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Primary and Secondary Isotope Effects in the Photooxidation of 2,5-Dimethyl-2,4-hexadiene. Elucidation of the Reaction Energy Profile

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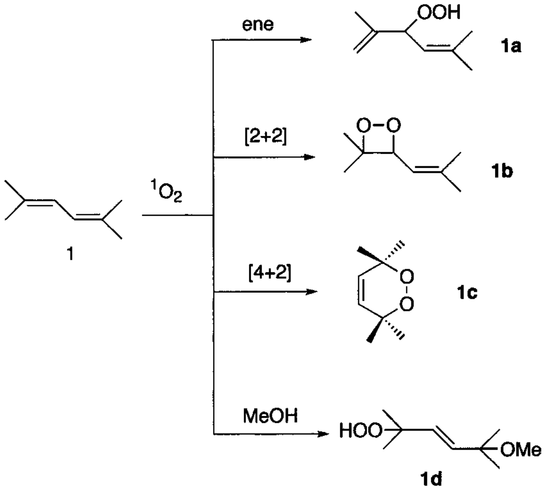
Introduction

Conjugated dienes react smoothly with singlet oxygen to form [4 + 2] adducts.[1] The reaction is synthetically useful, especially with dienes bearing a polar stereogenic center[2] at an adjacent position to the double bond. In this case, a highly diastereoselective formation of endoperoxides due to favorable or unfavorable interactions with the polar substituents was reported. The photooxygenation of 1,3-dienes was initially considered to proceed via a concerted pathway since it was found to occur in a suprafacial manner.[3] Recent studies, however, have indicated that the transition state of the [4 + 2] product formation is preceded by an exciplex intermediate.[4] The photooxygenation of dienes with constraints of rotation around the single C−C bond to adopt the reactive s-cis conformation is not stereospecific.[5] For instance, the reaction of $^1O_2$ with the isomeric 2,4-hexadienes has been studied extensively.[6] It was found that the [4 + 2] pathway was not stereospecific. (*E,E*)-2,4-Hexadiene afforded in addition to the endoperoxide with the cis stereochemistry (suprafacial process) a small amount of the endoperoxide, where the methyls had a trans configuration. Also, (*E,Z*)-2,4-hexadiene gave mixtures of the diastereomeric endoperoxides with the major being the adduct with the “wrong” stereochemistry. These results were rationalized by the formation of an open zwitterionic intermediate.

The reaction of singlet oxygen with the sterically hindered 2,5-dimethyl-2,4-hexadiene (DMHD, **1**) forms a mixture of ene product **1a**, 1,2-dioxetane **1b**, endoperoxide **1c**, and the 1,4-methoxy hydroperoxide adduct **1d** in methanol solvent (Scheme 1).[7] The initially formed ene product **1a** was reported to rearrange to 2,5-dimethylhexa-3,5-diene-2-hydroperoxide[8] via the corresponding peroxy radical. The rearrangement of the ene hydroperoxides has been studied extensively by Porter and coworkers.[9] The [4 + 2] adduct could be further attributed to reaction of DMHD with $^3O_2$ by a free-radical process. Indeed, a sample of DMHD left for prolonged time in air is gradually contaminated with significant amounts of endoperoxide.[10] The ratio of these adducts depends on solvent and temperature conditions. Polar protic solvents and low temperatures favor the dioxetane pathway.

Scheme 1. Photooxygenation and MeOH Trapping Products of the Reaction of DMHD with $^1O_2$



Foote and Manring[7b] measured the activation parameters of the reaction and found them to be identical with those of the photooxygenation of the simple trisubstituted alkene, 2-methyl-2-pentene. They concluded that both reactions proceed through a perepoxide intermediate. The perepoxide may open to a zwitterionic intermediate that leads to the dioxetane. A significant feature of the reaction is that there is a remarkably fast rate of nonreactive quenching[11] in solvents other than methanol. This was attributed to the transformation of the zwitterionic intermediate to a singlet diradical, which collapses through intersystem crossing to **1** and $^3O_2$.

Although the mechanistic details (stereoisotopic studies) of the ene reaction of alkenes with $^1O_2$ have been established, there is no analogous study concerning the reaction of dienes with $^1O_2$. For example, isotope effect studies of the ene reaction of singlet oxygen with alkenes have been reported previously by us[12−14] and others.[15−17] The primary isotope effects measured in these reactions

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are small and depend on the stereochemistry of the perepoxide intermediate, whereas the secondary isotope effects are negligible. For example, the intermolecular competition[12,15−17] of singlet oxygen with alkenes possesses a very small isotope effect ($k_H/k_D = 1.08-1.10$) and negligible secondary isotope effect. However, the value of $k_H/k_D = 1.38-1.40$ was measured for tetramethylethylenes-d_6, when the competing methyl groups are in cis configuration, and $k_H/k_D = 1.04-1.10$, when the competing methyl groups are in a trans configuration. These results (negligible intermolecular and substantial intramolecular isotope effects) were interpreted by the irreversible formation of a perepoxide intermediate in a rate-determining step. A perepoxide intermediate was also recently supported by additional experimental results.[18]

Results and Discussion

In this paper, we report the mechanistic details of the ene, [2 + 2], and methanol-trapping pathways in the sensitized photooxygenation of the 2,5-dimethyl-2,4-hexadiene. To measure the intramolecular primary isotope effect for the ene reaction, and the β-secondary isotope effects for the [2 + 2] and methanol-trapping pathways, we chose the appropriately labeled DMHD at the geminal methyls, 2,5-dimethyl-2,4-hexadiene-*1,1,1,2′,2′,2′*-d_6 (DMHD-d_6, **2**). Diene **2** was prepared by Wittig coupling of triphenylphosphoranylidene-3-methyl-2-butene with acetone-d_6. Photooxygenations were carried out in $CHCl_3$ where the ene is the major product and in MeOH to obtain the [2 + 2] and 1,4-trapping adducts. A Xenon Eimac Cermax 300 W lamp was used as the light source.

Irradiation of an oxygen-saturated solution of **2** (1×10^{-2} M) and tetraphenylporphine (TPP) as the sensitizer (1×10^{-4} M) in $CHCl_3$ containing a drop of pyridine to prevent dye bleaching, at 0 °C, gave the ene as the major product, accompanied by a small amount of dioxetane (~5%). Since the ene hydroperoxide easily rearranges[8] on standing, it was immediately reduced with PPh_3 to the bisallylic alcohol, which was chromatographed with a silica gel column prewashed with triethylamine and identified from its spectral properties and by comparison with literature data.[7b] No rearranged allylic alcohol was detected, which was reported recently[8b] to be the sole ene product in the reaction of **1** with $^1O_2$ induced by a chiral phosphite ozonide.

To confirm these results, photooxygenation was carried out in the presence of equimolar amounts of Ti(*i*-PrO)$_4$ to form the more stable epoxy alcohols by in situ epoxidation.[19] Also, if Ti(*i*-PrO)$_4$ is added instead of PPh_3 to the hydroperoxide mixture, the same epoxy alcohols can be isolated in excellent yield. The primary isotope effect k_H/k_D of the ene reaction, which is a result of an intramolecular isotopic competition, is proportional to the ratio **3a**/**3b** or to **4a**/**4b**, (Scheme 2). For instance, integration of the vinylic hydrogens H_a and H_b of **4a** at 5.09 and 4.97 ppm, whose sum is proportional to the quantity of $2k_H$, and the hydrogens H_c and H_e of **4a** and **4b** next to the hydroxyl group at 3.83 ppm ($k_H + k_D$) or the hydrogens next to the epoxide H_d and H_f at 2.80 ppm (also $k_H + k_D$) measures the isotope effect of $k_H/k_D = 1.61 \pm 0.05$ (Figure 1). The same value can be obtained by integrating the single resonance of the allylic methyl group at 1.72 ppm of **4a** and the two diastereotopic methyls of **4b**, which resonate at 1.29 and 1.27 ppm, respectively. Similar integration of the proper peaks of **3a** and **3b** (see Experimental Section) affords a $k_H/k_D = 1.58 \pm 0.05$.

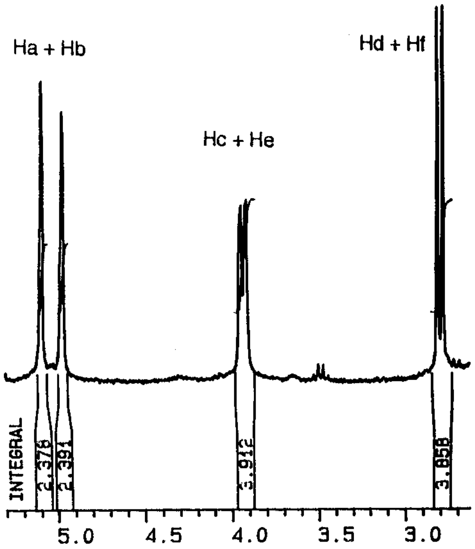
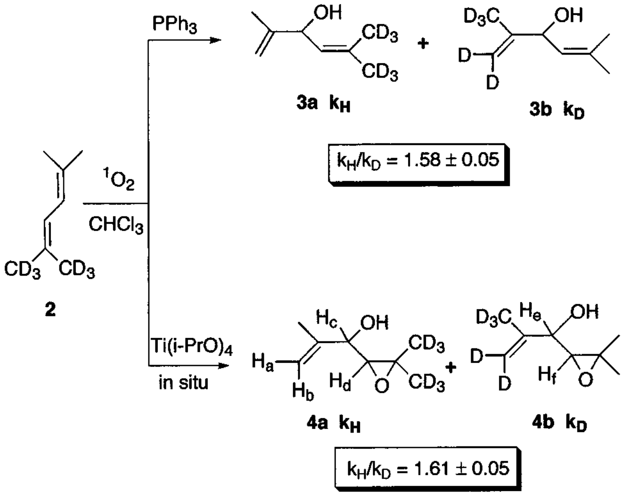


Figure 1. ^{1}NMR measurement of k_H/k_D by the integration of the proper hydrogen absorptions of products **4a** and **4b**: H_a (k_H) and H_b (k_H) at 5.09 and 4.97 ppm, H_c and H_e at 3.83 ppm ($k_H + k_D$), H_d and H_f at 2.80 ppm ($k_H + k_D$).

Scheme 2. Primary Isotope Effects in the *Ene* Reaction of $^1O_2$ with DMHD-d_6 in $CHCl_3$



When the photooxygenation of **2** was run in methanol (methylene blue as sensitizer) at 0 °C, the dioxetanes **5a** and **5b** and the 1,4-methanol-trapping adducts **6a** and **6b** (Scheme 3) were the major products in a ratio **5**/**6** = 60/20, along with a 20% of ene and traces of [4 + 2] adduct. After the end of the photooxygenation of **2**, triphenylphosphine was added as a reducing agent and the products were fractionated by column chromatogra-

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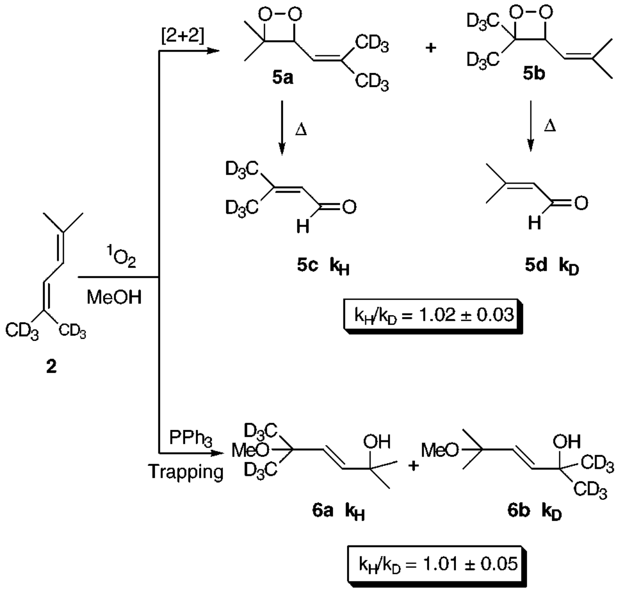
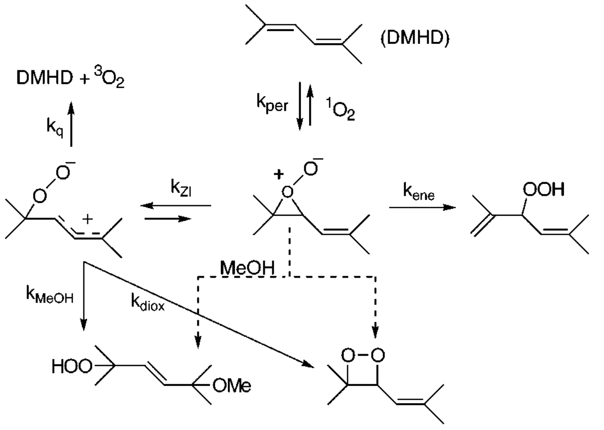
Scheme 3. Secondary Isotope Effects for the [2 + 2] and MeOH Trapping Adducts in the Reaction of $^1O_2$ with DMHD-d_6



phy. Under the experimental conditions, the labile dioxetanes decomposed to acetone and 3-methylbuten-2-al. For the 1,4-methanol-trapping adducts, we define as k_H the percent of product where the new C−OOH bond is formed next to the geminal protonated methyls and k_D the percent of product where the C−OOH bond is formed next to the geminal deuterated methyls. The isotope effect was measured by direct integration of the single peaks at 1.35 ppm corresponding to the two geminal methyls of **6a** and at 1.27 ppm for the two methyls of **6b** and found to be $k_H/k_D = 1.01 \pm 0.05$. It is interesting to note that the two methoxy groups next to the geminal CH_3 methyls in **6b**, and next to the geminal CD_3 methyls in **6a**, resonate at 3.152 and 3.149 ppm, respectively. The small but significant chemical shift change of the methoxy groups is due to a H/D substitution five bonds away from the resonating methoxy hydrogens. Thus, the electronegativity of the six hydrogens, which is larger than the six deuteria, causes a higher diamagnetic deshielding. For this reason, the methoxy group next to the protonated methyl absorbs at lower field (3.152 ppm).

For the dioxetane pathway, k_H is proportional to the **5a** product where the new C−O bond is formed next to the protonated methyls, while k_D is proportional to the **5b** product where the dioxetane is formed next to the deuterated methyls. The isotope effect was measured by GC−MS integration of the two 3-methyl-buten-2-als (**5c** and **5d**) resulting from the quantitative thermal cleavage of the initially formed labile dioxetanes. The capillary column 50%−50% phenyl methyl silicone separates the aldehydes **5c** and **5d** sufficiently to be measured. Mass spectroscopy showed that the deuterated aldehyde, 3-methyl-buten-2-al-*4,4,4,3′,3′,3′*-d_6, **5c**, has a shorter retention time than the protio aldehyde **5d**. The isotope effect k_H/k_D is proportional to the product ratio of **5c**/**5d** and was measured to be $k_H/k_D = 1.02 \pm 0.03$, which is identical with that measured from the 1,4-methanol-trapping path.

Scheme 4. Proposed Energy Profile in the Reaction of DMHD with Singlet Oxygen



The significant primary isotope effect of $k_H/k_D = 1.6$ measured in the ene reaction of singlet oxygen with DMHD-d_6 could be the result of partial reversion of the perepoxide intermediate to the starting materials, since the direct isotopic competition is impossible in an intermediate of this geometry (Scheme 4). Subsequent H/D abstraction in the rate-determining step accounts for the observed primary isotope effect. This is in contrast to the energy profile of trisubstituted[20] or tetrasubstituted alkenes,[13] where formation of the perepoxide, as we already mentioned, is the rate-limiting step. However, in the reaction of $^1O_2$ with the highly unreactive *trans*-2-butene-d_3, the unexpected substantial $k_H/k_D = 1.25$ was rationalized[14] in terms of partial reversion of the perepoxide intermediate to the starting materials. The proposed inversion of the intermediate to the products, in the photooxygenation of DMHD, could be attributed to the fact that the diene is more nucleophilic than the simple trisubstituted alkenes and the energy barrier for the formation of the perepoxide is lower.

When the photooxygenation of **2** was carried out in methanol, the dioxetanes and the methoxy-trapping adducts were the major detected products. These products have been proposed to arise probably from an open zwitterionic intermediate. Significant evidence for the existence of an open intermediate comes from results reported by Manring and Foote.[7b] Formation of the dipolar zwitterion in polar solvents is expected to have a higher negative value of entropy, due to the additional solvation, compared to the more rigid perepoxide. Indeed, as the temperature decreases, the ratio of the products arising from the proposed open intermediate in methanol (dioxetane and trapping) vs the ene product from the perepoxide, increases; at ambient temperature (dioxetane + trapping)/ene = 3/1, whereas at −78 °C (dioxetane + trapping)/ene = 15/1. The secondary isotope effects measured in the photooxygenation of **2** either in the dioxetane or in the methanol trapping pathways, are practically unity, $k_H/k_D = 1.0$.

These and previous results[11] are consonant with the formation of a perepoxide as a common intermediate in the first step for all reaction paths. Dioxetane and methoxy adducts are probably formed via an open zwitterionic intermediate, which is produced by rearrangement of the perepoxide in a faster step ($k_{ZI} > k_{per}$, Scheme 4). The perepoxide is formed reversibly in a fast step compared to the competing ene step ($k_{per} > k_{ene}$). Al-

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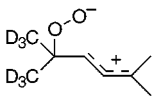
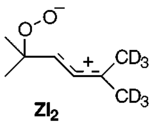
[20] Stratakis, M.; Orfanopoulos, M.; Chen, J. S.; Foote, C. S. *Tetrahedron Lett.* **1996**, 37, 4105- 4108.

though the ene pathway is energetically unfavorable ($k_{ZI} > k_{ene}$), it becomes predominant in aprotic solvents, due to the significant collapse of the zwitterionic intermediate to starting materials. The zwitterionic intermediate must involve some biradical character in order to decompose in a spin-allowed proccess. It is well established[11] that the rate of disappearance (k_r) of DMHD in methanol is close to the total rate of interaction between DMHD and $^1O_2$ ($k_r + k_q$). This indicates that DMHD does not quench $^1O_2$ by a nonreactive pathway in methanol. The physical quenching (PQ) is about 4%. In contrast, in aprotic solvents, k_r of DMHD is much less than the total interaction rate between DMHD and $^1O_2$ ($k_r + k_q$). In this case, the major interaction between DMHD and $^1O_2$ leads to nonreactive quenching (PQ), e.g., 72% in CH_3CN, 73% in CH_2Cl_2, 81% in $(CH_3)_2CO$, and 93% in C_6H_6. Thus, in aprotic solvents, because the zwitterionic intermediate collapses exclusively through the nonreactive pathway k_q to starting materials, the ene product predominates even if $k_{ZI} > k_{ene}$. However, in methanol ($k_{MeOH} + k_{diox} > k_q$), a dramatic increase in dioxetane and methanol-trapping products was observed. While the zwitterionic intermediate finds also support from experimental results reported by Foote and Manring,[11] the present negligible secondary isotope effects in the dioxetane and in the methanol-trapping experiments do not exclude an alternative mechanistic pathway in which the [2 + 2] and 1,4-methanol-trapping adducts (Scheme 4) are formed from the perepoxide without intervention of a zwitterion. Recently, common perepoxide intermediates have been also proposed for the ene and [4 + 2] pathways in the photooxygenation of chiral 1,2-dihydronaphthalenes[21] and a cyclic diene.[22] Although it is difficult to distingush between the two mechanistic pathways, we favor the formation of the zwitterionic intermediate in a faster step from a preceding perepoxide intermediate.

In case the dipolar intermediate has been formed in a slow step, the methoxy adduct next to the geminal CH_3 methyls and the [2 + 2] adduct next to the geminal CD_3 methyls resulting from ZI_1 would be expected to predominate over the corresponding adducts produced from ZI_2 because hyperconjugation effect[23] favors formation of ZI_1 over ZI_2.



ZI_1



ZI_2

In conclusion, we have presented an energy profile for the reaction of 2,5-dimethyl-2,4-hexadiene with $^1O_2$ that is consistent with kinetic primary and secondary isotope effects. The reaction proceeds through the formation of a perepoxide as a common intermediate for the ene and [2 + 2] pathways. For the ene pathway, the hydrogen abstraction is the rate-determining step, whereas the dioxetane and methanol-trapping pathways proceed either through an open zwitterionic intermediate, which is formed in a faster step compared to perepoxide formation or directly from the perepoxide intermediate.

Experimental Section

Nuclear magnetic resonance spectra were recorded on 400 and 250 MHz spectrometers. Isomeric purities were determined by ^1H NMR and by analytical gas chromatography equipped with a 50%−50% phenyl methyl silicone capillary column and a 5971A MS detector.

2,5-Dimethyl-2,4-hexadiene-*1,1,1,2′,2′,2′-d*$_6$ (1) was prepared by Wittig coupling of triphenylphosphoranylidene-3-methyl-2-butene with acetone-d_6 in ether at 0 °C (65% yield). ^1H NMR ($CDCl_3$): δ 5.96 (s, 2H), 1.78 (s, 3H), 1.72, (s, 3H). Exact mass for $C_8H_8D_6$: calcd 116.1472, found 116.1458. The precursor to ylide phosphonium salt was prepared in 90% yield by heating neat 4-bromo-2-methyl-2-butene (Aldrich) and an equimolar amount of triphenyl phosphine in a tight tube for 12 h at 100 °C. The phosphonium salt was collected as a white solid and was washed with hot toluene. ^1H NMR: δ 7.90−7.63 (m, 15H), 5.13 (m, 1H), 4.52 (dd, $J_{H-P} = 14.5$ Hz, $J_{H-H} = 7.7$ Hz, 2H), 1.67 (d, $J = 5.8$ Hz, 3H), 1.28 (d, $J = 3.9$ Hz, 3H).

Ene Products from the Reaction of 2 with $^1O_2$ in $CHCl_3$. After reduction of the initially formed hydroperoxides with excess PPh_3 at 0 °C, the bis allylic alcohols were purified by flash column chromatography over silica gel, prewashed with triethylamine using ether/hexane = 1:1 as eluent. M^+: 132. ^1H NMR ($CDCl_3$): δ 5.16 (d, $J = 8.7$ Hz, 1H of **3a** + 1H of **3b**), 5.00 (br. s, 1H of **3a**), 4.80 (br s, 1H of **3a**), 4.75 (d, $J = 8.7$ Hz, 1H of **3a** + 1H of **3b**), 1.71 (s, 3H of **3a**), 1.70 (s, 3H of **3b**), 1.69 (s, 3H of **3b**), 1.25 (br s, 1H, hydroxyl).

In a separate experiment, photooxygenation was carried out in the presence of equimolar amounts of Ti(*i*-PrO)$_4$. After the end of the reaction, 5 mL of ether was added and then 1−2 mL of a saturated solution of Na_2SO_4. The mixture was extracted with ether, and the residue was chromatographed with petroleum ether/ether = 2/1 to obtain the pure epoxy alcohols **4a** and **4b**. The same epoxy alcohols were also obtained in the same ratio if Ti(*i*-PrO)$_4$ was added to the mixture of the initially formed allylic hydroperoxides. ^1H NMR ($CDCl_3$): δ 5.09 (s, 1H of **4a**), 5.00 (s, 1H of **4a**), 3.93 (d, $J = 7.5$ Hz, 1H of **4a** + 1H of **4b**), 2.80 (d, $J = 7.5$ Hz, 1H of **4a** + 1H of **4b**), 1.72 (s, 3H of **4a**), 1.53 (br s, 1H, hydroxyl), 1.29 (s, 3H of **4b**), 1.27 (s, 3H of **4b**).

Dioxetanes from the Reaction of 2 with $^1O_2$ in MeOH. Although the labile dioxetanes were not isolated, the thermally cleaved products 3-methyl-buten-2-al and 3-methylbuten-2-al-*4,4,4,3′,3′,3′-d*$_6$ were analyzed by GC−MS ($T_{col} = 40$ °C). The aldehyde-d_6 ($M^+ = 90$) has a retention time of 4.81 min, whereas the aldehyde-d_0 ($M^+ = 84$) has a retention time of 4.91 min.

1,4-Methanol Adducts from the Reaction of 2 with $^1O_2$ in MeOH. After reduction of the initially formed methoxy hydroperoxides with excess PPh_3, the resulting isomeric (*E*)-5-methoxy-2,5-dimethyl-hex-3-en-2-ol-*1,1,1,2′,2′,2′-d*$_6$, **6a**, and (*E*)-5-methoxy-2,5-dimethylhex-3-en-2-ol-*6,6,6,5′,5′,5′-d*$_6$, **6b**, were purified by column chromatography (hexane/ethyl acetate = 3/1). M^+: 164. ^1H NMR (CDCl3): δ 5.74 (d, $J = 16.1$ Hz, 1H of **6a** + 1H of **6b**), 5.62 (d, $J = 16.1$ Hz, 1H of **6a** + 1H of **6b**), 3.15 (s, 3H of **6a** + 3H of **6b**), 1.50 (br s, 1H, hydroxyl), 1.27 (s, 6H of **6b**), 1.35 (s, 6H of **6a**).

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Supporting Information Available: NMR spectra (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, see any current masthead page for ordering information.

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[23] Recent experimental results show a significant inverse secondary isotope effect of $k_H/k_D = 0.72$ in the [2 + 2] cycloaddition of TCNE to diene **2**, and it is due to the hyperconjugation effect. See: Vassilikogiannakis, G.; Orfanopoulos, M. *Tetrahedron Lett.* **1996**, 37, 3075−3078.