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Homogeneous Decatungstate-Catalyzed Photooxygenation of Tetrasubstituted Alkenes: A Deuterium Kinetic Isotope Effect Study

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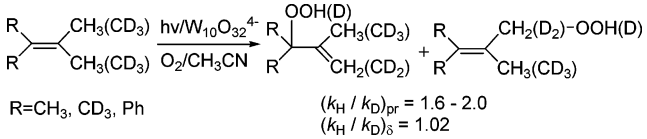

The decatungstate $W_{10}O_{32}^{4-}$ homogeneous photocatalyzed oxygenation of tetrasubstituted alkenes has been mechanistically studied. In all cases, allylic hydroperoxides are the major products. The primary inter- and intramolecular as well as the remote δ-secondary deuterium kinetic isotope effects for the photooxidation of the 2,3-dimethyl-2-butene and 1,1,1-trideuterio-7-methyl-2-(trideuteriomethyl)octa-2,6-diene along with product analysis suggest a hydrogen abstraction in the rate-determining step. For comparison, singlet oxygen photosensitized oxidations of the above substrates were also studied.

Introduction

Photocatalyzed reactions induced by polyoxometalates[1,2] and especially by the decatungstate[2] anion $W_{10}O_{32}^{4-}$, in the presence of molecular oxygen, lead to the oxygenation of virtually any organic substrate.[2−15] It is generally accepted that illumination of $W_{10}O_{32}^{4-}$ leads to the formation of a charge-transfer excited state $W_{10}O_{32}^{4-*}$ that decays in less than 30 ps to an extremely reactive transient,[11] with a distorted geometry[12] with respect to $W_{10}O_{32}^{4-}$, which has been designated as wO.[2,11,12] The wO reactivity provides an interesting new mechanistic tool for studies of light-induced oxidations, since it proceeds exclusively via free-radical pathways.[10b]

In general, the two well-established mechanisms of photosensitized oxidations classified as Type I and Type II, according to the initial interaction of the excited sensitizer (Sen*), are shown in Scheme 1.[16]

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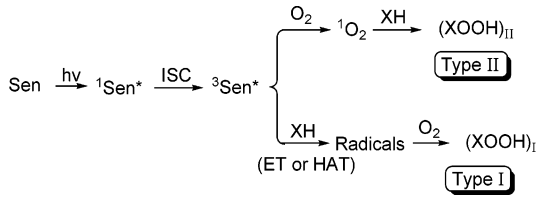
SCHEME 1. Type I and Type II Mechanisms in Photosensitized Oxygenations



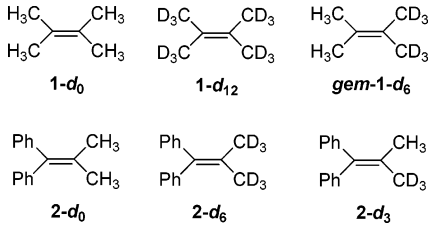
Sen=Sensitizer, XH=Alkene, ET=Electron Transfer, HAT=Hydrogen Atom Transfer

In Type I reactions, the excited sensitizer reacts directly with the substrate XH or the solvent to give electron transfer (ET)[17] or hydrogen atom transfer (HAT),[18] producing radicals. These radicals then react with molecular oxygen to give oxygenated products. In the alternative Type II mechanism, the excited sensitizer interacts directly with molecular oxygen by energy transfer to produce singlet molecular oxygen ($^1O_2$,$^1\Delta_g$).[19] Subsequently, this reactive species adds to a variety of substrates giving oxygenated products. In the case of $W_{10}O_{32}^{4-}$ as the photocatalyst, hydrogen atom transfer (HAT)[2,7−14] and electron transfer (ET)[10a] pathways can compete in the overall process, both leading to the formation of peroxides. Thus, in the oxidation of organic substrates, such as alkanes,[7a,8a,13] alkylarenes,[14b] alcohols,[4,6] arylalkanols,[14a] and cycloalkenes,[7b] a HAT mechanism has been reported. However, in the decatungstate-catalyzed photooxygenation of alkenes,[10a] both ET and HAT mechanisms have been proposed, with the ET being the predominant with long irradiation times and high alkene concentrations.

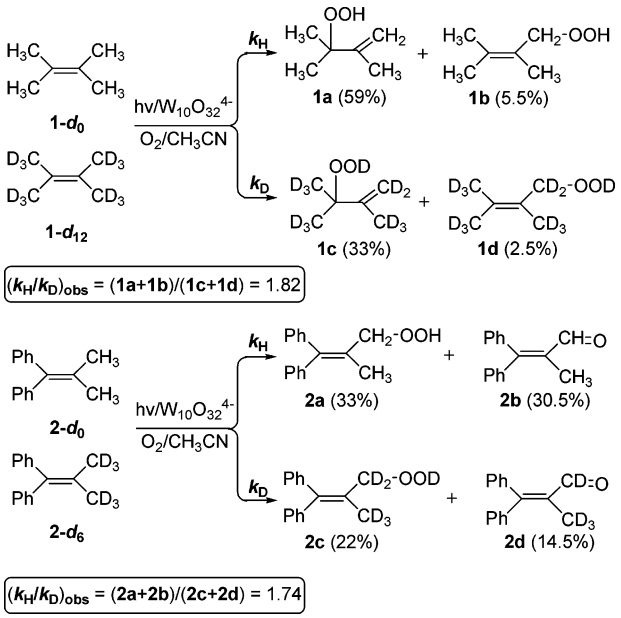
Results and Discussion

Following our general interest in the photosensitized oxygenation of alkenes in the presence of molecular oxygen,[20] we present here a detailed mechanistic study on the decatungstate-photocatalyzed oxygenation of symmetrically tetrasubstituted alkenes in the presence of O_2. This was accomplished by determining the intra- and intermolecular kinetic isotope effects (KIEs) of the title reaction. Since KIEs have not been previously measured, their values may shed more light on the factors controlling the formation of the alkene-oxygenated products. For this purpose, we have investigated the $W_{10}O_{32}^{4-}$-catalyzed photooxygenation of a series of perprotium and deuterium-labeled tetrasubstituted alkenes such as: **1-*d*$_0$**, **1-*d*$_{12}$**, ***gem*-1-*d*$_6$**, **2-*d*$_0$**, **2-*d*$_6$**, and **2-*d*$_3$**, shown in Chart 1. It is noteworthy that the symmetrically tetrasubstituted 2,3-dimethylbut-2-enes (TMEs) **1-*d*$_0$**, **1-*d*$_6$**, and **1-*d*$_{12}$** have been previously used as efficient probes to determine the mechanism of several enophiles, such as singlet oxygen ($^1O_2$),[20] triazolinediones (TADs),[21] and nitrosoarenes (ArNO).[22]

CHART 1. Tetrasubstituted Alkenes Used for the Decatungstate-Photocatalyzed Oxygenations



SCHEME 2. Intermolecular KIEs in the Decatungstate Photooxygenation of TMEs



The homogeneous decatungstate-photocatalyzed oxygenations of the symmetrically substituted, deuterium-labeled alkenes were carried out as follows: A solution of the alkene (5.0×10^{-3} M) and $W_{10}O_{32}^{4-}$ (5×10^{-5} M), in oxygen-bubbled acetonitrile, was irradiated with a Variac Eimac 300 W Xenon lamp ($\lambda >$ 300 nm) as the light source. To avoid deactivation of the photocatalyst, due to the formation of a long-lived complex between the catalyst and alkenes at higher alkene concentrations (1×10^{-1} M),[10a] lower alkene concentrations (5.0×10^{-3} M) were used in this work. The product distribution was measured by integration of the appropriate peaks in the ^{1}H NMR spectra, as well as by GC analysis of the allylic alcohols produced from the reduction of the initially formed allylic hydroperoxides by triphenylphosphine. The intermolecular KIEs were obtained by the competitive oxidation of equimolar mixtures of the TMEs **1-*d*$_0$** vs **1-*d*$_{12}$** and 2-methyl-1,1-diphenylpropene **2-*d*$_0$** vs **2-*d*$_6$** in separate experiments (Scheme 2). For better accuracy, intra- and intermolecular KIEs were obtained by keeping the conversion of each competition reaction lower than 40%.

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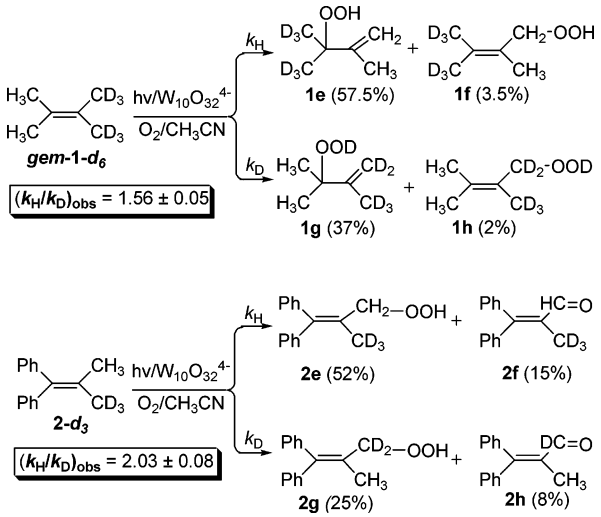
SCHEME 3. Intramolecular Kinetic Isotope Effects in the Decatungstate Photooxygenation of *gem*-1-d_6 and 2-d_3

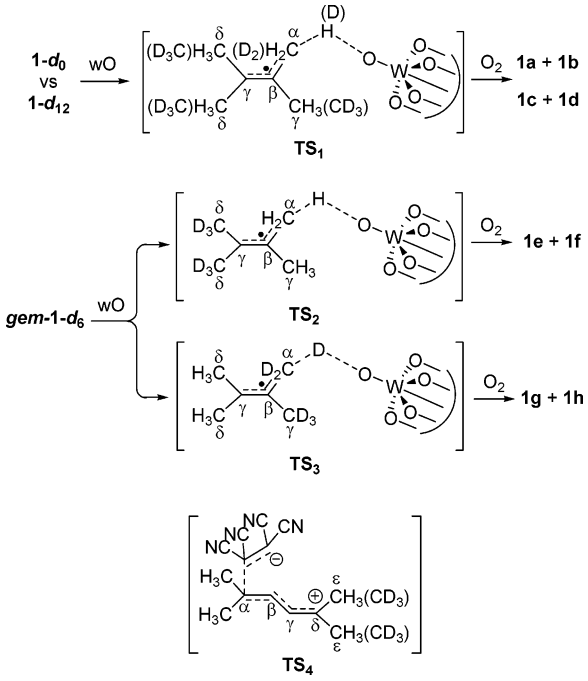


Irradiation of **1-d_0** vs **1-d_{12}** at 5−10 °C gave the corresponding tertiary hydroperoxides **1a** and **1c** as the major products, in about 92% relative yield. The hydroperoxide ratio of (**1a** + **1b**)/(**1c** + **1d**), determined by ^{1}H NMR, is proportional to the observed intermolecular isotope effect and was found to be $(k_H/k_D)_{obs}$ = 1.82 ± 0.03. The isotopic ratio may also be determined from the integration of the well-separated (capillary column) GC signals of the allylic alcohols protio vs deuterium after reduction of the initially formed allylic hydroperoxides by triphenylphosphine, as well as from the remaining alkenes[23] **1-d_0** and **1-d_{12}** (see the Supporting Information). It is interesting to mention that the capillary column (60 m, 5% phenyl methylpolysiloxane) was capable of separating with baseline resolution of the protio allylic alcohol and starting alkene from their corresponding deuterium-labeled analogues.

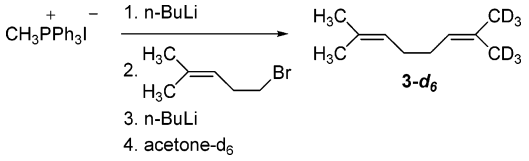
The photooxidation of the mixture **2-d_0** vs **2-d_6**, according to the above procedure, gave apart from the primary hydroperoxides **2a** and **2c** substantial amounts of the aldehydes **2b** and **2c**, as well as small amounts of benzophenone and epoxides (less than 10% relative yield). The photooxygenation results with decatungstate as a photocatalyst are shown in Scheme 2.

Again in this case, a substantial primary intermolecular isotope effect was measured and found to be $(k_H/k_D)_{obs}$ = 1.74 ± 0.03. This isotope effect was determined from the ratio of protio vs deuterium hydroperoxides and aldehydes (**2a** + **2b**)/(**2c** + **2d**), as well as from the ratio of the remaining alkenes **2-d_0** vs **2-d_6**, by the use of gas chromatography. Aldehydes **2b** and **2d** were formed due to further oxidation and/or decomposition[24] of the initially formed primary hydroperoxides **2a** and **2c**, respectively. When the photooxygenation of **2-d_0** vs **2-d_6** was run in the presence of 2 equiv of Et_3SiH, the corresponding relative yield of the primary hydroperoxides **2a** and **2c** increased from 55% to 90%. In this case, the ratio of protio and deuterium hydroperoxides and aldehydes (**2a** + **2b**)/(**2c** + **2d**), which is proportional to the intermolecular KIE, was found to be $(k_H/k_D)_{obs}$ = 1.79, similar (within experimental error) to the one found in the absence of Et_3SiH. The increase of the primary hydroperoxides was attributed previously[14b] to the fact that the corresponding peroxy radical intermediates are trapped by Et_3-SiH.[25] Also, the primary KIEs were measured in three different conversions, all of them lower than 40%, and was found to be in the range of 1.74−1.79. These results suggest that the aldehyde formation, which is the result of partial hydroperoxide decomposition, has a negligible influence in the overall primary intermolecular KIE of this oxidation.

SCHEME 4. Proposed Transition States in the Decatungstate Allylic Hydrogen Abstraction and in the Cycloaddition of TCNE to 2,4-Hexadiene



SCHEME 5. Synthesis of 1,1,1-Trideuterio-7-methyl-2-(trideuteriomethyl)octa-2,6-diene (3-d_6)



The primary isotope effects suggest that a C− H(D) bond cleavage occurs in the rate-determining step of the oxygenation.[26,27] The relatively modest, for organic reactions, value of the primary isotope effects, measured in these reactions [$(k_H/k_D)_{obs}$ = 1.74−1.82], may be attributed either to a bent transition state (i.e., nonlinear hydrogen atom transfer)[28] and/or to an early transition state,[29] in which C−H(D) bond cleavage is not extensively developed.

It was previously reported that the dicyanoanthracene (DCA)-sensitized photooxygenation of phenyl-substituted alkenes leads

(23) For the equation used to calculate the isotope effect, see: Stratakis, M.; Orfanopoulos, M.; Foote, C. S. *J. Org. Chem.* **1998**, *63*, 1315−1318.
(24) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871−3877.
(25) For Et_3SiH as a hydrogen donor, see: (a) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229−1251.. (b) Chatgilialoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67−112. (c) Lucarini, M.; Marchesi, E.; Pedulli, F. G.; Chatgilialoglu, C. *J. Org. Chem.* **1998**, *63*, 1687−1693.and ref 14b.
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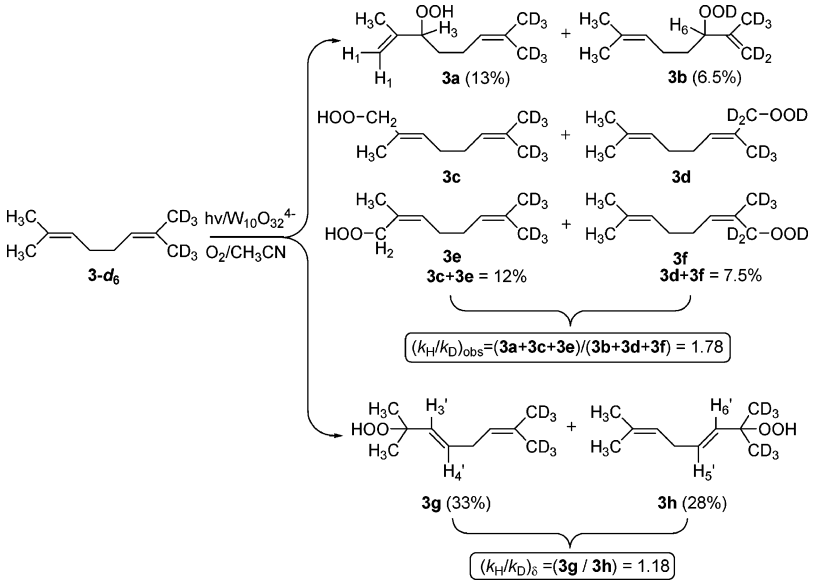
(28) (a) More, O'Ferrall, R. A. *J. Chem. Soc.* **1970**, *13*, 785−790. (b) Karabatsos, G. J.; Tornaritis, M. *Tetrahedron Lett.* **1989**, *30*, 5733−5736.
(29) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334−338.

SCHEME 6. Intramolecular Kinetic Isotope Effects in the Decatungstate Photooxygenation of 3-d_6



mainly to benzophenone and the corresponding epoxide of the alkene by an electron-transfer mechanism.[17] Benzophenone was the cleavage product from the decomposition of the corresponding 3,3-dimethyl-4,4-diphenyl-1,2-dioxetane. In this work, the formation of small amounts of benzophenone and epoxide products through the decatungstate photocatalyzed oxygenation of **2-d_0** indicates that the electron-transfer mechanism possesses a minor contribution to the overall oxidative process.

To assess further the extent of bond making and bond breaking in the transition state, we measured the intramolecular isotope effects of the sensitized photooxygenations of the two alkenes, ***gem*-1-d_6** and **2-d_3**, in separate experiments, under the experimental conditions described above (Scheme 3). In the case of ***gem*-1-d_6**, the product ratio (**1e** + **1f**)/(**1g** + **1h**), is proportional to the isotopic ratio $(k_H/k_D)'_{obs}$. ^{1}H NMR integrations of the **1e** vinyl protons at 4.98−5.02 ppm and the **1f** methylene protons at 4.05 ppm, as well as the integrals at 1.39 and 1.85 ppm of the two methyl groups of **1g** and **1h**, correspondingly, determine the intramolecular primary isotope effect ratio, which is equal to $(k_H/k_D)'_{obs} = 1.56 \pm 0.05$. Similarly, the proper proton integrations determine the product ratio (**2e** + **2f**)/(**2g** + **2h**), which is proportional to the intramolecular primary isotope effect $(k_H/k_D)'_{obs}$. This isotopic ratio was found to be $(k_H/k_D)'_{obs} = 2.03 \pm 0.08$.

These results, primary intramolecular $(k_H/k_D)'_{obs} = 1.56-2.03$ and primary intermolecular isotope effect, $(k_H/k_D)_{obs} = 1.74-1.82$, suggest an extensive C−H(D) bond cleavage in the rate-determining step,[26,27] leading to a radical intermediate.[7b] This radical intermediate is then trapped by molecular oxygen to form mainly allylic hydroperoxides and further oxidation products such as aldehydes. This conclusion, derived from the present isotope effect studies of tetrasubstituted alkenes, is in agreement with previous studies of decatungstate-sensitized oxygenation of cycloalkenes.[3b,7b,30]

A further analysis of the observed isotope effects provides an estimate of the remote KIEs, which contribute to the overall reaction rates. For example, in both inter- and intramolecular competitions of **1-d_0** vs **1-d_{12}** and ***gem*-1-d_6** (Scheme 4), the observed isotope effects can be factored into a primary ($k_H/k_D)_{pr}$, a α-secondary $[(k_H/k_D)_\alpha]^2$, a γ-secondary $[(k_H/k_D)_\gamma]^3$, and a δ-secondary isotope effect $[(k_H/k_D)_\delta]^6$ and $[(k_H/k_D)_\delta]^{-6}$ respectively (Scheme 4), according to eqs 1 and 2.[26]

$$(k_H/k_D)_{obs} = [(k_H/k_D)_{pr}]\cdot[(k_H/k_D)_\alpha]^2\cdot[(k_H/k_D)_\gamma]^3\cdot[(k_H/k_D)_\delta]^6 = 1.83 \quad (1)$$

$$(k_H/k_D)'_{obs} = [(k_H/k_D)_{pr}]\cdot[(k_H/k_D)_\alpha]^2\cdot[(k_H/k_D)_\gamma]^3\cdot[(k_H/k_D)_\delta]^{-6} = 1.56 \quad (2)$$

Although the primary, the α-secondary, and the γ-secondary isotope effects in both cases (**1-d_0** vs **1-d_{12}** and ***gem*-1-d_6**) have contributions that are in the same direction (i.e., they all favor hydrogen abstraction), the δ-secondary isotope effect favors hydrogen abstraction in **1-d_0** vs **1-d_{12}** but deuterium abstraction in ***gem*-1-d_6** (inverse contribution). We therefore propose that the small difference in the observed, overall isotope effects in the competitions **1-d_0** vs **1-d_{12}** $[(k_H/k_D)_{obs} = 1.82]$ and ***gem*-1-d_6** $[(k_H/k_D)'_{obs} = 1.56)]$ may be attributed to the opposite contributions of the δ-secondary isotope effects. Assuming that $(k_H/k_D)_{pr}$, $(k_H/k_D)_\alpha$, and $(k_H/k_D)_\gamma$ are the same for **1-d_0** vs **1-d_{12}** (intermolecular) and ***gem*-1-d_6** (intramolecular) competitions, the ratio of eq 1/eq 2 gives $[(k_H/k_D)_\delta]^{12} = 1.82/1.56 = 1.17$, which corresponds to a $(k_H/k_D)_\delta \approx 1.02$ per deuterium atom. This value is reasonable for a remote secondary isotope effect[31a] and comparable to a normal remote ϵ-secondary isotope effect, found previously in the dipolar cycloaddition of TCNE to 2,4-hexadiene (**TS$_4$**, Scheme 4).[31b]

To test this mechanism and directly obtain the remote isotope effect contribution to the reaction rate, we designed substrate **3-d_6** (1,1,1-trideuterio-7-methyl-2-(trideuteriomethyl)octa-2,6-diene). In this substrate, unlike TME-d_6 (***gem*-1-d_6**), the geminal methyls are placed apart from the deuterium methyl groups. This compound was prepared according to the procedure shown in Scheme 5.

The photocatalyzed oxidation of **3-d_6** was carried out under the above-described reaction conditions. In order to avoid the

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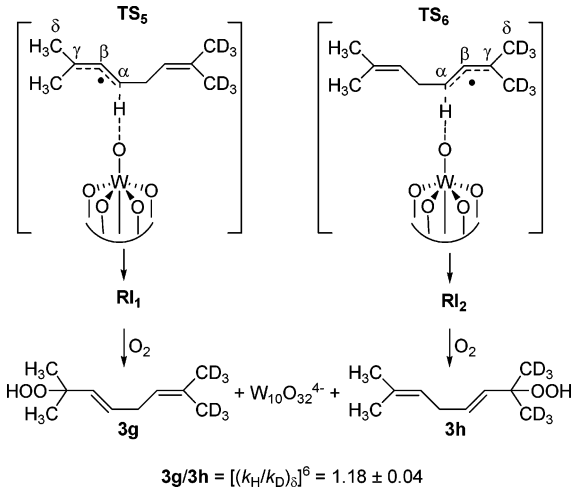
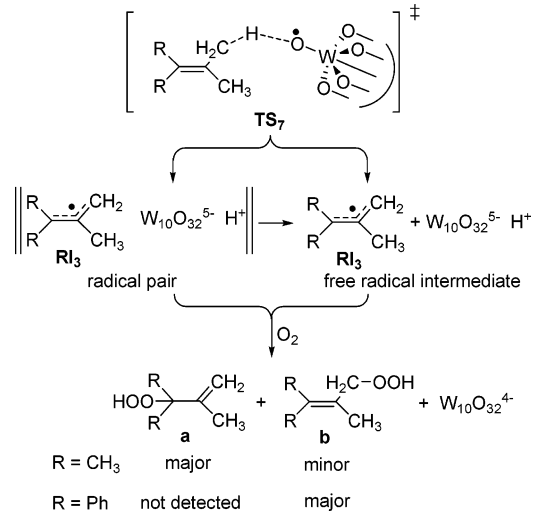
(31) (a) Shiner, V. J.; Kritz, G. S., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 2643−2645. (b) Vassilikogiannakis, G.; Orfanopoulos, M. *Tetrahedron Lett.* **1996**, *37*, 3075−3078.

SCHEME 7. δ-Secondary Kinetic Isotope Effect in the Decatungstate Photooxidation of 3-d_6



SCHEME 8. Transition State of the Decatungstate-Photosensitized Oxygenation of the Alkenes 1 and 2



formation of the dihydroperoxides observed in previous studies of similar substrates with singlet oxygen as the enophile,[32] the reactions were kept at low conversions (<10%). The product distribution was measured by integrating the appropriate peaks in the ^{1}H NMR spectra. These results are summarized in Scheme 6.

Irradiation of **3-d_6** for 30 s at 5 °C afforded the corresponding allylic tertiary hydroperoxides **3g** and **3h** as the major products (61% relative yield), along with primary, **3c**−**f**, and secondary, **3a** and **3b**, hydroperoxides in 19.5% and 19.5% relative yields. No dihydroperoxides were observed during the photocatalyzed reaction. The ratio of the tertiary hydroperoxides **3g**/**3h** is directly proportional to a remote δ-secondary isotope effect, which was calculated to be $(k_H/k_D)_\delta = 1.18 \pm 0.04$, (1.03 per deuterium atom). This **3g**/**3h** ratio was determined by ^{1}H NMR integration of the two methyls at 1.33 ppm for **3g** and the two methyls at 1.71 ppm for **3h** (Scheme 6). This small δ-secondary isotope effect supports the formation of radical intermediates, **RI$_1$** and **RI$_2$**, in the rate-determining step through the transition states **TS$_5$** and **TS$_6$** (Scheme 7). This value, obtained directly from the intramolecular isotopic competition in substrate **3-d_6**, is very similar, within experimental error, to the value of δ-secondary isotope effect calculated from eq 1 and eq 2, in the case of substrates **1-d_0** vs **1-d_{12}** and ***gem*-1-d_6**. This is also comparable to a normal remote secondary isotope effect obtained previously in other systems, where dipolar transition states were proposed $[(k_H/k_D)_{secondary} = 1.05-1.10$ per deuterium$]$.[26,27,33] Moreover, the hydroperoxides ratio of (**3a** + **3c** + **3e**)/(**3b** + **3d** + **3f**) is proportional to the observed intramolecular isotope effect, which was calculated to be $(k_H/k_D)'_{obs} = 1.78 \pm 0.07$. This KIE is the result of the combination of both the primary and the α-secondary isotope effects.

The significant inter- and intramolecular primary isotope effects in the decatungstate-catalyzed photooxygenation of symmetrically tetrasubstituted alkenes support a hydrogen abstraction in the rate-determining step, as shown by transition state **TS$_7$** (Scheme 8). The mechanism of this reaction, based on the KIEs and literature results,[2,3,7,10] can be summarized as follows: In the first step of the overall reaction and under irradiation conditions, the decatungstate anion changes into the established relatively long-lived excited intermediate wO.[2,10−12] This reactive intermediate abstracts an allylic hydrogen from the tetrasubstituted alkene (**TS$_7$**), producing the corresponding reduced forms of $H^+W_{10}O_{32}^{5-}$ and/or $HW_{10}O_{32}^{4-}$ and a radical intermediate (**RI$_3$**).[2,3,7,13] These radicals can exist either as a solvent cage radical pair or as a free-radical intermediate (Scheme 8). However, the radical pair can also diffuse freely through the solution to the corresponding free-radical intermediate.[13c] From both radical intermediates the one-electron-reduced species of decatungstate reoxidizes in the presence of O_2 into $W_{10}O_{32}^{4-}$ and the corresponding hydroperoxide.[3,7,10] In a previous study, the adsorption spectra of the decatungstate during the alkene photooxygenation reaction showed the formation of both one- and two-electron reduced forms of the decatungstate, with the former as the major in low irradiation time and low substrate concentration.[10a] It is noteworthy that in the present work all the reactions were carried out in less than 15 min irradiation time and the alkene concentrations were as low as 5.0×10^{-3} M. The continuous flow of O_2 into the reaction mixture during the irradiation enhances the reoxidation pathway, regenerating the decatungstate anion. Under these conditions and according to the present isotope effect results found in the decatungstate-photocatalyzed oxygenation of tetrasubstituted alkenes, a HAT mechanism is the predominant.

As we mentioned previously in this work, unlike the alkyl-substituted alkenes **1-d_0**, **1-d_6**, and **1-d_{12}**, the photooxidations

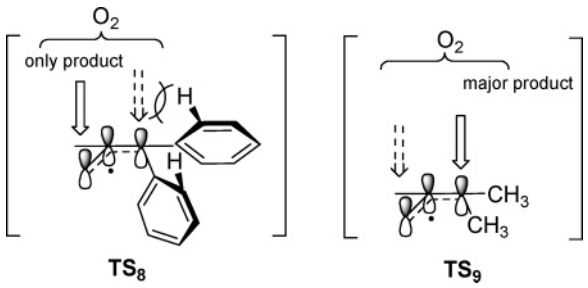
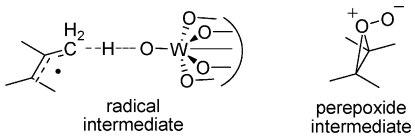


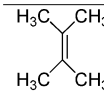
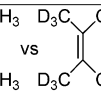
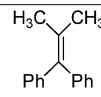
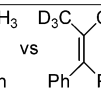
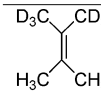
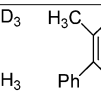
FIGURE 1. Regioselective addition of molecular oxygen due to steric and electronic factors.

(32) Tanielian, C. Ghaineaux, J. *Photochem. Photobiol.* **1978**, *28*, 487−492.

(33) (a) Shiner, V. J.; Murr, B. L.; Heineman, G. *J. Am. Chem. Soc.* **1963**, *85*, 2413−2416. (b) Shiner, V. J.; Byddnbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418−426.

TABLE 1. Inter- and Intramolecular KIEs in Decatungstate and Singlet Oxygen Photosensitized Oxidations of Tetrasubstituted Alkenes



	k_H / k_D values					
	Intermolecular				Intramolecular	
enophile	 **1-d_0**	 **1-d_{12}**	 **2-d_0**	 **2-d_6**	 ***gem*-1-d_6**	 **2-d_3**
wO	1.82		1.74		1.56	2.03
$^1O_2$	1.02		1.03		1.40[20]	1.02

of diarylalkenes **2-d_0**, **2-d_3**, and **2-d_6** gave mainly primary hydroperoxides. Examination of the possible transition states leading to the primary (when R is phenyl) and the tertiary (when R is methyl) hydroperoxides may provide a satisfactory explanation (Figure 1). In transition state **TS_8**, the oxygen approach on the terminal carbon, leading to the primary hydroperoxide, is expected to be more favorable than the attack on the tertiary carbon, where the nonbonding interactions between the large phenyl groups (substantially out of the radical plane) and the incoming oxygen are relatively stronger. In addition, the observed regioselective addition of molecular oxygen shown by **TS_8**, may also be attributed to electronic factors. The two phenyl groups next to the conjugated allyl-radical moiety, although not coplanar to the radical plane, must provide significant stabilization to this radical through resonance. This effect decreases kinetically the reactivity toward molecular oxygen,[34] compared to the other terminal radical carbon, where this resonance stabilization is absent. However, in transition state **TS_9**, where the previous relative steric interactions and electronic effects are diminished,[34] the major product is the tertiary hydoperoxide. Thus, both stereo- and electronic effects lead to the observed regioselective formation of primary hydroperoxides for the diarylalkenes, whereas in the case of TMEs, the major products are the tertiary allylic hydroperoxides.

For comparison purposes, we also measured the inter- and intramolecular isotope effects in the singlet oxygen $^1O_2$ ene reaction with alkenes **1-d_0**, **1-d_{12}**, **2-d_0**, **2-d_6**, ***gem*-1-d_6**, and **2-d_3**. According to previous mechanistic studies,[20−22] based on the inter- and intramolecular isotope effects of TMEs reactions with singlet oxygen,[20] a stepwise mechanism with an irreversible formation of a singlet oxygen−alkene perepoxide intermediate has been established (Table 1). Later on, Singleton and co-workers, based on theoretical and experimental work, proposed a two-step no-intermediate mechanism with a rate-limiting transition state, resembling that for the formation of a perepoxide intermediate in the initially proposed stepwise process.[35] In the present work, the isotope effect values of the decatungstate-photocatalyzed reaction with alkenes leading to allylic hydroperoxides are completely different than those of singlet oxygen reactions with the same substrates (Table 1). This is clearly demonstrated by the photooxygenation of substrates **1-d_0** vs **1-d_{12}**. In the case of decatungstate as the catalyst, a substantial primary intermolecular isotope effect $k_H/k_D = 1.82$ was found in contrast to the negligible or absent $k_H/k_D = 1.02$ when the photosensitized singlet oxygen was the reactive species. Similarly, in the case of **2-d_3**, a substantial intramolecular isotope effect $k_H/k_D = 2.03$ was obtained with wO/O_2 as the oxidizing system, whereas again a negligible $k_H/k_D = 1.02$ was measured with $^1O_2$. These isotope effect results also confirm the otherwise previously known different mechanistic routes of these two oxidizing systems.

Conclusion

In conclusion, the primary and the normal secondary kinetic isotope effects, as well as the product analysis of the $W_{10}O_{32}^{4-}$ photocatalytic oxidations of symmetrically tetrasubstituted deuterium-labeled alkenes, support an allylic hydrogen atom abstraction in the limiting step. In the decatungstate-catalyzed photooxygenation of tetrasubstituted alkenes the allylic hydroperoxides are formed as the only or major products. This result is consistent with a HAT mechanism. In the case of diaryl-substituted olefins, a part of the dominant HAT mechanism, the small amounts of epoxides or cleavage products are attributed to a simultaneous but less extended electron-transfer mechanism. In the case of substrate **3-d_3**, the remote δ-secondary kinetic isotope effect indicates again that hydrogen abstraction occurs in the rate-determining step. With simple alkenes, the decatungstate catalyst abstracts an allylic hydrogen from the tetrasubstituted alkene in the rate-determining step, producing the corresponding reduced forms $H^+W_{10}O_{32}^{5-}$ and/or $HW_{10}O_{32}^{4-}$ together with a radical intermediate. These radicals, which can exist as a radical pair and/or as free radical intermediates, are trapped by molecular oxygen producing the $W_{10}O_{32}^{4-}$ and the corresponding allylic hydroperoxides.

Experimental Section

General Procedure for the Decatungstate Catalytic Photooxidations. ^1H NMR and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$. The catalytic photooxidations were monitored by using gas chromatography with a 60 m capillary column (5% phenyl methylpolysiloxane) and ^1H NMR spectros-

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(35) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 1319−1328.

copy. Catalytic photooxidations were achieved with a Xenon Variac Cermax 300 W lamp. Flash chromatography was carried out on SiO_2 (silica gel 60, SDS, 230−400 mesh ASTM). Drying of organic extracts during workup of reactions was performed over anhydrous $MgSO_4$. Evaporation of solvents was accomplished with a rotary evaporator. The solvent used was HPLC-grade acetonitrile, sample size was 4 mL, and the concentrations of $[Bu_4N]_4W_{10}O_{32}$ and alkenes were 5×10^{-4} and 5×10^{-3} M, respectively. The photooxidations were carried out in a quartz cell. Samples were irradiated for 30 s to 15 min with oxygen bubbling. During irradiation, the reaction mixtures were cooled with ice water and monitored by gas chromatography. Acetonitrile was removed under reduced pressure. Tetrabutylammonium decatungstate was synthesized and purified by literature procedures.[36] The ^{1}H and ^{13}C NMR spectroscopic data for **1-*d*$_0$**, **1-*d*$_6$**, **1-*d*$_{12}$**, **2-*d*$_0$**, **2-*d*$_3$**, **2-*d*$_6$**, and **3-*d*$_6$** are given below:

2,3-Dimethylbyt-2-ene (1-*d*$_0$). This compound is commercially available.^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66 (s, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.4, 20.3.

3-Hydroxy-2,2-dimethyl-3-(trideuterio)methyl-3-hydroxybutyric Acid-*4,4,4*-*d*$_3$. This β-hydroxy acid was prepared according to the procedure reported in the literature.[37] A flame-dried, 500 mL, three-necked round-bottomed flask, equipped with a magnetic stirrer, reflux condenser, and an additional funnel, was charged with 14 mL (100 mmol) of dry diisopropylamine in dry THF (100 mL) under N_2. Cooling of the solution to −78 °C was followed by dropwise addition of 100 mmol of *n*-BuLi, (62.5 mL 1.6 M in *n*-hexane). Following the completion of the addition, the mixture was left for 1 h at room temperature and then cooled to −78 °C again. Next, 4.41 g (50 mmol) of isobutyric acid (1 M solution in dry THF) was added dropwise. After the completion of the addition, the mixture was left for 1 h at room temperature and then cooled to 0 °C. Then, 3.7 mL (50 mmol) of acetone-d_6 was added as a 2.5 M solution in dry THF. After being stire at room temperature for 12 h, the reaction mixture was poured on ice and transferred to a separatory funnel. Following several extractions with Et_2O, the aqueous layer was acidified with 6 N HCl, and the aqueous mixture was extracted with Et_2O (5 × 50 mL). The combined extracts were dried and evaporated to afford 6.5 g of β-hydroxy acid (85% yield), which was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.01 (brs, 2H, −COOH + −OH), 1.26 (s, 6H).

3,3-Di(trideuterio)methyl-4,4-dimethyl-β-lactone. A one-necked, 500 mL, round-bottomed flask equipped with a magnetic stirrer was charged with 1.52 g (10 mmol) of the above β-hydroxy acid in 60 mL of dry pyridine. To this solution, after cooling to 0−5 °C, was added 3.8 g (20 mmol) of *p*-toluenesulfonyl chloride. After the reaction mixture was stirred for 10 min, the flask was tapped and left in the freezer for 12 h. The reaction mixture was then poured on crushed ice (four to five times larger in volume) and extracted with Et_2O (5 × 50 mL). The combined organic layers were washed with aq satd $NaHCO_3$ and H_2O, dried, and evaporated to afford 0.7 g (52% yield) of the β-lactone. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 6H).

1,1,1-(Trideuterio)methyl-3-methyl-2-(trideuteriomethyl)but-2-ene (*gem*-1-*d*$_6$). A Schlenk flask which was connected to a rotaflo trap, cooled at −78 °C, was charged with 0.5 g (3.72 mmol) of the above β-lactone. The flask was heated at 160 °C with concomitant decomposition of the β-lactone to the deuterated alkene and CO_2. With the help of a slow N_2 stream, 0.26 g of the alkene (77% yield) was collected in the trap. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.4, 123.2, 20.3, 19.4 (septet, J_{CD} = 19 Hz).

1,1,1,4,4,4-Hexadeuterio-2,3-bis(trideuteriomethyl)-2,3-butanediol (Pinacol-*d*$_{12}$). Pinacol hydrate was prepared according to the literature procedure.[37b] A flame-dried, 100 mL, round-bottomed flask, equipped with a magnetic stirrer, reflux condenser, and an addition funnel, was charged with 1.6 g (65.8 mmol) of magnesium turnings and 16 mL of dry benzene. A solution of mercuric chloride (1.8 g) in acetone-d_6 (10 mL, 138 mmol) was added gradually through the addition funnel. When the first vigorous reaction was over, a mixture of 5.2 mL of acetone-d_6 and 4 mL of dry benzene was added, and the flask was heated on a water bath until no further reaction was evident (about 3 h). Through the addition funnel was then added 4 mL of H_2O, and the reaction mixture was heated for another 1 h, cooled to about 50 °C, and filtered. The solid was returned to the flask and heated with fresh benzene (10 mL) to dissolve any remaining pinacol. The combined filtrates were then condensed to one-half in order to remove the acetone; the remaining benzene solution was treated with 6 mL of H_2O and cooled to 10−15 °C. Pinacol hydrate was precipitated, filtered, and washed with benzene to afford 6.5 g (43% yield based on the magnesium used). The pinacol hydrate was then dehydrated and distilled to yield 2.5 g anhydrous pinacol. MS m/z = 130 (100, m/z = 65).

1,1,1,4,4,4-Hexadeuterio-2,3-bis(trideuteriomethyl)but-2-ene (1-*d*$_{12}$). A Schlenk flask which was connected to a rotaflo trap, cooled to −78 °C, was charged with 2.2 g (16.95 mmol) of the diol and 2.52 g of ethyl orthoformate. The flask was heated from 125 to 140 °C over 8 h, and 1.9 mL ethanol was distilled. The remaining colorless liquid (2-ethoxy-4,4,5,5-tetramethyl-1,3-dioxolane-d_{12}) was heated at 150−160 °C for 10 h, during which time CO_2 was evolved and 2.2 mL of distillate was collected. This distillate, which was mainly TME-d_{12} and ethanol, was further purified by preparative GC to afford 800 mg (6.15 mmol) **1-*d*$_{12}$**. ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.4, 19.4 (septet, J_{CD} = 19 Hz). MS m/z = 96 (100, m/z = 46).

1,1-Diphenyl-2-methylpropene (2-*d*$_0$). This compound was prepared according to the procedure described below:

1,1-Diphenyl-2-methyl-1-propanol. This compound was prepared by Grignard reaction of 3.6 g (20.0 mmol) of benzophenone, 0.85 g (35 mmol) of Mg, and 4 g (24 mmol) of isopropyl iodide, in dry ether, under argon atmosphere, at 0 °C. A total of 3.8 g of the tertiary alcohol (85% yield) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, 2H, J = 7.4 Hz), 7.59 (d, 2H, J = 7.3 Hz), 7.39 (t, 2H, J = 7.3 Hz), 2.85 (m, 1H), 0.92 (d, 6H, J = 6.7 Hz).

1,1-Diphenyl-2-methylpropene (2-*d*$_0$). The tertiary alcohol 1,1-diphenyl-2-methyl-1-propanol-d_0 (3.8 g) was heated at 120 °C, and after 1 h, 2.8 g of the tetrasubstituted alkene **1-*d*$_0$** (79% yield) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, 4H, J = 7.4 Hz), 7.21 (t, 2H, J = 7.3 Hz), 7.17 (d, 4H, J = 7.3 Hz), 1.83 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 138.8, 130.9, 129.7, 127.8, 125.9, 22.4. MS m/z = 208 (100, m/z = 208).

1,1-Diphenyl-(3,3,3-trideuterio-2-(trideuteriomethyl)propene (2-*d*$_6$). This compound was prepared according to the procedure described below:

1,1-Diphenyl-(3,3,3-trideuterio-2-(trideuteriomethyl)-2-propanol. This compound was prepared by the Grignard reaction of 0.7 g (3.0 mmol) of diphenylacetic methyl ester, 0.29 g (12 mmol) of Mg, and 0.56 mL (9 mmol) of CD_3I in dry ether, under argon atmosphere, at 0 °C. The tertiary alcohol was isolated after 4 h and directly heated in the presence of a catalytic amount of *p*-toluenesulfonic acid, producing the corresponding deuterium-labeled alkene **2-*d*$_6$** (0.3 g, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, 4H, J = 7.4 Hz), 7.21 (t, 2H, J = 7.3 Hz), 7.17 (d, 4H, J = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 138.8, 130.9, 129.7, 127.8, 125.9, 21.7 (septet, J_{CD} = 19 Hz). MS m/z = 214 (100, m/z = 214).

1,1-Diphenyl-3,3,3-trideuterio-2-methylpropene (2-*d*$_3$). This compound was prepared according to the procedure described below:

3,3-Diphenyl-2-methylpropenate methyl ester. This compound was prepared by the Wittig−Horner reaction. A solution of methyl

(36) Chemseddine, A.; Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M. *Inorg. Chem.* **1984**, *23*, 2609−2613.

(37) (a) Crank, G.; Eastwood, F. W. *Aust. J. Chem.* **1964**, *17*, 1392−1398. (b) Adams, R.; Adams, E. W.; Clarke, H. T.; Phillips, R. In *Organic Syntheses*; John Wiley and Sons: New York, 1932; pp 448−450.

diethyl 2-phosphonopropionate (7.84 g, 35 mmol) in dry DME (25 mL) was added to a mixture of NaH (60% in parafin oil, 1.45 g, 37 mmol) in dry DME (50 mL), under an Ar atmosphere, at room temperature. To the resulting solution, after 1 h of stirring at room temperature, a solution of benzophenone (5.5 g, 30 mmol) in 10 mL of dry DME was added dropwise. After overnight stirring at room temperature, the reaction was quenched with MeOH and washed with H_2O. The resulting residue, following its concentration, was chromatographed by using a mixture of 4:1 hexane/ethyl acetate as eluent and yielded the corresponding ester in 55% yield (4.1 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (m, 6H), 7.19 (d, 2H, J = 7.6 Hz), 7.13 (d, 2H, J = 7.5 Hz), 3.75 (s, 3H), 2.05 (s, 3H).

3,3-Diphenyl-1,1-dideuterio-2-methylprop-2-en-1-ol. To a mixture of $LiAlD_4$ (0.5 g, 12 mmol) in dry ether 40 mL), under Ar at 0 °C, was added dropwise a solution of the previous ester (4.1 g, 17 mmol) in dry ether (10 mL). The mixture was stirred at room temperature for 3 h. The reaction was quenched at 0 °C by adding 0.5 mL of H_2O, 0.5 mL of 15% NaOH, and 1.5 mL of H_2O, followed by filtration. The mixture was washed with 5% $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated carefully to give allylic alcohol-d_2 (3.1 g, 80% yield).

1,1-Diphenyl-3-bromo-3,3-dideuterio-2-methylpropene. To a solution of triphenylphosphine (3.9 g, 14 mmol) in dry CH_2Cl_2 under Ar at 0 °C was added dropwise 0.7 mL (14 mmol) of Br_2. The PPh_3Br_2 complex precipitated immediately. After 1 h of stirring at room temperature, the reaction mixture was cooled at 0 °C, and a solution of the corresponding allylic alcohol (3.1 g, 14 mmol) in dry CH_2Cl_2 was added dropwise. The solution was concentrated, and the resulting solid residue afforded the corresponding bromide (2.8 g, 70% yield) after chromatographic purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 7.0 Hz), 7.58 (t, 2H, J = 7.3 Hz), 7.49 (t, 4H, J = 8.0 Hz), 1.98 (s, 3H).

1,1-Diphenyl-3,3,3-trideuterio-2-methylpropene (2-d_3). A solution of the deuterium-labeled bromide (2.8 g, 10 mmol) in dry ether (10 mL) was added dropwise to a mixture of $LiAlD_4$ (0.2 g, 5 mmol) in dry ether (30 mL) under Ar at 0 °C. The mixture was stirred at room temperature for 3 h. The reaction was quenched at 0 °C by the addition of 0.2 mL of H_2O, 0.2 mL of 15% NaOH, and 0.6 mL of H_2O, followed by filtration. The mixture was washed with 5% $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated carefully to give alkene **2-d_3** (1.6 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, 4H, J = 7.4 Hz), 7.21 (t, 2H, J = 7.3 Hz), 7.17 (d, 4H, J = 7.3 Hz), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 138.8, 130.9, 129.7, 127.8, 125.9, 22.4, 21.7 (septet, J_{CD} = 19 Hz). MS m/z = 211 (100, m/z = 211).

1,1,1-Trideuterio-7-methyl-2-(trideuteriomethyl)octa-2,6-diene (3-d_6). A flame-dried, 100 mL, round-bottomed flask, equipped with a magnetic stirrer, was charged with 3.32 g (8.2 mmol) methyltriphenylphosphonium iodide in 20 mL of dry THF, under Ar. The solution was cooled to 0 °C, and 5.15 mL of 1.6 M *n*-butyllithium (solution in hexanes) was added dropwise. The orange solution was left at room temperature for 30 min and cooled to 0 °C, and 1.1 mL (8.2 mmol) of 5-bromo-2-methyl-2-pentene in 5 mL of THF was added dropwise. The flask was left at room temperature for 1 h and cooled again to 0 °C, and 5.15 mL of 1.6 M *n*-butyllithium solution was added dropwise. The solution was left at room temperature for 15 min and cooled to 0 °C, and 3 mL of acetone-d_6 (40 mmol) was added. The solution was concentrated to 10 mL, at the rotary evaporator, and 40 mL of pentanes was added and the mixture stirred for 30 min. Filtration, evaporation of the solvents, and purification by preparative GC gave 472 mg (3.28 mmol, 40% yield) of the desired **3-d_6**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.12 (t, 2H), 2.73 (t, 4H), 2.02 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.5, 131.3, 124.5, 28.4, 28.3, 25.7, 24.8 (septet, J_{CD} = 19 Hz), 17.7, 16.8 (septet, J_{CD} = 19 Hz). MS m/z = 144 (100, m/z = 69).

Decatungstate-Catalyzed Photooxygenations. The photooxygenations were carried out as described in general procedures. The ^{1}H NMR spectroscopic data of the hydroperoxides and carbonyl compounds, formed by the photooxidation of the corresponding alkenes are the following. **2a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, OOH), 7.50−7.17 (m, 10H), 4.58 (s, 2H), 1.93 (s, 3H). **2c**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, OOH), 7.50−7.17 (m, 10H). **2b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (s, CH═O), 7.84 (d, 2H, J = 7.3 Hz), 7.62 (t, 1H, J = 7.3 Hz), 7.51 (t, 2H, J = 7.3 Hz), 7.40−7.17 (m, 5H), 2.00 (s, 3H). **2d**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, 2H, J = 7.3 Hz), 7.62 (t, 1H, J = 7.3 Hz), 7.51 (t, 2H, J = 7.3 Hz), 7.40−7.17 (m, 5H). **2e**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, OOH), 7.50−7.17 (m, 10H), 4.58 (s, 2H). **2g**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, OOH), 7.50−7.17 (m, 10H), 1.93 (s, 3H). **2f**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (s, CH═O), 7.84 (d, 2H, J = 7.3 Hz), 7.62 (t, 1H, J = 7.3 Hz), 7.51 (t, 2H, J = 7.3 Hz), 7.40−7.17 (m, 5H). **2h**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, 2H, J = 7.3 Hz), 7.62 (t, 1H, J = 7.3 Hz), 7.51 (t, 2H, J = 7.3 Hz), 7.40−7.17 (m, 5H), 2.00 (s, 3H). **3g** + **3h**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (s, OOH, for **3h** hydroperoxide), 7.20 (s, OOH, for **3g** hydroperoxide), 5.68 (m, 2H), 5.53 (d, 2H, J= 16 Hz), 5.12 (m, 2H), 2.75 (t, 4H), 1.71 (s, 3H), 1.54 (s, 3H), 1.33 (s, 6H). **3a** + **3b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (s, OOH, for **3a** hydroperoxide), 7.69 (s, OOH, for **3b** hydroperoxide), 5.12 (m, 2H), 5.02 (d, 2H, J= 6 Hz), 4.32 (t, 2H), 1.49 (m, 8H), 1.69 (s, 3H), 1.59 (s, 6H). **3c** + **3d** + **3e** + **3f**. ^{1}H NMR (500 MHz,$CDCl_3$): δ 7.81 (s, OOH), 7.80 (s, OOH), 7.76 (s, OOH), 7.75 (s, OOH), 5.66 (m, 2H), 5.12 (m, 2H), 4.51 (s, 2H (**3e**)), 4.38 (s, 2H (**3c**)), 2.03 (m, 8H), 1.74 (s, 3H), 1.70 (s, 6H).

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for labeled alkenes as well as GC chromatograms of the oxidations. This material is available free of charge via the Internet at http://pubs.acs.org.

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