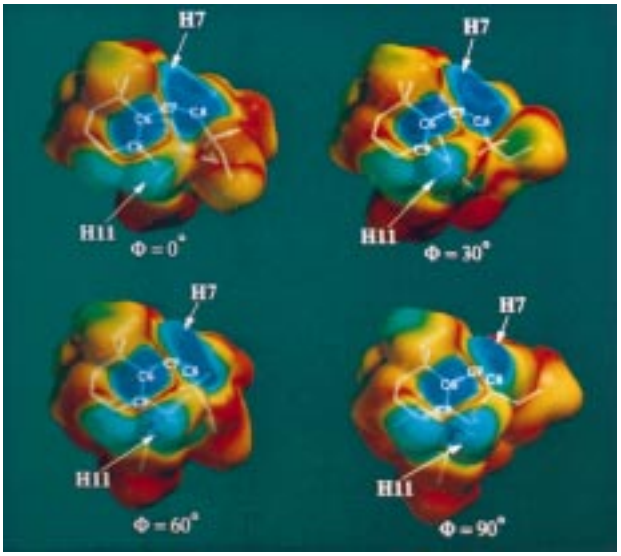

Figure 6. Electron density surface of rotational isomers of **2d-2** encoded by the electron density of HOMO, which was calculated at the HF/6-31G* level. Torsion angles (C5−C6−C7−C8) of the depicted molecules are 0° (top, left), 30° (top, right), 60° (bottom, left), and 90° (bottom, right). Scale: 0.000 e/Å^3 (red) to 0.012 e/Å^3 (blue).

software packages SPARTAN versions 3.1 and 4.0 (Wavefunction, Inc., Irvine CA). The results of the calculations are shown in Figure 5. The depth of the blue color indicates the relative frontier electron density, and the central blue part represents the cyclohexene double bond; also, the upper and lower right parts with the blue color represent the C7 vinyl hydrogen and the C11 allyl hydrogen, respectively. The results show that the frontier electron density around the C7 vinyl hydrogen is slightly richer than that around the C11 allyl hydrogen, and these calculation results are well in accord with the obtained experimental results. Thus, the relative frontier electron densities around these hydrogens have satisfactorily reflected their reactivity toward the singlet oxygen.

Furthermore, we compared the calculated electron densities of the frontier orbitals around both the C7 vinyl hydrogen and the C11 allyl hydrogen of various rotational isomers around the C6−C7 bond of **2d-2**. Those of four representative rotational isomers (dihedral angle $\Phi = 0$, 30, 60, and 90°) are shown in Figure 6. In this picture, the color tone shows the relative frontier electron densities in a manner similar to that of Figure 5. They gradually increased with the enlargement of the torsion angle between the two double bonds, and they were greatest at 90°. These calculated results can be rationalized by considering that the σ^* orbital of the C7 vinyl C−H bond interacts with the π orbital of the C5−C6 double bond in significantly twisted **2d-2**, as shown in Figure 3. *Thus, the vinyl hydrogen in a significantly twisted 1,3-diene would be highly activated by the large σ^*−π orbital interaction between the vinyl C−H bond and another double bond.* To the best of our knowledge, this is the first example of these interactions in 1,3-dienes.

The previous calculation results revealed that the vinyl hydrogen in significantly twisted 1,3-dienes bears a close reactivity to the allyl hydrogen, and the obtained novel experimental results in **11b** of a significantly twisted 1,3-diene also show that the inherent reactivity of the vinyl hydrogen Ha is close to that of the allyl hydrogen Hc as previously described. Now, we can discuss the regioselectivity of the ene reaction of significantly twisted 1,3-dienes by the "nonbonding large group effect" because

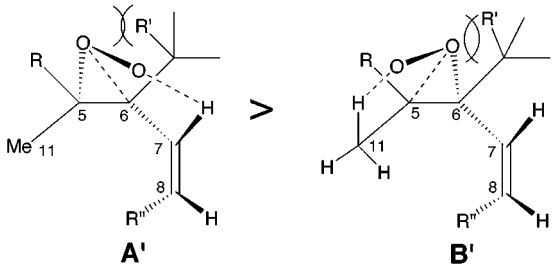

Figure 7. Nonbonding large group effect in **2d-2**, **2e**, and **11d**−**e**.

this idea is applicable for such hydrogens that possess close reactivity to one another. Thus, if the significantly twisted vinyl group could be regarded as a common alkyl group, the results obtained from **2d-2**, **2e**, and **11d**−**e** are readily understandable by the idea of the "nonbonding large group effect" as shown in Figure 7. Obviously, the intermediate A′ is more favorable than B′ because of the smaller nonbonding interactions. In the case of the compound **11c** having a propyl substituent, however, the amount of the ene reaction product of the vinyl hydrogen Ha, compound **13c**, was only 1.4 times greater than that of the allyl hydrogen Hb, compound **14c**. In this case, the "nonbonding large group effect" would not be applicable.

The results of Table 2 also led us to the following considerations: In compound **11c**, the isopropyl hydrogen Hc should be less reactive to photooxygenation because its calculated most stable conformation shows that the isopropyl C−Hc bond is placed on the coplanar with the C5−C6 double bond and the rotation of Hc toward the perpendicular position from the coplanar is necessary for the ene reaction of this hydrogen with the singlet oxygen. In addition, it had been reported that the photooxygenation of 2,4-dimethyl-2-pentene (**17**) in Figure 8 gave two products, which were produced by the abstraction of the C1 primary hydrogen and the C4 tertiary hydrogen in a ratio of 93:7.[34] Contrary to these results, in the case of

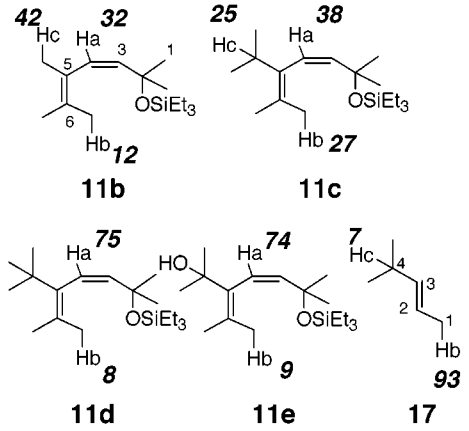

Figure 8. Abstracted hydrogens of acyclic systems; the numbers represent abstracted proportion.

11c, which has the same partial structure as **17**, the isopropyl hydrogen Hc was totally abstracted in 25% yield (**15c** plus **16**), whose value was nearly the same as that of the Hb abstraction product (27% yield) as summarized in the results of the photooxygenation of **11** in Figure 8. This result may be attributable to the characteristic nature of the significantly twisted vinyl group. The characteristic substituent effect of the significantly twisted vinyl group is also remarkable in the methyl-substituted twisted 1,3-diene **11b**. The ratio between the C5 and the C6 hydroxy products from this compound was 12:74% (32% of **13b** plus 42% of **15b**). Thus, the twisted vinyl substituent at the double bond may prevent the attack to the C5 sp^2 carbon of the singlet oxygen.

In conclusion, the remarkable regioselectivity of the vinyl hydrogen ene reaction of the significantly twisted 1,3-dienes with a singlet oxygen would be attributed to the following three factors: (1) large $\sigma^*-\pi$ orbital interaction between the vinyl C−H bond and another double bond, (2) the "nonbonding large group effect", and (3) some special electronic interactions involving the perpendicular π orbital of the significantly twisted double bond with the singlet oxygen.

Experimental Section

All commercially available reagents were used without further purification. All solvents were used after distillation. Tetrahydrofuran, diethyl ether, and hexane were refluxed over and distilled from sodium. Dichloromethane and diisopropylamine were refluxed over and distilled from CaH_2. Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure. Methanol was refluxed over and distilled from magnesium. Preparative separation was usually performed by column chromatography on silica gel (FUJI Silysia Ltd., BW-200 and BW-300). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, and chemical shifts were represented as δ values relative to internal standard TMS. Melting points were uncorrected.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-1-buten-3-ol (1b). To a THF (50 mL) solution of *cis*-β-ionone 2.0 g (10.4 mmol), which was prepared by the reported procedure,[12] was added a 2.0 M solution of methylmagnesium iodide in ether prepared from methyl iodide (6.18 mL, 104 mmol), magnesium turnings (2.52 g, 98.8 mmol), and ether (44 mL) at 65 °C until the starting material was completely consumed (2−4 equiv of Grignard reagent was required). After the reaction mixture was stirred at 65 °C for 15 min, saturated aqueous NH_4Cl solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (3% ether in hexane) gave **1b** (1.65 g, 76%): IR (neat, cm^{-1}) 3544, 1464, 1378, 1362; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (1H, brd, J = 12.4 Hz), 5.49 (1H, d, J = 12.4 Hz), 3.42 (1H, s), 1.98 (2H, m), 1.72 (3H, s), 1.62−1.43 (4H, m), 1.29 (3H, s), 1.26 (3H, s), 1.05 (3H, s), 1.03 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.22, 136.49, 130.15, 122.45, 73.31, 38.90, 34.43, 31.87, 30.67, 29.28, 28.94, 28.58, 22.34, 19.00; EI HRMS *m/e* calcd for $C_{14}H_{24}O$ (M^+) 208.1821, found 208.1828.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-1-penten-3-ol (1c). To a THF (115 mL) solution of *cis*-β-ionone 5.05 g (26.2 mmol) and tetra-*n*-butylammonium iodide 11.0 g (34.1 mmol) was added ethylmagnesium bromide (3.0 M in ether, 18 mL, 52 mmol) at 65 °C. After the reaction mixture was stirred at 65 °C for 3 min, saturated aqueous NH_4Cl solution was added and the resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (from 0.7% to 1% ethyl acetate in hexane) gave **1c** (2.86 g, 49%) as a mixture of conformational isomers: IR (neat, cm^{-1}) 3544, 1464, 1376, 1364; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79−5.82 (1H, m), 5.51 ($^1/_2$ × 1H, d, J = 12.7 Hz), 5.46 ($^1/_2$ × 1H, d, J = 12.7 Hz), 3.37 ($^1/_2$ × 1H, s), 3.33 ($^1/_2$ × 1H, s), 1.95−2.00 (2H, m), 1.75 ($^1/_2$ × 13H, s), 1.72 ($^1/_2$ × 3H, s), 1.43−1.64 (6H, m), 1.25 ($^1/_2$ × 3H, s), 1.21 ($^1/_2$ × 3H, s), 1.08 ($^1/_2$ × 3H, s), 1.06 ($^1/_2$ × 3H, s), 1.04 ($^1/_2$ × 3H, s), 1.03 ($^1/_2$ × 3H, s), 0.94 ($^1/_2$ × 3H, t, J = 7.8 Hz), 0.92 ($^1/_2$ × 3H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.72, 137.55, 136.59, 136.54, 130.53, 130.26, 123.47, 123.32, 75.57, 75.42, 39.03, 39.00, 36.33, 35.29, 34.58, 31.97, 31.93, 29.18, 29.08, 28.69, 28.67, 27.33, 26.44, 22.65, 19.01, 18.98, 8.58, 8.50; EI HRMS *m/e* calcd for $C_{15}H_{26}O_1$ (M^+) 222.1977, found 222.1992.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-1,4-pentadien-3-ol (1d). To a THF (80 mL) solution of *cis*-β-ionone (3.0 g, 15.8 mmol) was added a 2.0 M solution of vinylmagnesium bromide in THF prepared from vinyl bromide (8.70 mL, 123 mmol), magnesium turnings (1.65 g, 67.9 mmol), and THF (33 mL) at 65 °C until the starting material was completely consumed (2−4 equiv of Grignard reagent was required). After the reaction mixture was stirred at 65 °C for 15 min, saturated aqueous NH_4Cl solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (2% ether in hexane) gave **1d** (2.69 g, 78%) as a mixture of conformational isomers: IR (neat, cm^{-1}) 3528, 1655, 1462, 1364; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 ($^5/_{13}$ × 1H, dd, J = 17.0, 10.5 Hz), 5.90 ($^8/_{13}$ × 1H, dd, J = 17.0, 10.5 Hz), 5.82 (1H, d, J = 11.5 Hz), 5.52 ($^8/_{13}$ × 1H, d, J = 11.5 Hz), 5.50 ($^5/_{13}$ × 1H, d, J = 11.5 Hz), 5.22 ($^5/_{13}$ × 1H, J = 17.0, 1.2 Hz), 5.21 ($^8/_{13}$ × 1H, dd, J = 17.0, 1.5 Hz), 4.99 ($^8/_{13}$ × 1H, dd, J = 10.5, 1.5 Hz), 4.96 ($^5/_{13}$ × 1H, dd, J = 10.5, 1.5 Hz), 3.57 ($^5/_{13}$ × 1H, s), 3.46 ($^8/_{13}$ × 1H, s), 1.98 (2H, m), 1.73 ($^5/_{13}$ × 3H, s), 1.52 ($^8/_{13}$ × 3H, s), 1.47−1.73 (4H, m), 1.35 ($^5/_{13}$ × 3H, s), 1.31 ($^8/_{13}$ × 3H, s), 1.08 ($^8/_{13}$ × 3H, s), 1.05 ($^8/_{13}$ × 3H, s), 1.02 ($^5/_{13}$ × 3H, s), 1.01 ($^5/_{13}$ × 3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.15, 142.79, 136.61, 135.99, 135.64, 135.31, 130.83, 130.30, 123.61, 123.34, 110.85, 110.73, 75.74, 75.62, 38.91, 34.86, 34.42, 31.96, 31.90, 29.38, 29.02, 28.94, 28.64, 28.51, 27.80, 22.40, 22.36, 19.02; EI HRMS *m/e* calcd for $C_{15}H_{24}O$ (M^+) 220.1821, found 220.1820.

(1*Z*)-3-Phenyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-1-buten-3-ol (1e). To a THF (4 mL) solution of *cis*-β-ionone 256 mg (1.33 mmol) was added a 1.8 M solution of phenylmagnesium bromide in ether prepared from bromobenzene (1.29 mL, 12.4 mmol), magnesium turnings (328 mg, 13.5 mmol), and ether (7 mL) at 65 °C until the starting material was completely consumed (2−4 equiv of Grignard reagent was required). After the reaction mixture was stirred at 65 °C for 2 h, saturated aqueous NH_4Cl solution was added, and the

(34) Wasserman, H. H.; Murray, R. W. Singlet Oxygen; Academic Press Inc.: New York, 1979; p 342.

resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (1% ethyl acetate in hexane) gave **1e** (277 mg, 77%) as a mixture of conformational isomers: mp 57.0−57.5 °C; IR (KBr disk, cm^{-1}) 3500, 1958, 1600, 1446, 1334, 1210; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50−7.51 (2H, m), 7.30−7.33 (2H, m), 7.18−7.22 (1H, m), 6.03 ($^2/_3 \times$ 1H, d, J = 12.4 Hz), 5.87 ($^2/_3 \times$ 1H, d, J = 12.7 Hz), 5.86 ($^1/_3 \times$ 1H, d, J = 13.0 Hz), 5.83 ($^1/_3 \times$ 1H, d, J = 12.9 Hz), 4.09 ($^1/_3 \times$ 1H, s), 3.93 ($^2/_3 \times$ 1H, s), 1.80−2.04 (2H, m), 1.82 ($^1/_3 \times$ 3H, s), 1.30−1.66 (4H, m), 1.64 ($^1/_3 \times$ 3H, s), 1.61 ($^2/_3 \times$ 3H, s), 1.29 ($^2/_3 \times$ 3H, s), 1.15 ($^2/_3 \times$ 3H, s), 1.08 ($^2/_3 \times$ 3H, s), 0.97 (1/3 × 3H, s), 0.89 ($^1/_3 \times$ 3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.19, 147.77, 137.47, 136.81, 136.68, 136.15, 131.23, 131.03, 128.00, 127.92, 126.26, 126.22, 124.85, 124.72, 123.30, 123.15, 76.37, 38.97, 38.93, 34.97, 34.48, 32.80, 31.98, 30.40, 29.15, 28.90, 28.66, 28.53, 22.52, 22.02, 18.98; EI HRMS *m/e* calcd for $C_{19}H_{26}O$ (M^+) 270.1977, found 270.1974.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-1-penten-4-yn-3-ol (1f). To a THF (8 mL) solution of *cis*-β-ionone (300 mg, 1.56 mmol) was added a 0.5 M solution of ethynylmagnesium chloride in THF prepared from acetylene and *n*-butylmagnesium chloride (magnesium turnings (2.43 g 100 mmol), *n*-butyl chloride (10.7 mL, 100 mmol), and THF (200 mL) at 65 °C until the starting material was completely consumed (2−4 equiv of Grignard reagent was required). After the reaction mixture was stirred at 65 °C for 2 h, saturated aqueous NH_4Cl solution was added, and the resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (0.7% ethyl acetate in hexane) gave **1f** (289 mg, 85%) as a mixture of conformational isomers: IR (neat, cm^{-1}) 3508, 3312, 2936, 2872, 1464, 1364, 1260, 1154, 1058; ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 (1H, d, J = 12.2 Hz), 5.78 ($^5/_{18} \times$ 1H, d, J = 12.2 Hz), 5.56 ($^{13}/_{18} \times$ 1H, d, J = 12.0 Hz), 3.93 ($^{13}/_{18} \times$ 1H, s), 3.79 ($^5/_{18} \times$ 1H, s), 2.49 ($^{13}/_{18} \times$ 1H, s), 2.46 ($^5/_{18} \times$ 1H, s), 2.02−1.94 (2H, m), 1.80 ($^{13}/_{18} \times$ 3H, s), 1.69 ($^5/_{18} \times$ 3H, s), 1.57 ($^5/_{18} \times$ 3H, s), 1.55 ($^{13}/_{18} \times$ 3H, s), 1.67−1.42 (4H, m), 1.05 (3H, s), 1.02 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) 136.31, 134.87, 133.88, 133.79, 131.52, 130.86, 125.32, 124.62, 87.12, 86.19, 71.25, 70.93, 69.19, 68.86, 38.83, 38.76, 34.26, 31.93, 31.83, 31.10, 30.95, 30.60, 30.38, 28.97, 28.67, 28.60, 28.40, 22.30, 22.06, 18.94; EI HRMS *m/e* calcd for $C_{15}H_{22}O$ (M^+) 218.1665, found 218.1682.

(1*Z*)-3-Triethylsiloxy-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-1-butene (2a). To a solution of **1a** (3.0 g, 15.4 mmol), 4-(dimethylamino)pyridine (188 mg, 1.54 mmol), and triethylamine (3.2 mL, 23.0 mmol) in DMF (80 mL) was added triethylsilyl chloride (3.1 mL, 18.5 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was poured into H_2O, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (3% triethylamine in hexane) gave a colorless oil. The oil was evacuated in vacuo (1−2 mmHg) at 80 °C for 3 days in order to remove triethylsiloxane to give pure silyl ether **2a** (3.6 g, 73%): IR (neat, cm^{-1}) 1418, 1366, 1238, 1112, 1070; ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (1H, ddtq, J = 11.5, 2.4, 1.2, 0.7 Hz), 5.51 (1H, dd, J = 11.5, 8.7 Hz), 4.37 (1H, ddq, J = 8.7, 6.4, 0.7 Hz), 1.95 (2H, t, J = 6.3 Hz), 1.64−1.59 (2H, m), 1.57 (3H, brs), 1.46−1.43 (2H, m), 1.20 (3H, d, J = 6.4 Hz), 0.99 (6H, s), 0.94 (9H, t, J = 7.2 Hz), 0.59 (6H, q, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.33, 135.20, 127.98, 126.54, 65.92, 39.15, 34.20, 31.94, 28.78, 28.59, 23.89, 21.96, 19.29, 6.95, 5.49; EI HRMS *m/e* calcd for $C_{19}H_{36}OSi$ (M^+) 308.2526, found 308.2545.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-3-triethylsiloxy-1-butene (2b). To a solution of **1b** (244 mg, 1.2 mmol), 4-(dimethylamino)pyridine (14 mg, 0.15 mmol), and triethylamine (0.49 mL, 3.5 mmol) in DMF (8 mL) was added triethylsilyl chloride (0.51 mL, 3.0 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 18.5 h, saturated aqueous $NaHCO_3$ solution was added, and the resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **2b**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-3-triethylsiloxy-1-pentene (2c). To a solution of **1c** (303 mg, 1.4 mmol), 4-(dimethylamino)pyridine (50 mg, 0.41 mmol), and triethylamine (0.78 mL, 5.5 mmol) in DMF (7 mL) was added triethylsilyl chloride (0.82 mL, 4.9 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 66 h, saturated aqueous $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **2c**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-3-trimethylsiloxy-1,4-pentadiene (2d-1). To a solution of **1d** (308 mg, 1.4 mmol), 4-(dimethylamino)pyridine (17 mg, 0.14 mmol), and triethylamine (0.48 mL, 3.5 mmol) in dichloromethane (7 mL) was added trimethylsilyl chloride (0.41 mL, 3.2 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 4 h, saturated aqueous $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **2d-1**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-3-triethylsiloxy-1,4-pentadiene (2d-2). To a solution of **1d** (308 mg, 1.4 mmol), 4-(dimethylamino)pyridine (17 mg, 0.14 mmol), and triethylamine (0.78 mL, 5.6 mmol) in DMF (7 mL) was added triethylsilyl chloride (0.84 mL, 5.0 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 5 days, saturated aqueous $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **2d-2**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

(1*Z*)-3-Phenyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-3-(triethylsiloxy)-1-butene (2e). To a solution of **1e** (299 mg, 1.1 mmol), 4-(dimethylamino)pyridine (14 mg, 0.11 mmol), and triethylamine (0.61 mL, 4.4 mmol) in DMF (6 mL) was added triethylsilyl chloride (0.67 mL, 4.0 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 19.5 h, saturated aqueous $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **2e**, which was used for photosensitized oxygenation without any purification because of their instability for column chromatography.

(1*Z*)-3-Methyl-1-(2′,2′,6′-trimethylcyclohex-1′-enyl)-3-triethylsiloxy-1-penten-4-yne (2f). To a solution of **1f** (300 mg, 1.4 mmol), 4-(dimethylamino)pyridine (50 mg, 0.41 mmol), and triethylamine (0.76 mL, 5.5 mmol) in DMF (7 mL) was added triethylsilyl chloride (0.83 mL, 5.0 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 16 h, saturated aqueous $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried

over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **2f**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

General Procedure for Photosensitized Oxygenation. To a solution of *cis*-*β*-ionol derivatives **1** or **2** (1−2 mmol) in dichloromethane (8 mL) were added 1 equiv of triphenylphosphine or triethyl phosphite and a catalytic amount of 5,10,15,20-tetraphenyl-21*H*, 23*H*-porphine (TPP), and the solution was cooled to 0 °C. The mixture was irradiated with a Riko-HGA-300A Halogen lamp under oxygen atmosphere, and the reaction was monitored by TLC. After the starting material was consumed, the reaction mixture was flushed with argon. To complete the reduction of the intermediary peroxides, another 1 equiv of triphenylphosphine or triethyl phosphite was added, and the mixture was stirred until the peroxides were completely consumed. It was concentrated in vacuo to give crude products that were purified by column chromatography on silica gel to yield the pure allene **3** and exomethylene **4**.

General Procedure of Desilylation. In the case of silyl ether, the following procedures were performed in addition to those above. To a THF solution of the mixture, which was treated with a reducing agent, was added 1−2 equiv of *n*-tetrabutylammonium fluoride (TBAF) at room temperature at 0 °C, and the mixture was stirred at the same temperature until the starting material was consumed. It took overnight for the desilylation of triethylsilyl ether. The reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution and was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (from 17% to 75% ether in hexane) gave pure oxygenated products.

Photosensitized Oxygenation of 2a. Following the general procedure of photosensitized oxygenation, **2a** (500 mg, 1.56 mmol), TPP (9 mg, 0.015 mmol), and triphenylphosphine (409 mg, 1.56 mmol, and after oxidation 409 mg, 1.56 mmol) in dichloromethane (10 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (450 mg, 1.72 mmol) in THF (10 mL) gave **3a** (56 mg, 17% for two steps) and **4a** (263 mg, 80% for two steps) as a nearly 1:1 mixture of diastereoisomers, respectively, after the usual workup and column chromatography (from 17% to 50% ethyl acetate in hexane). In addition, exomethylene **4a** contained about 10% unidentified products that could not be removed by column chromatography.

1-(2′-Hydroxy-2′,6′,6′-trimethylcyclohexylidene)-1-buten-3-ol (3a) (mixture of diastereoisomers): IR (neat, cm^{-1}) 3368, 1958, 1456, 1374, 1072, 1024; ^1H NMR (400 MHz, $CDCl_3$) δ 5.43 ($^1/_2 \times$ 1H, d, J = 5.4 Hz), 5.40 ($^1/_2 \times$ 1H, d, J = 6.1 Hz), 4.34−4.28 (1H, m), 1.94−1.72 (3H, m), 1.58−1.48 (3H, m), 1.37 ($^1/_2 \times$ 1H, s), 1.36 ($^1/_2 \times$ 1H, s), 1.29 (1H, d, J = 6.3 Hz), 1.29 ($^1/_2 \times$ 3H, s), 1.21 ($^1/_2 \times$ 3H, s), 1.07 ($^1/_2 \times$ 3H, s), 1.06 ($^1/_2 \times$ 3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.98, 196.89, 120.42, 120.16, 100.04, 70.57, 66.56, 66.16, 40.50, 40.42, 40.33, 40.29, 34.05, 34.02, 31.32, 31.27, 31.01, 30.89, 29.53, 29.43, 23.24, 23.16, 18.48, 18.42; EI HRMS *m/e* calcd for $C_{13}H_{22}O_2$ (M^+) 210.1614, found 210.1631.

(1*Z*)-1-(1′-Hydroxy-2′-methylidene-6′,6′-dimethylcyclohexyl)-1-buten-3-ol (4a) (mixture of diastereoisomers): IR (neat, cm^{-1}) 3372, 1644, 1456, 1368, 1094, 1046; ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 ($^1/_2 \times$ 1H, dd, J = 12.2, 1.5 Hz), 5.82 ($^1/_2 \times$ 1H, dd, J = 12.4, 1.5 Hz), 5.56 ($^1/_2 \times$ 1H, dd, J = 12.2, 7.3 Hz), 5.53 ($^1/_2 \times$ 1H, dd, J = 12.4, 6.6 Hz), 5.00 ($^1/_2 \times$ 1H, dd, J = 1.7, 1.0 Hz), 4.98 ($^1/_2 \times$ 1H, dd, J = 1.7, 0.7 Hz), 4.94−4.81 (2H, m), 2.45−2.12 (2H, m), 1.62−1.46 (4H, m), 1.27 ($^1/_2 \times$ 3H, d, J = 6.6 Hz), 1.22 ($^1/_2 \times$ 3H, d, J = 6.3 Hz), 0.97 ($^1/_2 \times$ 3H, s), 0.96 ($^1/_2 \times$ 3H, s), 0.93 ($^1/_2 \times$ 3H, s), 0.91 ($^1/_2 \times$ 3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.35, 151.23, 136.29, 134.99, 132.87, 132.37, 108.11, 107.36, 81.31, 80.40, 64.10, 63.05, 37.17, 37.10, 33.32, 32.89, 24.15, 23.83, 23.45, 22.77, 22.70, 22.62, 22.41, 22.01; EI HRMS *m/e* calcd for $C_{13}H_{22}O_2$ (M^+) 210.1614, found 210.1631.

Photosensitized Oxygenation of 1b. Following the general procedure of photosensitized oxygenation, **1b** (302 mg, 1.45 mmol), a catalytic amount of TPP, and triphenylphosphine (380 mg, 1.45 mmol, and after oxidation 760 mg, and 2.90 mmol) in dichloromethane (8 mL) gave, after the usual workup and column chromatography (from 25% to 75% ether in hexane), **3b** (129 mg, 40%) and **4b** (175 mg, 54%).

Photosensitized Oxygenation of 2b. Following the general procedure of photosensitized oxygenation, **2b** (ca. 1.20 mmol), a catalytic amount of TPP, and triphenylphosphine (316 mg, 1.20 mmol, and after oxidation 316 mg, 1.20 mmol) in dichloromethane (7 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (315 mg, 1.20 mmol) in THF (7 mL) gave **3b** (138 mg, 51% for three steps) and **4b** (79 mg, 29% for three steps), after the usual workup and column chromatography (from 25% to 75% ether in hexane).

1-(2′-Hydroxy-2′,6′,6′-trimethylcyclohexylidene)-3-methyl-1-buten-3-ol (3b): mp 94.0−94.5 °C; IR (KBr disk, cm^{-1}) 3452, 1965, 1655, 1452, 1396, 1374, 1258, 1166, 1100; ^1H NMR (400 MHz, $CDCl_3$) δ 5.45 (1H, s), 1.77−1.98 (3H, m), 1.50−1.56 (3H, s), 1.36 (3H, s), 1.34 (6H, s), 1.23 (3H, s), 1.07 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.51, 120.76, 104.21, 70.66, 69.95, 40.58, 40.49, 34.24, 31.41, 31.06, 29.91, 29.83, 29.44, 18.48. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.47; H, 10.76.

(1*Z*)-1-(1′-Hydroxy-2′-methylidene-6′,6′-dimethylcyclohexyl)-3-methyl-1-buten-3-ol (4b): mp 59.0−60.0 °C; IR (KBr disk, cm^{-1}) 3350, 3220, 1646, 1380, 1172, 1120; ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (1H, d, J = 13.4 Hz), 5.53 (1H, d, J = 13.2 Hz), 4.92 (1H, brd, J = 2.0 Hz), 4.84 (1H, m), 2.47 (1H, brdt, J = 13.1, 6.1 Hz), 2.16 (1H, brdt, J = 13.1, 6.8 Hz), 1.56−1.68 (4H, m), 1.40 (3H, s), 1.36 (3H, s), 0.92 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.50, 137.29, 130.93, 107.85, 79.42, 71.94, 39.72, 36.84, 32.80, 31.74, 30.06, 24.00, 23.20, 23.09; EI HRMS *m/e* calcd for $C_{14}H_{24}O_2$ (M^+) 224.1770, found 224.1776.

Photosensitized Oxygenation of 1c. Following the general procedure of photosensitized oxygenation, **1c** (311 mg, 1.40 mmol), a catalytic amount of TPP, and triphenylphosphine (367 mg, 1.40 mmol, and after oxidation 417 mg, 1.59 mmol) in dichloromethane (7 mL) gave **3c** (64 mg, 19%), its diastereoisomer (70 mg, 21%), and **4c** (147 mg, 44%) as a nearly 1:1 mixture of diastereoisomers, after the usual workup and column chromatography (from 17% to 71% ether in hexane).

Photosensitized Oxygenation of 2c. Following the general procedure of photosensitized oxygenation, **2c** (ca. 1.36 mmol), a catalytic amount of TPP, and triphenylphosphine (360 mg, 1.37 mmol, and after oxidation 360 mg, 1.37 mmol) in dichloromethane (7 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (356 mg, 1.36 mmol) in THF (7 mL) gave **3c** (87 mg, 26% for three steps), its diastereoisomer (87 mg, 26% for three steps), and **4c** (117 mg, 15% for three steps) as a nearly 1:1 mixture of diastereoisomers, after workup and column chromatography (from 17% to 71% ether in hexane). In addition, **4c** contained triethylsilanol, which could not be removed by column chromatography. The yield of **4c** was calculated on the integral basis of the values of **4c** and triethylsilanol in the NMR spectrum.

1-(2′-Hydroxy-2′,6′,6′-trimethylcyclohexylidene)-3-methyl-1-penten-3-ol (3c): mp 113.5−114.5 °C; IR (KBr disk, cm^{-1}) 3408, 3320, 1964, 1454, 1364, 1120; ^1H NMR (400 MHz, $CDCl_3$) δ 5.39 (1H, s), 1.49−1.92 (8H, m), 1.36 (3H, s), 1.27 (3H, s), 1.24 (3H, s), 1.08 (3H, s), 0.95 (3H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.65, 121.05, 103.36, 72.10, 70.63, 40.48, 40.46, 35.55, 34.14, 31.64, 29.39, 27.19, 18.40, 8.61. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.53; H, 10.87. **Diastereoisomer:** mp 89.0−92.5 °C; IR (KBr disk, cm^{-1}) 3344, 1964, 1458, 1374, 1136; ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 (1H, s), 1.27−1.87 (8H, m), 1.39 (3H, s), 1.22 (3H, s), 1.21 (3H, s), 1.08 (3H, s), 0.94 (3H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.72, 121.12, 103.42, 72.20, 70.64, 40.64,

40.37, 35.54, 34.25, 31.07, 30.95, 29.83, 26.83, 18.60, 8.65. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.63; H, 11.08.

(1*Z*)-1-(1′-Hydroxy-2′-methylidene-6′,6′-dimethylcyclohexyl)-3-methyl-1-penten-3-ol (4c) (mixture of diastereoisomers): IR (KBr disk, cm^{-1}) 3340, 1640, 1462, 1382; ^1H NMR (400 MHz, $CDCl_3$) δ 5.81 ($^1/_2 \times$ 1H, d, J = 13.4 Hz), 5.79 ($^1/_2 \times$ 1H, d, J = 13.4 Hz), 5.45 ($^1/_2 \times$ 1H, d, J = 13.4 Hz), 5.44 ($^1/_2 \times$ 1H, d, J = 13.4 Hz), 4.96 ($^1/_2 \times$ 1H, d, J = 2.2 Hz), 4.93 ($^1/_2 \times$ 1H, d, J = 2.2 Hz), 4.84 ($^1/_2 \times$ 1H, m), 4.83 ($^1/_2 \times$ 1H, m), 2.47 (1H, brdt, J = 12.8, 6.4 Hz), 2.16 ($^1/_2 \times$ 1H, brdt, J = 13.2, 7.8 Hz), 2.14 ($^1/_2 \times$ 1H, brdt, J = 13.9, 7.1 Hz), 1.43−1.75 (6H, m), 1.35 ($^1/_2 \times$ 3H, s), 1.29 ($^1/_2 \times$ 3H, s), 0.93−0.97 (6H, m), 0.92 ($^1/_2 \times$ 3H, t, J = 7.6 Hz), 0.88 ($^1/_2 \times$ 3H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.15, 154.54, 136.39, 132.20, 131.48, 107.81, 107.62, 79.09, 74.57, 74.44, 39.72, 39.71, 39.66, 36.84, 36.77, 23.23, 23.15, 23.14, 23.10, 8.46, 8.04, 8.03; EI HRMS *m/e* calcd for $C_{15}H_{26}O_2$ (M^+) 238.1926, found 238.1932.

Photosensitized Oxygenation of 1d. Following the general procedure of photosensitized oxygenation, **1d** (304 mg, 1.38 mmol), a catalytic amount of TPP, and triethyl phosphite (0.47 mL, 2.76 mmol) in dichloromethane (7 mL) gave, after the usual workup and column chromatography (from 17% to 67% ether in hexane), **3d** (120 mg, 37%) and **4d** (179 mg, 55%) as a nearly 1:1 mixture of diastereoisomers, respectively.

Photosensitized Oxygenation of 2d-1. Following the general procedure of photosensitized oxygenation, **2d** (ca. 1.38 mmol), a catalytic amount of TPP, and triethyl phosphite (0.24 mL and after oxidation 0.24 mL, 1.38 and 1.38 mmol) in dichloromethane (7 mL) gave crude oxygenated products. To a THF (7 mL) solution of the oxygenated product was added two drops of 1 N HCl at 0 °C. After the reaction mixture was stirred at 0 °C for 1 h, saturated aqueous $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (from 25% to 67% ether in hexane) gave **3d** (130 mg, 40% for three steps) and **4d** (129 mg, 40% for three steps) as a mixture of diastereoisomers, respectively.

Photosensitized Oxygenation of 2d-2. Following the general procedure of photosensitized oxygenation, **2d-2** (ca. 1.40 mmol), a catalytic amount of TPP, and triethyl phosphite (0.49 mL, 2.85 mmol, and after oxidation 0.73 mL, 4.25 mmol) in dichloromethane (11 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (743 mg, 2.84 mmol) in THF (11 mL) gave **3d** (209 mg, 63% for three steps) and **4d** (165 mg, 32% for three steps) as a nearly 1:1 mixture of diastereoisomers, respectively, after the usual workup and column chromatography (from 25% to 67% ether in hexane). In addition, **4d** contained triethylsilanol, which could not be removed by column chromatography. The yield of **4d** was calculated on the basis of the integral values of **4d** and triethylsilanol in the NMR spectrum.

1-(2′-Hydroxy-2′,6′,6′-trimethylcyclohexylidene)-3-methyl-1,4-pentadien-3-ol (3d): mp 93.5−95.5 °C; IR (KBr disk, cm^{-1}) 3424, 1966, 1454, 1364, 1092; ^1H NMR (400 MHz, $CDCl_3$) δ 5.98 (1H, dd, J = 17.1, 10.5 Hz), 5.42 (1H, s), 5.28 (1H, dd, J = 17.1, 1.2 Hz), 5.05 (1H, dd, J = 10.5, 1.2 Hz), 1.78−1.88 (2H, m), 1.26−1.55 (4H, m), 1.39 (3H, s), 1.34 (3H, s), 1.24 (3H, s), 1.07 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.21, 143.94, 120.99, 111.75, 102.35, 72.13, 70.71, 40.52, 40.41, 34.26, 31.32, 30.93, 29.41, 27.87, 18.43; EI HRMS *m/e* calcd for $C_{15}H_{24}O_2$ (M^+) 236.1770, found 236.1770. **Diastereoisomer:** mp 95.5−100.5 °C; IR (KBr disk, cm^{-1}) 3372, 1962, 1450, 1386, 1148, 1102; ^1H NMR (400 MHz, $CDCl_3$) δ 5.97 (1H, dd, J = 17.3, 10.5 Hz), 5.42 (3H, s), 5.28 (1H, dd, J = 17.3, 1.2 Hz), 5.06 (1H, dd, J = 10.5, 1.2 Hz), 1.78−1.88 (2H, m), 1.26−1.55 (4H, m), 1.39 (3H, s), 1.36 (3H, s), 1.24 (3H, s), 1.05 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.17, 144.01, 121.17, 111.81, 102.30, 72.15, 70.71, 40.55, 40.42, 34.32, 31.31, 31.05, 29.38, 27.78, 18.45; EI HRMS *m/e* calcd for $C_{15}H_{24}O_2$ (M^+) 236.1770, found 236.1770.

(1*Z*)-1-(1′-Hydroxy-2′-methylidene-6′,6′-dimethylcyclohexyl)-3-methyl-1,4-pentadien-3-ol (4d): mp 31.5−34.0 °C; IR (KBr disk, cm^{-1}) 3352, 1640, 1464, 1366, 1120; ^1H NMR (400 MHz, $CDCl_3$) δ 6.03 (1H, dd, J = 17.3, 10.5 Hz), 5.81 (1H, d, J = 13.4 Hz), 5.64 (1H, d, J = 13.4 Hz), 5.20 (1H, dd, J = 17.3, 1.2 Hz), 5.02 (1H, dd, J = 10.5, 1.2 Hz), 4.89 (1H, d, J = 1.7 Hz), 4.86 (1H, m), 2.46 (1H, brdt, J = 13.4, 6.6 Hz), 2.16 (1H, brdt, J = 12.9, 6.4 Hz), 1.58−1.71 (4H, m), 1.42 (3H, s), 0.97 (3H, s), 0.96 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.30, 145.69, 135.31, 131.94, 111.67, 108.81, 80.01, 73.26, 39.53, 36.63, 32.58, 29.35, 24.04, 23.54, 22.91; EI HRMS *m/e* calcd for $C_{15}H_{24}O_2$ (M^+) 236.1770, found 236.1775. **Diastereoisomer:** mp 50.0−51.5 °C; IR (KBr disk, cm^{-1}) 3288, 1642, 1388, 1358, 1116, 1098; ^1H NMR (400 MHz, $CDCl_3$) δ 6.10 (1H, dd, J = 17.3, 10.5 Hz), 5.84 (1H, d, J = 13.2 Hz), 5.61 (1H, d, J = 13.2 Hz), 5.26 (1H, dd, J = 17.3, 1.2 Hz), 5.05 (1H, dd, J = 10.5, 1.2 Hz), 4.97 (1H, brd, J = 2.0 Hz), 4.88 (1H, m), 4.00 (2H, brs), 2.43 (1H, brdt, J = 13.6, 6.1 Hz), 2.18 (1H, brdt, J = 13.6, 6.4 Hz), 1.58−1.62 (4H, m), 1.39 (3H, s), 0.95 (3H, s), 0.93 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.25, 145.67, 135.28, 131.92, 111.67, 108.81, 80.00, 73.22, 39.52, 36.61, 29.33, 24.04, 23.53, 22.90; EI HRMS *m/e* calcd for $C_{15}H_{24}O_2$ (M^+) 236.1770, found 236.1775.

Photosensitized Oxygenation of 1e. Following the general procedure of photosensitized oxygenation, **1e** (302 mg, 1.11 mmol), a catalytic amount of TPP, and triphenylphosphine (292 mg, 1.11 mmol, and after oxidation 292 mg, 1.11 mmol) in dichloromethane (6 mL) gave **3e** (68 mg, 21%), its diastereoisomer (57 mg, 18%), and **4e** (163 mg, 51%) as a nearly 1:1 mixture of diastereoisomers after the usual workup and column chromatography (from 17% to 50% ether in hexane).

Photosensitized Oxygenation of 2e. Following the general procedure of photosensitized oxygenation, **2e** (ca. 1.10 mmol), a catalytic amount of TPP, and triphenylphosphine (285 mg, 1.11 mmol, and after oxidation 285 mg, 1.11 mmol) in dichloromethane (6 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (568 mg, 2.17 mmol) in THF (6 mL) gave **3e** (208 mg, 67% for three steps) and **4e** (76 mg, 24% for three steps) as a nearly 1:1 mixture of diastereoisomers, respectively, after the usual workup and column chromatography (from 17% to 60% ether in hexane).

1-(2′-Hydroxy-2′,6′,6′-trimethylcyclohexylidene)-3-phenyl-1-buten-3-ol (3e): mp 103.0−105.0 °C; IR (KBr disk, cm^{-1}) 3368, 1968, 1452, 1374, 1156, 1140, 1058; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.52 (2H, m), 7.31−7.35 (2H, m), 7.22−7.26 (1H, m), 5.65 (1H, s), 1.72−1.90 (2H, m), 1.65 (3H, s), 1.43−1.51 (4H, m), 1.31 (3H, s), 1.22 (3H, s), 1.02 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.16, 147.21, 128.04, 126.84, 125.09, 121.48, 104.09, 73.59, 40.51, 40.38, 34.38, 31.19, 30.90, 30.02, 29.41, 18.44. Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15, Found: C, 79.62; H, 9.20. **Diastereoisomer:** mp 152−154.5 °C; IR (KBr disk, cm^{-1}) 3292, 1954, 1452, 1160, 1096, 1070; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.53 (2H, m), 7.32−7.36 (2H, m), 7.23−7.26 (1H, m), 5.66 (1H, s), 2.49 (1H, s), 1.73−1.90 (2H, m), 1.65 (3H, s), 1.49−1.53 (4H, m), 1.36 (3H, s), 1.23 (3H, s), 1.08 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.11, 147.33, 128.09, 126.85, 125.05, 121.74, 104.11, 73.61, 70.84, 40.60, 40.34, 34.57, 31.09, 30.86, 30.04, 29.73, 18.57. Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.76; H, 9.30.

(1*Z*)-1-(1′-Hydroxy-2′-methylidene-6′,6′-dimethylcyclohexyl)-3-phenyl-1-buten-3-ol (4e) (mixture of diastereoisomers): IR (KBr disk, cm^{-1}) 3268, 1642, 1450, 1386, 1368, 1096, 1062; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20−7.52 (5H, m), 6.05 ($^3/_4 \times$ 1H, d, J = 13.2 Hz), 6.03 ($^1/_4 \times$ 1H, d, J = 13.1 Hz), 5.88 ($^1/_4 \times$ 1H, d, J = 13.2 Hz), 5.82 ($^1/_4 \times$ 1H, d, J = 13.4 Hz), 4.99 ($^3/_4 \times$ 1H, s), 4.90 ($^3/_4 \times$ 1H, s), 4.70 ($^1/_4 \times$ 1H, s), 4.56 ($^1/_4 \times$ 1H, s), 2.16−2.41 (2H, m), 1.63 ($^1/_4 \times$ 3H, s), 1.59 ($^3/_4 \times$ 3H, s), 1.43−1.70 (6H, m), 0.98 ($^1/_4 \times$ 1H, s), 0.94 ($^1/_4 \times$ 1H, s), 0.81 ($^3/_4 \times$ 3H, s), 0.75 ($^3/_4 \times$ 3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.25, 150.76, 149.51, 149.35, 138.08, 137.72, 131.19, 131.14, 128.17, 128.14, 126.68, 126.66, 124.94, 108.86, 108.77, 80.78, 80.72, 73.71, 73.63, 40.10, 39.54, 39.90, 36.75, 33.36,

32.79, 32.71, 32.57, 24.27, 23.93, 22.85, 22.69, 22.64. Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.79; H, 9.31.

Photosensitized Oxygenation of 2f. Following the general procedure of photosensitized oxygenation, **2f** (ca. 1.37 mmol), TPP (9 mg, 0.015 mmol), and triphenylphosphine (360 mg, 1.37 mmol, and after oxidation 360 mg, 1.37 mmol) in dichloromethane (7 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (611 mg, 2.34 mmol) in THF (7 mL) gave **3f** (176 mg, 55% for three steps) and **4f** (142 mg, 27% for three steps) as a nearly 1:1 mixture of diastereoisomers, respectively, after the usual workup and column chromatography (from 9% to 50% in hexane). In addition, **4f** contained triethylsilanol, which could not be removed by column chromatography. The yield of **4f** was calculated on the basis of the integral values of **4f** and triethylsilanol in the NMR spectrum.

1-(2′-Hydroxy-2′,6′,6′-trimethylcyclohexylidene)-3-methyl-1-penten-4-yn-3-ol (3f): mp 103.5−104 °C; IR (KBr disk, cm^{-1}) 3320, 2932, 2116, 1964, 1460, 1368, 1188, 1114; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (1H, s), 2.52 (1H, brs), 2.48 (1H, s), 1.77−1.91 (2H, m), 1.49−1.65 (4H, m), 1.59 (3H, s), 1.36 (3H, s), 1.24 (3H, s), 1.09 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.78, 121.95, 101.46, 86.54, 71.61, 70.82, 66.73, 40.55, 40.43, 34.46, 31.26, 30.87, 29.87, 29.14, 18.39. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.60; H, 9.50. **Diastereoisomer:** mp 79.5−81 °C; IR (KBr disk, cm^{-1}) 3316, 2932, 1960, 1452, 1366, 1166, 1120; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (1H, s), 2.90 (1H, brs), 2.48 (1H, s), 1.73−1.89 (2H, m), 1.60 (3H, s), 1.48−1.58 (4H, m), 1.42 (3H, s), 1.22 (3H, s), 1.09 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.66, 122.04, 101.73, 86.48, 71.70, 70.95, 66.92, 40.64, 40.37, 34.51, 30.92, 30.78, 30.04, 29.49, 18.56; EI HRMS *m/e* calcd for $C_{15}H_{26}O$ ($M - H_2O^+$) 216.1509, found 216.1521.

(1*Z*)-1-(1′-Hydroxy-2′-methylidene-6′,6′-dimethylcyclohexyl)-3-methyl-1-penten-4-yn-3-ol (4f): IR (neat, cm^{-1}) 3524, 3312, 2940, 2872, 1716, 1642, 1452, 1122; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (1H, d, J = 12.9 Hz), 5.75 (1H, d, J = 12.9 Hz), 4.97 (1H, brs), 4.91 (1H, dd, J = 2.6, 1.2 Hz), 2.53 (1H, s), 2.46 (1H, dt, J = 14.2, 7.1 Hz), 2.22 (1H, dt, J = 13.4, 5.9 Hz), 1.63 (3H, s), 1.56−1.79 (4H, m), 0.97 (3H, s), 0.96 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.21, 135.07, 132.92, 109.93, 89.09, 81.30, 71.42, 64.45, 39.34, 36.43, 32.22, 30.89, 24.22, 23.76, 22.54; EI HRMS *m/e* calcd for $C_{15}H_{20}O$ ($M - H_2O^+$) 216.1509, found 216.1518. **Diastereoisomer:** mp 65−65.5 °C; IR (KBr disk, cm^{-1}) 3292, 3036, 2936, 2116, 1646, 1452, 1152, 1094; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (1H, d, J = 12.9 Hz), 5.76 (1H, d, J = 12.9 Hz), 5.52 (1H, brs), 4.97 (1H, d, J = 1.2 Hz), 4.90 (1H, dd, J = 2.7, 1.2 Hz), 3.34 (1H, brs), 2.59 (1H, s), 2.41 (1H, dt, J = 14.0, 6.8 Hz), 2.21 (1H, dt, J = 14.0, 6.8 Hz), 1.61 (3H, s), 1.47−1.69 (4H, m), 1.01 (3H, s), 0.97 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.83, 135.49, 132.38, 109.68, 89.69, 81.78, 71.14, 64.21, 40.41, 36.96, 32.51, 31.00, 24.03, 22.90, 22.73. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.91; H, 9.54.

2,6-Dimethyl-2-hepten-4-yn-6-ol (9a). To a solution of 3-methyl-1-butyn-3-ol (9.0 mL, 93 mmol) in THF (200 mL) were added *n*-BuLi (1.6 M solution in hexane, 128 mL, 204 mmol) and HMPA (20 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h, and zinc chloride (29 g, 204 mmol) was added at the same temperature. The mixture was warmed to 0 °C and stirred for an additional 3 h. To this solution were added 1-bromo-2-methyl-2-propene (**5a**) (2.0 mL, 193 mmol) and tetrakis(triphenylphosphine)palladium (239 mg, 2.07 mmol). After being stirred at 65 °C for 33 h, the mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ether. The organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (17% ether in hexane) gave **9a** (2.14 g, 80%): IR (neat, cm^{-1}) 3364, 2980, 2212, 1632, 1380, 1244, 1166; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (1H, qq, J = 1.5, 0.5 Hz), 2.08 (1H, brs), 1.88 (3H, d, J = 0.5 Hz), 1.80 (3H, d, J = 1.5 Hz), 1.55 (1H, s);^{13}C NMR (100 MHz, $CDCl_3$) δ 148.67, 104.50, 95.90, 80.09, 65.71, 31.61, 24.68, 20.83; EI HRMS *m/e* calcd for $C_9H_{14}O$ (M^+) 138.1041, found 138.1052.

(4*Z*)-2,6-Dimethyl-2,4-heptadien-6-ol (10a). To a solution of **9a** (920 mg, 6.66 mmol) in hexane (95 mL) were added Lindlar catalyst (1.14 g) and quinoline (76 μL), and the mixture was stirred at room temperature for 10 min under hydrogen atmosphere. The reaction mixture was filtered and concentrated in vacuo to give crude products that were purified by column chromatography (9% ether in hexane) to afford **10a** (438 mg, 47%): IR (neat, cm^{-1}) 3384, 2972, 1650, 1450, 1380, 1200, 1142; UV_{max} (MeOH) 238 nm (ϵ = 26 900); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (1H, brd, J = 12.0 Hz), 6.12 (1H, dd, J = 12.0, 11.7 Hz), 5.40 (1H, brd, J = 11.7 Hz), 1.82 (3H, brs), 1.74 (3H, brs), 1.64 (1H, s), 1.41 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.15, 135.08, 124.74, 120.87, 71.93, 31.33, 26.50, 17.62; EI HRMS *m/e* calcd for $C_9H_{16}O$ (M^+) 140.1197, found 140.1225.

(4*Z*)-2,6-Dimethyl-6-(triethylsiloxy)-2,4-heptadiene (11a). To a solution of **10a** (290 mg, 2.07 mmol), 4-(dimethylamino)-pyridine (25 mg, 0.21 mmol), and triethylamine (0.72 mL, 5.17 mmol) in DMF (11 mL) was added triethylsilyl chloride (0.80 mL, 4.76 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 11 h, saturated aqueous NH_4Cl solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **11a**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

2,3,6-Trimethyl-2-hepten-4-yn-6-ol (9b). Compound **9b** was prepared according to the procedure for synthesis of **9a** using 2-(bromomethyl)-2-butene (**5b**) (2.50 mL, 20.7 mmol) in place of 1-bromo-2-methyl-2-propene (**5a**). The product **9b** was isolated by repeating medium-pressure column chromatography (4% ether in hexane) (1.42 g, 45%): IR (neat, cm^{-1}) 3368, 2980, 2204, 1374, 1236, 1166, 1136; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (1H, s), 1.91 (3H, brs), 1.78 (3H, brs), 1.73 (3H, brs), 1.56 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.07, 111.02, 95.10, 83.89, 65.70, 31.71, 23.42, 19.81, 18.51.

(4*Z*)-2,3,6-Trimethyl-2,4-heptadien-6-ol (10b). To a solution of **9b** (450 mg, 2.96 mmol) in hexane (50 mL) were added Lindlar catalyst (600 mg) and quinoline (38 μL), and the mixture was stirred at room temperature for 20 min under hydrogen atmosphere. The reaction mixture was filtered and concentrated in vacuo to give crude products that were purified by column chromatography (5% ether in hexane) to give **10b** (225 mg, 49%): IR (neat, cm^{-1}) 3452, 2976, 1454, 1374, 1140; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (1H, brd, J = 12.4 Hz), 5.40 (1H, d, J = 12.4 Hz), 2.96 (1H, s), 1.76 (3H, brs), 1.73 (3H, brs), 1.69 (3H, brs), 1.29 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.44, 128.15, 127.88, 126.57, 72.77, 30.16, 22.49, 19.62, 19.56; EI HRMS *m/e* calcd for $C_{10}H_{18}O$ (M^+) 154.1353, found 154.1372.

(4*Z*)-2,3,6-Trimethyl-6-(triethylsiloxy)-2,4-heptadiene (11b). To a solution of **10b** (69 mg, 0.45 mmol), 4-(dimethylamino)pyridine (6 mg, 0.05 mmol), and triethylamine (0.21 mL, 1.51 mmol) in DMF (3 mL) was added triethylsilyl chloride (0.27 mL, 1.43 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 17 h, saturated aqueous NH_4Cl solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **11b**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

1-(Tributylstannyl)-1-butyn-3-ol (8). To a solution of 3-methyl-1-butyn-3-ol (5.0 mL, 51.6 mmol) in THF (20 mL) was added *n*-BuLi (1.6 M solution in hexane, 71 mL, 114 mmol) at −78 °C and HMPA (10 mL) at 0 °C, and the mixture was stirred for 2 h. Tributyltin chloride (30.1 mL, 114 mmol) was then added at 0 °C, and the mixture was warmed to room temperature. After being stirred at room temperature for 38 h, the reaction mixture was diluted with saturated aqueous NH_4Cl solution and extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column

chromatography on silica gel (from 11% to 13% ether in hexane) gave **8** (17.2 g), which was used for the next reaction without further purification.

3-Isopropyl-2,6-dimethyl-2-hepten-4-yn-6-ol (9c). To a solution of lithium diisopropylamide prepared from diisopropylamine (7.35 mL, 52.4 mmol) and *n*-BuLi (1.6 M solution in hexane, 32.8 mL, 52.4 mmol) in THF (132 mL) was added 2,4-dimethyl-3-pentanone (3.7 mL, 26.2 mmol) at −78 °C. After the reaction mixture was stirred at −78 °C for 1.5 h, a THF solution of *N*-trifluoromethanesulfonimide (11.2 g, 31.5 mmol) was added. The mixture was stirred at room temperature for 38 h, diluted with saturated aqueous NH_4Cl solution, and extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (1% ether in hexane) gave enol triflate **7c** as an oil (5.21 g), which was used for the next reaction without further purification.

To a solution of **7c** in THF (105 mL) were added stanylacetylide **8** (9.32 g) and tetrakis(triphenylphosphine)palladium (1.22 g, 1.06 mmol). After the mixture was stirred at room temperature for 18 h, the reaction was quenched with aqueous NH_4Cl solution, and the mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (11% ether in hexane) gave **9c** (2.13 g, 45% for two steps): IR (neat, cm^{-1}) 3376, 2972, 2872, 2204, 1628, 1456, 1232, 1166; ^1H NMR (400 MHz, $CDCl_3$) δ 2.74 (1H, qq, J = 6.8, 6.8 Hz), 2.01 (1H, s), 1.91 (3H, s), 1.76 (3H, s),1.58 (6H, s), 1.02 (6H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.81, 123.23, 97.77, 80.32, 65.79, 31.77, 28.83, 23.85, 21.47, 19.38.

(4*Z*)-3-Isopropyl-2,6-dimethyl-2,4-heptadien-6-ol (10c). To a solution of **9c** (622 mg, 3.45 mmol) in hexane (18 mL) was added Lindlar catalyst (1.5 g), and the mixture was stirred at room temperature for 3 days under hydrogen atmosphere. The reaction mixture was filtered and concentrated in vacuo to give crude products that were purified by column chromatography (from 11% to 13% ether in hexane) to give **10c** (294 mg, 47%): IR (neat, cm^{-1}) 3540, 2972, 2872, 1468, 1378, 1362, 1146; ^1H NMR (400 MHz, $CDCl_3$) δ 5.67 (1H, dqq, J = 12.7, 2.0, 1.7 Hz), 5.52 (1H, d, J = 12.7 Hz), 3.41 (1H, s), 2.90 (1H, qq, J = 6.8 Hz), 1.78 (3H, d, J = 1.7 Hz), 1.72 (3H, d, J = 2.0 Hz), 1.28 (6H, s), 0.99 (6H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.50, 136.61, 127.05, 121.71, 73.19, 30.05, 29.72, 23.47, 21.37, 19.20; EI HRMS *m/e* calcd for $C_{12}H_{22}O$ (M^+) 182.1665, found 182.1665.

(4*Z*)-3-Isopropyl-2,6-dimethyl-2-(triethylsiloxy)-2,4-heptadiene (11c). To a solution of **10c** (268 mg, 1.47 mmol), 4-(dimethylamino)pyridine (18 mg, 0.15 mmol), and triethylamine (0.41 mL, 2.94 mmol) in DMF (8 mL) was added triethylsilyl chloride (0.41 mL, 2.65 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature for 11 h, aqueous saturated NH_4Cl solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **11c**, which was used for photosensitized oxygenation without any purification because of its instability for column chromatography.

3-*tert*-Butyl-2,6-dimethyl-2-hepten-4-yn-6-ol (9d). To a solution of lithium diisopropylamide prepared from diisopropylamine (2.2 mL, 16 mmol) and *n*-BuLi (1.6 M solution in hexane, 9.8 mL, 16 mmol) in THF (30 mL) was added 2,2,4-trimethyl-3-pentanone[20] (1.0 g, 7.8 mmol) at −78 °C. The solution was warmed to room temperature and maintained at the same temperature for an additional 30 min. To this solution was added *N*-trifluoromethansulfonimide (3.3 g, 9.2 mmol) in THF at 0 °C. After the reaction mixture was stirred at room temperature for 1.5 h, the reaction was quenched with saturated aqueous NH_4Cl solution, and the mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude **7d**. Obtained **7d** was used for the next reaction without any purification because of its instability for column chromatography.

To a solution of crude **7d** in THF (30 mL) were added stannylacetylide **8** (6.1 g) in THF (20 mL) and tetrakis-(riphenylphosphine)palladium (900 mg, 0.78 mmol). After the reaction mixture was stirred at room temperature for 2.5 h, the reaction was quenched with saturated aqueous NaCl solution, and the mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (from 7% to 9% ethyl acetate in hexane) gave **9d** (880 mg, 52% for two steps): IR (neat, cm^{-1}) 3360, 2972, 2208, 1466, 1366, 1212, 1148; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (3H, s), 1.92 (3H, s), 1.56 (6H, s), 1.23 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.27, 123.62, 98.13, 83.22, 65.94, 31.64, 31.00, 29.22, 26.57, 22.14.

(4*Z*)-3-*tert*-Butyl-2,6-dimethyl-2,4-heptadien-6-ol (10d). To a solution of **9d** (210 mg, 1.1 mmol) in hexane (10 mL) was added $Pd/BaSO_4$ (530 mg), and the mixture was stirred at room temperature for 50 min under hydrogen atmosphere. The reaction mixture was filtered and concentrated in vacuo to give crude products that were purified by column chromatography (17% ethyl acetate in hexane) to give **10d** (128 mg, 61%): IR (neat, cm^{-1}) 3540, 2972, 1470, 1364, 1162; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (1H, dqq, J = 12.5, 1.9, 1.8 Hz), 5.36 (1H, d, J = 12.5 Hz), 3.32 (1H, s), 1.86 (3H, d, J = 2.4 Hz), 1.78 (3H, d, J = 1.7 Hz), 1.28 (3H, s), 1.27 (3H, s), 1.20 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.94, 135.07, 128.95, 126.32, 72.96, 34.94, 31.05, 30.47, 29.47, 25.88, 22.08; EI HRMS *m/e* calcd for $C_{13}H_{24}O_1$ 196.1821, found 196.1850.

(4*Z*)-3-*tert*-Butyl-2,6-dimethyl-6-(trimethylsiloxy)-2,4-heptadiene (11d). To a solution of **10d** (300 mg, 1.50 mmol), 4-(dimethylamino)pyridine (56 mg, 0.46 mmol), and triethylamine (0.85 mL, 6.10 mmol) in DMF (8 mL) was added triethylsilyl chloride (0.92 mL, 5.50 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After the reaction mixture was stirred at the same temperature overnight, aqueous saturated $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude silyl ether **11d**, which was used for photosensitized oxygenation without any purification because of its instability for a column chromatography.

3-Bromo-2,4-dimethyl-2-penten-4-ol (5e). To a solution of methyl 3,3-dimethylacryrate (4.1 mL, 30.4 mmol) in dichloromethane (110 mL) was added bromine (2.4 mL, 45.7 mmol) at 0 °C. After being stirred at 0 °C for 10 h, the reaction mixture was diluted with aqueous saturated $Na_2S_2O_3$ solution, poured into aqueous saturated $NaHCO_3$ solution, and extracted with dichloromethane. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (2% ethyl acetate in hexane) gave dibromide (7.41 g, 73%): IR (neat, cm^{-1}) 2984, 1754, 1440, 1350, 1246, 1146, 1102, 1030; ^1H NMR (400 MHz, $CDCl_3$) δ 4.65 (1H, s), 3.81 (3H, s), 2.05 (3H, s), 1.95 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.08, 61.60, 54.15, 52.89, 33.69, 28.44.

To a solution of the obtained dibromide (6.4 g, 23.4 mmol) in THF (110 mL) was added DBU (3.49 mL, 23.4 mmol) at −78 °C. After being stirred at −78 °C for 1.5 h, the reaction mixture was diluted with aqueous saturated NH_4Cl solution and extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (1% ethyl acetate in hexane) gave vinyl bromide (4.0 g, 89%): IR (neat, cm^{-1}) 2956, 1722, 1438, 1252, 1218, 1096, 1016; ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 (3H, s), 2.15 (3H, s), 2.06 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.50, 149.05, 108.15, 52.66, 27.16, 23.18.

To a solution of the obtained vinyl bromide (8.24 g, 42.7 mmol) in THF (150 mL) was added methylmagnesium iodide prepared from magnesium turnings (6.7 g, 277 mmol) and methyl iodide (16.5 mL, 264 mmol) in ether (130 mL), until the starting material disappeared. After being stirred at 0

°C for 8 h, the reaction mixture was diluted with aqueous saturated NH_4Cl solution and extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (11% ethyl acetate in hexane) gave **5e** (5.81 g, 71%): IR (KBr disk, cm^{-1}) 3304, 2980, 1624, 1380, 1144; ^1H NMR (400 MHz, $CDCl_3$) δ 2.06 (3H, s), 1.98 (1H, s), 1.94 (3H, s), 1.56 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.51, 128.35, 75.78, 31.06, 28.99, 22.27.

5-Isopropylidene-2,6-dimethyl-2-(triethylsiloxy)-3-heptyn-6-ol (9e). To a solution of 3-methyl-1-butyn-3-ol (12 mL, 124 mmol), 4-(dimethylamino)pyridine (1.51 g, 12.4 mmol), and triethylamine (25.8 mL, 18.6 mmol) in DMF (240 mL) was added triethylsilyl chloride (24.9 mL, 149 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature. After being stirred at the same temperature for 2 days, the reaction mixture was diluted with aqueous saturated NH_4Cl solution and then extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (3% triethylamine in hexane) gave silyl ether as an oil (25 g), which was used for the next reaction without further purification.

To a solution of the silyl ether (4.0 g) in THF (40 mL) was added *n*-BuLi (1.6 M solution in hexane, 3.9 mL, 22.2 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h, and zinc chloride (3.15 g, 22.2 mmol) was added at the same temperature. The mixture was warmed to room temperature and stirred for an additional 3 h. To this solution were added the alcohol **5e** (1.0 g, 5.18 mmol), and tetrakis-(triphenylphosphine)palladium (600 mg, 0.518 mmol) was added. After being stirred at 65 °C for 4 h, the reaction mixture was diluted with aqueous saturated NH_4Cl solution and extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude products. Column chromatography on silica gel (3% ethyl acetate and 3% triethylamine in hexane) gave **9e** (1.35 g, 84%): IR (neat, cm^{-1}) 3432, 2960, 2204, 1464, 1380, 1160, 1040; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (3H, s), 1.98 (3H, s), 1.74 (1H, brs), 1.52 (6H, s),1.47 (6H, s), 0.96 (9H, t, J = 8.0 Hz), 0.66 (6H, q, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.10, 124.36, 99.49, 81.90, 72.56, 66.80, 33.21, 30.77, 25.91, 21.61, 6.97, 5.95.

(3*Z*)-5-Isopropylidene-2,6-dimethyl-2-(triethylsiloxy)-3-hepten-6-ol (11e). To a solution of **9e** (300 mg, 0.97 mmol) in MeOH (6 mL) was added Pd−C (90 mg), and the mixture was stirred at room temperature for 40 min under hydrogen atmosphere. The reaction mixture was filtered and concentrated in vacuo to give crude products that were purified by column chromatography on silica gel (2% triethylamine in hexane) to give **11e** (271 mg, 90%): IR (neat, cm^{-1}) 3452, 2964, 1466, 1378, 1150, 1042; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (1H, dqq, J = 12.7, 2.2, 1.5 Hz), 5.54 (1H, d, J = 12.7 Hz), 2.60 (1H, s), 1.86 (3H, d, J = 2.2 Hz), 1.68 (3H, d, J = 1.5 Hz), 1.44 (6H, s), 1.37 (6H, s), 0.95 (9H, t, J = 7.8 Hz), 0.61 (6H, q, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.45, 137.50, 127.19, 127.14, 74.07, 72.37, 30.67, 30.20, 25.26, 21.37, 7.01, 6.65.; EI HRMS *m/e* calcd for $C_{17}H_{31}O_1Si_1$ ($M - H_2O - CH_3^+$) 279.2136, found 279.2178.

Photosensitized Oxygenation of 11a. Following the general procedure of photosensitized oxygenation, **11a** (ca. 2.07 mmol), TPP (7 mg, 0.01 mmol), and triphenylphosphine (542 mg, 2.07 mmol, and after oxidation 813 mg, 3.10 mmol) in dichloromethane (11 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (1.22 mg, 4.65 mmol) in THF (11 mL) gave **13a** (144 mg, 45% for three steps) and **14a** (93 mg, 29% for three steps), after the usual workup and column chromatography (from 2% to 9% hexane in ether).

2,6-Dimethyl-3,4-heptadiene-2,6-diol (13a): IR (KBr disk, cm^{-1}) 3368, 2980, 1968, 1468, 1366, 1152; ^1H NMR (400 MHz, $CDCl_3$) δ 5.51 (1H, s), 2.63 (2H, brs), 1.36 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.53, 104.63, 69.65, 30.02, 29.83.; FAB HRMS *m/e* calcd for $C_9H_{15}O_1$ ($M - OH^+$) 139.1119, found 139.1124.

(4*Z*)-2,6-Dimethyl-1,4-heptadiene-3,6-diol (14a): IR (neat, cm^{-1}) 3324, 2976, 1652, 1454, 1374, 1170, 1064, 1008; ^1H NMR (400 MHz, $CDCl_3$) δ 5.60 (1H, dd, J = 12.0, 1.5 Hz), 5.39 (1H, dd, J = 12.2, 6.8 Hz), 5.15 (1H, d, J = 6.8 Hz), 5.03 (1H, m), 4.85 (1H, m), 1.78 (3H, s), 1.39 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.29, 139.42, 129.44, 110.74, 71.86, 71.68, 31.79, 30.64, 18.44; EI HRMS *m/e* calcd for $C_9H_{14}O_1$ ($M - H_2O^+$) 138.1041, found 138.1046.

Photosensitized Oxygenation of 11b. Following the general procedure of photosensitized oxygenation, **11b** (ca. 0.45 mmol), TPP (2 mg, 0.002 mmol), and triphenylphosphine (117 mg, 0.45 mmol, and after oxidation 117 mg, 0.45 mmol) in dichloromethane (3 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (175 mg, 0.67 mmol) in THF (3 mL) gave **13b** (24 mg, 32% for three steps), **14b** (9 mg, 12% for three steps), and **15b** (32 mg, 42% for three steps) after the usual workup and column chromatography (from 20% to 67% ethyl acetate in hexane).

2,3,6-Trimethyl-3,4-heptadiene-2,6-diol (13b): IR (KBr disk, cm^{-1}) 3496, 3252, 2980, 1978, 1370, 1156; ^1H NMR (400 MHz, $CDCl_3$) δ 5.38 (1H, q, J = 2.9 Hz), 1.79 (3H, d, J = 2.9 Hz), 1.36 (6H, s), 1.34 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.68, 115.51, 103.04, 71.02, 69.92, 29.97, 29.86, 28.84, 28.56, 14.90; EI HRMS *m/e* calcd for $C_{10}H_{17}O_1$ ($M - OH^+$) 153.1275, found 153.1268.

(4*Z*)-2,3,6-Trimethyl-1,4-heptadiene-3,6-diol (14b): IR (neat, cm^{-1}) 3220, 2980, 1644, 1452, 1366, 1300, 1148; ^1H NMR (400 MHz, $CDCl_3$) δ 5.51 (1H, d, J = 12.9 Hz), 5.43 (1H, d, J = 12.9 Hz), 5.08 (1H, dq, J = 1.7, 0.7 Hz), 4.81 (1H, dq, J = 1.6, 1.5 Hz), 1.85 (3H, dd, J = 1.7, 1.5 Hz), 1.66 (1H, brs), 1.43 (3H, s), 1.39 (3H, s), 1.36 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.27, 136.56, 134.48, 109.33, 74.61, 72.20, 31.50, 30.16, 29.14, 19.18; EI HRMS *m/e* calcd for $C_{10}H_{16}O_1$ ($M - H_2O^+$) 152.1197, found 152.1189.

(3*Z*)-5-Methylidene-2,6-dimethyl-3-heptene-2,6-diol (15b): IR (neat, cm^{-1}) 3352, 2976, 1626, 1464, 1364, 1254, 1152; ^1H NMR (400 MHz, $CDCl_3$) δ 5.99 (1H, ddd, J = 12.4, 1.8, 1.7 Hz), 5.62 (1H, d, J = 12.4 Hz), 5.21 (1H, dd, J = 1.7, 1.6 Hz), 4.91 (1H, dd, J = 1.8, 1.7 Hz), 2.95 (2H, brs), 1.39 (6H, s), 1.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.50, 139.68, 124.78, 110.49, 72.90, 71.94, 31.28, 29.00; EI HRMS *m/e* calcd for $C_{10}H_{16}O_1$ ($M - H_2O^+$) 152.1197, found 152.1190.

Photosensitized Oxygenation of 11c. Following the general procedure of photosensitized oxygenation, **11c** (ca. 1.47 mmol), TPP (5 mg, 0.005 mmol), and triphenylphosphine (386 mg, 1.47 mmol, and after oxidation 386 mg, 1.47 mmol) in dichloromethane (8 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (769 mg, 2.94 mmol) in THF (8 mL) gave **13c** (111 mg, 38% for three steps), **14c** (80 mg, 27% for three steps), **15c** (24 mg, 8% for three steps), and **16** (48 mg, 17% for three steps) after the usual workup and column chromatography (from 25% to 95% ether in hexane).

3-Isopropyl-2,6-dimethyl-3,4-heptadiene-2,6-diol (13c): IR (neat, cm^{-1}) 3396, 2972, 2872, 1958, 1464, 1366, 1210, 1148; ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (1H, d, J = 0.5 Hz), 2.34 (1H, dqq, J = 6.8, 6.6, 0.5 Hz), 2.17 (2H, brs),1.37 (6H, s), 1.35 (6H, s), 1.09 (3H, d, J = 6.8 Hz), 1.06 (3H, d, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.48, 123.85, 106.76, 71.52, 69.85, 30.12, 29.97, 29.32, 29.12, 27.09, 24.78, 24.08; EI HRMS *m/e* calcd for $C_{12}H_{21}O_1$ ($M - OH^+$) 181.1587, found 181.1589.

(4*Z*)-3-Isopropyl-2,6-dimethyl-1,4-heptadiene-3,6-diol (14c): mp 69.0−69.5 °C; IR (KBr disk, cm^{-1}) 3272, 3132, 2972, 1640, 1454, 1294, 1154, 1044; ^1H NMR (400 MHz, $CDCl_3$) δ 5.50 (2H, d, J = 3.4 Hz), 5.07 (1H, m), 4.85 (1H, m), 1.92 (1H, qq, J = 6.8 Hz), 1.78 (3H, m), 1.40 (3H, s), 1.35 (3H, s), 0.93 (3H, d, J = 6.8 Hz), 0.86 (3H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.55, 136.84, 133.24, 110.43, 79.58, 71.97, 34.45, 31.68, 30.06, 19.49, 17.07, 16.23. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19. Found: C, 72.75; H, 11.19.

(3*Z*)-5-Isopropylidene-2,6-dimethyl-3-heptene-2,6-diol (15c): IR (neat, cm^{-1}) 3404, 2976, 1632, 1466, 1250, 1170; ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (1H, dqq, J = 12.2, 2.2, 1.7 Hz), 5.50 (1H, d, J = 12.2 Hz), 3.00 (1H, brs), 2.47 (1H, brs),

1.94 (3H, d, J = 2.2 Hz), 1.76 (3H, d, J = 1.7 Hz), 1.43 (6H, brs), 1.30 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.19, 137.52, 129.23, 125.40, 72.83, 72.35, 30.19, 25.11, 21.46; EI HRMS *m/e* calcd for $C_{12}H_{20}O$ (M − H_2O^+) 180.1509, found 180.1514.

3-(1-Hydroxy-1-methylethyl)-2,6-dimethyl-3,4-heptadiene-2,6-diol (16): mp 76.0−77.0 °C; IR (neat, cm^{-1}) 3344, 2976, 1956, 1464, 1378, 1124; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (1H, s), 4.28, 4.34 (2H, brs), 2.43, 2.48 (1H, brs),1.48 (6H, s), 1.47 (6H, s), 1.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.36, 120.48, 104.38, 73.50, 70.02, 32.43, 31.69, 29.92; FAB HRMS *m/e* calcd for $C_{12}H_{22}O_3Na$ (M + Na^+) 237.1476, found 237.1455.

Photosensitized Oxygenation of 11d. Following the general procedure of photosensitized oxygenation, **11d** (ca. 1.50 mmol), TPP (9 mg, 0.015 mmol), and triphenylphosphine (400 mg, 1.5 mmol, and after oxidation 600 mg, 2.3 mmol) in dichloromethane (8 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (600 mg, 2.3 mmol) in THF (13 mL) gave **13d** (244 mg, 75% for three steps) and **14d** (28 mg, 8% for three steps) after the usual workup and column chromatography (from 9% to 25% ethyl acetate in hexane). In addition, **14d** contained triethylsilanol that could not be removed by column chromatography. The yield of **14d** was calculated on the basis of the integral values of **14d** and triethylsilanol in the NMR spectrum.

3-*tert*-Butyl-2,6-dimethyl-3,4-heptadiene-2,6-diol (13d): IR (KBr disk, cm^{-1}) 3372, 2972, 1952, 1468, 1362, 1244, 1136; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (1H, s), 1.83 (2H, brs), 1.48 (3H, s),1.46 (3H, s), 1.35 (6H, s), 1.23 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.80, 103.48, 72.86, 69.90, 32.95, 32.45, 31.59, 29.92, 29.82; EI HRMS *m/e* calcd for $C_{13}H_{22}O$ (M − H_2O^+) 194.1655, found 194.1694.

(4*Z*)-3-*tert*-Butyl-2,6-dimethyl-1,4-heptadiene-3,6-diol (14d): IR (KBr disk, cm^{-1}) 3196, 2972, 1486, 1364, 1172, 1100; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (1H, d, J = 13.4 Hz), 5.44 (1H, d, J = 13.2 Hz), 5.05 (1H, dq, J = 1.7, 1.2 Hz), 5.02 (1H, dq, J = 1.7, 1.5 Hz), 1.86 (3H, dd, J = 1.5, 1.2 Hz), 1.40 (3H, s), 1.35 (3H, s), 1.00 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.89, 135.87, 133.04, 113.84, 80.34, 72.19, 38.69, 31.59, 30.10, 25.81, 22.78; EI HRMS *m/e* calcd for $C_{13}H_{22}O$ (M − H_2O^+) 194.1655, found 194.1645.

Photosensitized Oxygenation of 11e. Following the general procedure of photosensitized oxygenation, **11e** (475 mg, 1.62 mmol), TPP (10 mg, 0.016 mmol), and triphenylphosphine (840 mg, 320 mmol, and after oxidation 420 mg, 1.60 mmol) in dichloromethane (8 mL) gave crude oxygenated products. Following the general procedure of desilylation, the oxygenated products and TBAF (562 mg, 1.92 mmol) in THF (8 mL) gave **13e** (240 mg, 74% for two steps) and **14e** (26 mg, 8% for three steps) after the usual workup and column chromatography (from 33% to 80% ethyl acetate in hexane).

13e = 16.

(3*Z*)-5-Isopropyl-2,6-dimethyl-3-heptene-2,5,6-triol (14e): IR (KBr disk, cm^{-1}) 3416, 3248, 2980, 1478, 1358, 1166, 1054; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (1H, d, J = 13.2 Hz), 5.51 (1H, d, J = 13.2 Hz), 5.07 (1H, m), 5.03 (1H, dq, J = 1.6, 1.5 Hz), 2.50 (1H, brs), 1.91 (3H, dd, J = 1.5, 1.4 Hz), 1.40 (3H, s), 1.35 (3H, s), 1.27 (3H, s), 1.24 (3H, s);^{13}C NMR (100 MHz, $CDCl_3$) δ 150.60, 136.73, 131.32, 114.01, 80.44, 75.35, 72.10, 31.25, 30.17, 25.38, 24.91, 22.13; FAB HRMS *m/e* calcd for $C_{12}H_{23}O_3$ (M + H^+) 215.1641, found 215.1651.

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Supporting Information Available: Full details of the crystal structure of **1e** and 400 MHz ^{1}H NMR and ^{13}C NMR spectra of **1d**, **3d**, **4d**, **10d**, **13d**, and **14d** (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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