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Thionin-Sensitized Intrazeolite Photooxygenation of Trisubstituted Alkenes: Substituent Effects on the Regioselectivity As Probed through Isotopic Labeling

Manolis Stratakis,* Radim Nencka,† and Constantinos Rabalakos

Department of Chemistry, University of Crete, 71409 Iraklion, Greece

Waldemar Adam and Oliver Krebs

Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

stratakis@chemistry.uoc.gr

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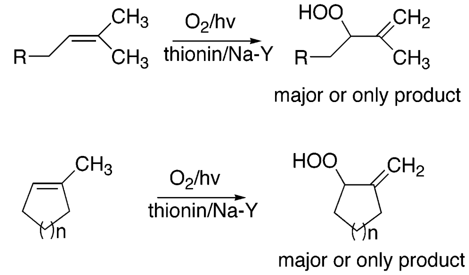
The regioselectivity for the intrazeolite photooxygenation of several trisubstituted alkenes with geminal dimethyl groups was examined. The length of the alkyl chain at the lone position was varied, and as end groups, the phenyl or the cyclohexyl functionalities were chosen. The general trend for all alkenes is a significant increase of the reactivity at the twin position compared to the photooxygenation in solution. For the cyclohexyl-substituted alkenes, it was found that the regioselectivity is nearly independent of the alkyl chain length. However, for the phenyl-substituted alkenes, the ene reactivity of the allylic methylene hydrogen atoms at the lone position and the twix/twin regioselectivity depend significantly on the distance of the phenyl group from the double bond. These trends are discussed in terms of cation−π interactions and conformational effects. Intramolecular and intermolecular isotope effects in the intrazeolite photooxygenation of deuterium-labeled alkenes suggest that a perepoxide-type intermediate is formed in the rate-determining step. Type I photooxygenation that involves reaction of the radical cations of the alkenes with superoxide ion are unlikely.

Introduction

In recent years, the photooxygenation of alkenes, adsorbed within the dye-supported zeolite Na−Y, has attracted considerable mechanistic and synthetic attention.[1] For the intrazeolite photooxygenation of trisubstituted alkenes, it was reported[2] that the reaction is regioselective with preferential double-bond formation at the more substituted carbon of the double bond. This is in contrast to the reaction in solution, in which lack of Markovnikov selectivity is found. Also, with 1-methylcycloalkenes,[3] the formation of the double bond occurs preferentially at the methyl group, in contrast to the photooxygenation reaction in solution (Scheme 1). Recent work by us and by Clennan has shown independently[4] that the "*cis effect*" selectivity[5] in the photooxygenation of some trisubstituted alkenes does not necessarily operate within the zeolite.

SCHEME 1. Regioselectivity in the Intrazeolite Photooxygenation of Trisubstituted Alkenes



Several models have been presented so far to explain the low reactivity of the allylic hydrogens at the lone[6] position (Scheme 2). Originally, Ramamurthy and coworkers postulated[3] that steric effects inside the cavity place the bulkier alkyl group (R) away from the cation; therefore, the methylene hydrogen atoms adopt an unreactive conformation toward singlet-oxygen attack (model

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* Corresponding author. Fax: +30-2810-393601.

† Visiting student via the SOCRATES/ERASMUS program (2000-2001), Charles University, Faculty of Pharmacy in Hradec Kralove, Czech Republic.

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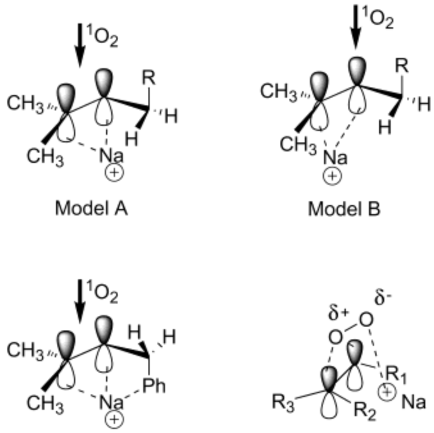
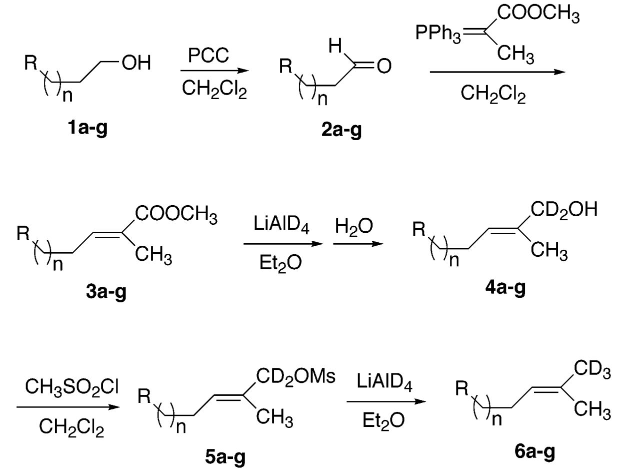
[6] For the terminology lone, twin, and twix, see: Adam, W.; Bottke, N.; Krebs, O. *J. Am. Chem. Soc.* **2000**, *122*, 6791−6792.

10.1021/jo020350z CCC: $22.00

SCHEME 2. Proposed Models of Intrazeolite $^1O_2$ Ene Reaction with Alkenes



SCHEME 3. Synthesis of Labeled Alkenes 6a−g



a) R = Ph, n = 0
b) R = Ph, n = 1
c) R = Ph, n = 2
d) R = Ph, n = 3
e) R = Cy, n = 0
f) R = Cy, n = 1
g) R = Cy, n = 2

[a] Ph = phenyl, Cy = cyclohexyl

A). Later, the same group postulated[1a] an alternative explanation, according to which the polarization of the alkene by interaction of the double bond with the cation occurs in such a way that the more substituted carbon atom bears a partial positive charge (model B). Thus, the electrophilic $^1O_2$ attacks the more nucleophilic monosubstituted olefinic carbon atom, and allylic hydrogen abstraction occurs at the alkyl substituents of the geminal disubstituted site. For the substrate in which R = Ph, we have proposed[4a] simultaneous interaction of the cation with the phenyl group and the alkene double bond to result in a conformation in which none of the allylic hydrogen atoms at the benzylic position are perpendicular to the olefinic plane to become reactive for abstraction by singlet oxygen (model C). Clennan and Sram[7] proposed the mechanistic model D based on the regioselectivity for the photooxygenation of some tetrasubstituted alkenes. They have argued that the alkali-metal cation forms a complex with the pendant oxygen in the intermediate perepoxide, which leads to a greater positive charge on the carbon framework, while steric interactions between the cation and the alkyl substituents affect the stability of the transition states that lead to the intermediate perepoxide. In the perepoxide of model D, the C−O bonds are highly unsymmetric and, therefore, account for the Markovnikov-type selectivity. This type of intermediate resembles the aziridinium imide[8a] and the aziridine *N*-oxide,[8b] which are formed in the reaction of triazolinediones (TADs) and nitrosoarenes (ArNO) with trisubstituted alkenes. To explain the enhanced reactivity of the allylic hydrogen atoms at the less substituted side of the trisubstituted alkenes (twin position), it was proposed[4] that the electrostatic interaction of the pendant negatively charged oxygen atom of the perepoxide with the alkali metal cation within the cages of Na−Y stabilizes the transition state in which the oxygen is directed toward the less substituted side of the alkene.

Results

To shed more light on the factors that control the regioselectivity of the ene hydroperoxidation reaction within zeolite Na−Y, we performed the intrazeolite photooxygenation of a series of deuterium-labeled *gem*-dimethyl trisubstituted alkenes **6a**−**g**, by varying the position of a phenyl or a cyclohexyl substitutent at the end of the alkyl chain. We chose the phenyl and cyclohexyl groups as substituents, because they have similar steric demands but different electronic character, since a phenyl group may strongly coordinate[9] with the Na^+ cations of the Na−Y supercages. The preparation of the alkenes **6a**−**g** was accomplished in 90−95% purity for the *E* configuration (Scheme 3).

The photooxygenation results in solution (dichloromethane with methylene blue as sensitizer) and within the thionin-supported zeolite Na−Y are presented in Table 1. The intrazeolite photooxygenations were accomplished as described in the Experimental Section. We have used dye−zeolite samples that had been dried under vacuum at 110−120 °C prior to use, until the color of the purple solid turned to light blue. The product distribution was measured by integration of the appropriate peaks in the ^1H NMR spectrum and by GC analysis of the allylic alcohols produced after reduction of initially formed allylic hydroperoxides by triphenylphosphine. The loading level of the alkenes in the zeolite was low (approximately 10 mg of the alkene per 1 g of thionin/Na−Y). The ene reactivity of the allylic hydrogen atoms expressed in % abstraction was very reproducible (the error of three measurements for each substrate was ±4%). To prevent the competing intrazeolite isomerization of the reacting alkenes and the decomposition of the more labile tertiary allylic hydroperoxides, a short reaction time (less than 2 min) was followed, and the irradiation was performed almost immediately after the addition of the alkene to the zeolite slurry. Under the reaction conditions, 15−95% of the alkenes had been transformed to the allylic hydroperoxides. The reactivity

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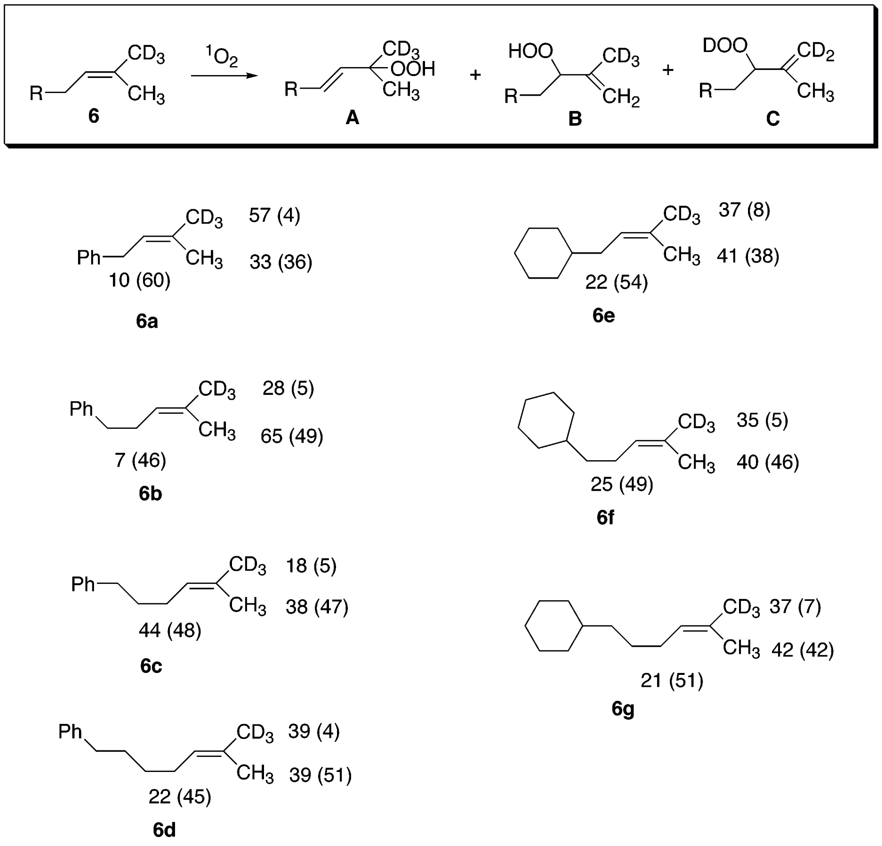
TABLE 1. Ene Reactivities[a] for the Photooxygenation of the Deuterium-Labeled Alkenes 6a−g



[a] The values in parentheses indicate the ene reactivity at the allylic position when the photooxygenation is carried out in solution; the ene reactivities at the twin and twix positions have been corrected for 100% purity of the (*E*)-configurated **6a**−**g**.

of the phenyl-substituted alkenes **6a**−**d** was >80%, while for the cyclohexyl substrates **6e**−**g** it was 15−30%. Control experiments have shown that alkenes **6a**−**d** are completely adsorbed in Na−Y after 2−3 min, whereas for **6e**−**g** only 50−60% have been adsorbed for the same period of time. This accounts for the higher reactivity of the phenyl-substituted alkenes compared to the cyclohexyl-substituted ones, since confinement of the alkene in the zeolite is probably necessary to achieve ene hydroperoxidation. Prolonged irradiation time within the zeolite resulted in the partial or even complete decomposition of the tertiary allylic hydroperoxides without affecting, however, the ratio of the twin/twix reactivity (ratio B/C in Table 1). Treatment of the zeolite with 2 equiv of pyridine[1a] relative to the substrate for 5 min prior to the introduction of the alkene to the zeolite slurry significantly retarded the unwanted side reactions.

The mass balance for all reactions as measured by using an external standard[10] was always higher than 83%. Furthermore, the hydroperoxide mixture obtained from the photooxygenation of the alkene in solution was introduced to the thionin/Na−Y and irradiated under a constant flow of oxygen gas for 2 min. After extraction of the hydroperoxides with tetrahydrofuran, it was found that the ratio of tertiary/secondary hydroperoxide, as well as the twin/twix ratio (B/C), was almost the same (up to 4% deviation) prior to and after the zeolite treatment. Generally, the tertiary hydroperoxides vanish slowly on prolonged intrazeolite treatment. For example, in the intrazeolite photooxygenation of the more sensitive alkene **6a**, the tertiary hydroperoxide disappears after 15 min of stirring in Na−Y; however, photooxygenation times from 15 s to 2 min gave reliable results, with a ratio of tertiary/secondary hydroperoxide of ca. 10/90.

To establish the reaction profile for the intrazeolite photooxygenation of trisubstituted alkenes, the alkenes **6a-*d*$_0$** (prenylbenzene) and **6a-*d*$_6$** (prenylbenzene-*d*$_6$) were prepared by Wittig reaction, and the ene reactivities were assessed by intermolecular competition (Scheme 4). For this purpose, an equimolar mixture of the two alkenes was photooxygenated to 40% conversion[11] and the analysis of the product mixture (after reduction with PPh_3) was submitted to GC. The alkenes **6a-*d*$_0$** and **6a-*d*$_6$**, as well as their photooxygenation products (as allylic alcohols), that differ by six D over six H, are well separable on a 60-m capillary column. The relative photooxygenation rate, as found from the consumption of the reactants or from the formation of the products, was $k_H/k_D = 1.03 \pm 0.02$.[12] The same competition experiment in solution gave $k_H/k_D = 1.01 \pm 0.02$.

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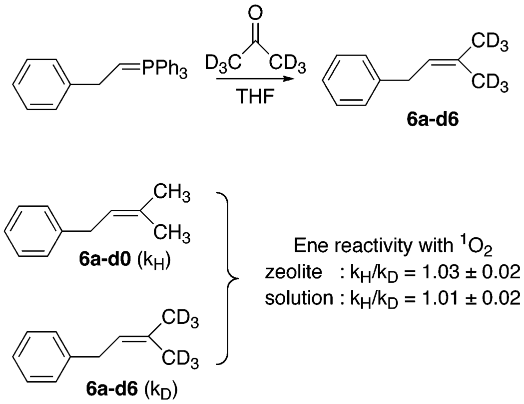
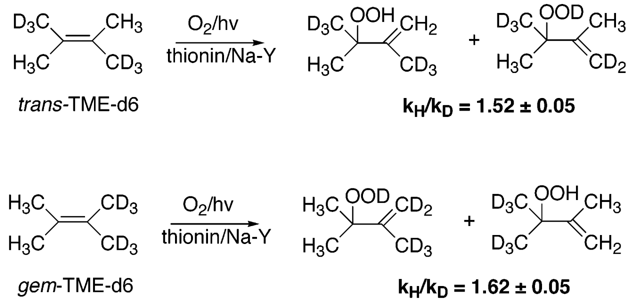
[10] After the extraction of the hydroperoxides and the unreacted alkene from the zeolite with moistened tetrahydrofuran, excess triphenylphosphine was added. The extract was mixed with a solution of hexane that contained a precisely weighed amount the external standard (nonane, dodecane, or *trans*-decahydronaphthalene). The mass balance was determined by GC analysis from the peak areas of the external standard and the sum of the allylic alcohols and alkene.

[11] *n*-Dodecane was used as internal standard.

SCHEME 4. Intermolecular Kinetic Isotope Effect in the Intrazeolite Photooxygenation of Prenylbenzene



SCHEME 5. Kinetic Isotope Effects for the Photooxygenation of Deuterium-Labeled Tetramethylethylenes within Thionin-Supported Zeolite Na−Y



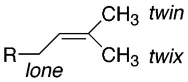
Discussion

Before the regioselectivity results of Table 1 shall be analyzed, it is necessary to assess whether the intrazeolite formation of the allylic hydroperoxides arises from a type I or a type II photooxygenation. This clarification is important in the light of our recent observations[13] that an electron-transfer-induced pathway subordinated to acid catalysis may be responsible for the isomerization of the alkenes or the decomposition of the hydroperoxides within the thionin-supported zeolite Na−Y. Furthermore, we would like to exclude the photooxygenation process reported by Frei and co-workers,[14] in which the irradiation of the alkene−O_2 charge-transfer complex within Na−Y proceeds through the reaction of the alkene radical cation with superoxide ion.

Photooxygenation of the isomeric *cis*-, *trans*-, and *gem*-tetramethylethylenes(TME)-d_6 is an ideal tool (Stevenson's isotope effect test)[15] to delineate the mechanism of these ene-type reactions. For *cis*-TME-d_6 Clennan and Sram[7] recently reported a negligible isotope effect ($k_H/k_D = 1.04$) within methylene blue-supported Na−Y. We performed the intrazeolite photooxygenation of *trans*-TME-d_6 and *gem*-TME-d_6 and found for the *trans*-TME-d_6 $k_H/k_D = 1.52 \pm 0.05$, whereas for the *gem*-TME-d_6 it was $k_H/k_D = 1.62 \pm 0.05$ (Scheme 5). These intrazeolite isotope effects are very similar to those reported for the photooxygenation in solution.[15] Therefore, formation of radical cations and their subsequent reaction with superoxide ion to afford a zwitterionic intermediate is unlikely to occur within the thionin/Na−Y.

We consider an irreversibly formed perepoxide as the most likely intermediate that arises from the reaction of singlet oxygen with the alkenes (type II photooxygenation). The negligible isotope effect of $k_H/k_D = 1.03 \pm 0.02$ in the intrazeolite competition of **6a-*d*$_0$** versus **6a-*d*$_6$** also indicates that in the photooxygenation of trisubstituted alkenes the formation of a perepoxide-type intermediate is rate-determining.

As seen in Table 1, for all the alkenes **6a**−**g**, a significant increase in the twin-methyl reactivity is found, as reported[4] earlier for other substrates. For the phenyl-substituted alkenes **6a**−**d**, there is a significant variation of the reactivity at the allylic positions (twin, twix, or lone) by changing the length of the phenyl-substituted alkyl chain. The reactivity at the lone position is 10% for **6a**, slightly drops to 7% in **6b**, increases significantly to 44% in **6c**, and then drops again to 22% in **6d**. For the same phenyl-substituted substrates, the twin/twix reactivity ratio is higher (63/37) for substrate **6a**, where the phenyl group is closer to the double bond. By increasing the length of the alkyl chain the twin/twix reactivity ratio drops to 30/70 in **6b** and to 32/68 in **6c**, and finally for alkene **6d** it is 50/50. These results are in contrast to the cyclohexyl-substituted alkenes **6e**−**g**, for which the twin/twix reactivity ratio is quite similar (approximately 47/53); also a nearly constant lone reactivity is found (21−25%). The novel feature of the regioselectivities for the substrates **6a**−**d** is that the lone and the twin/twix reactivity ratios depend significantly on the position of phenyl group. This effect is not evident in the case of the cyclohexyl-substituted alkenes **6e**−**g**. For derivative **6c**, the lone position is surprisingly as reactive as in solution. Direct comparison of substrates **6c** and **6g**, which possess similar steric demand, indicates that presumably interaction between the Na^+ and the π system of the phenyl ring are responsible for this differentiation.



We propose that the changes in the ene reactivity at the lone position for **6a**−**d** is controlled by cation−π interactions and conformational effects within the Na−Y supercages. Simultaneous coordination of the Na^+ with the phenyl ring[1f,9] and the double bond places the allylic methylene hydrogen atoms in a favorable (perpendicular to the double bond) or unfavorable position for ene reaction, as seen in Figure 1.

For derivative **6c**, we suggest that coordination of the Na^+ with the phenyl group induces a conformation in which the methylene hydrogen atoms are more perpendicular to the olefinic plane compared to the other alkenes and thus more reactive. For the three cyclohexyl-

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[12] For the equation used to calculate the isotope effect, see: Stratakis, M.; Orfanopoulos, M.; Foote, C. S. *J. Org. Chem.* **1998**, *63*, 1315−1318.

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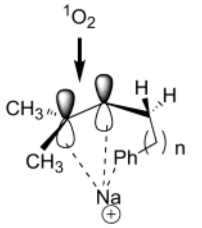

FIGURE 1. Conformational changes through the simultaneous coordination of the sodium ion with the phenyl group and alkene double bond.

substituted substrates **6e**–**d**, the coordination of the Na^+ to the alkene double bond affords similar conformations for the allylic methylene hydrogen atoms and, therefore, they are approximately equally reactive. This is also corroborated by the fact that the twix/twin reactivity ratio is the same for all cyclohexyl-substituted alkenes. The change in the twix/twin ratio with the remoteness of the phenyl group in alkenes **6a**–**d** is difficult to rationalize. It certainly has to do with the conformational changes of each specific alkene after confinement within Na–Y.

In conclusion, we have presented in this study evidence that cation–π interactions have conformational consequences on the alignment of the allylic hydrogen atoms for ene reaction. This coordination significantly influences the regioselectivity of the dye-sensitized intrazeolite photooxygenation of trisubstituted alkenes. The most important finding is that a phenyl group at a remote position with respect to the double bond can significantly affect the regioselectivity of the intrazeolite singlet oxygen ene reaction.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a 500-MHz instrument. Isomeric purities were determined by ^1H NMR and by GC analysis on a 60-m capillary column. All spectra reported herein were taken in $CDCl_3$.

The general procedures for the preparation of the labeled alkenes **6a**–**g** are as follows.

Preparation of the Aldehydes (2b–g). Except phenylacetaldehyde (**2a**), which is commercially available, the rest of the aldehydes were prepared by pyridinium chlorochromate (PCC) oxidation of the corresponding alcohols in 65–75% yield. The following are the ^1H NMR data of **2b**–**g**. **2b**: 9.86 (s, 1H), 7.22–7.34 (m, 5H), 2.99 (t, 2H, J = 7.5 Hz), 2.82 (t, 2H, J = 7.5 Hz). **2c**: 9.79 (s, 1H), 7.19–7.33 (m, 5H), 2.69 (t, 2H, J = 7.5 Hz), 2.48 (t, 2H, J = 7.5 Hz), 2.01 (m, 2H). **2d**: 9.78 (s, 1H), 7.20–7.34 (m, 5H), 2.68 (t, 2H, J = 7.5 Hz), 2.49 (m, 2H), 1.71 (m, 4H). **2e**: 9.86 (s, 1H), 2.30 (d, 2H, J = 6.5 Hz), 1.00–1.85 (m, 11 H). **2f**: 9.77 (s, 1H), 2.44 (t, 2H, J = 7.5 Hz), 1.63–1.72 (m, 4H), 1.53 (m, 2H), 1.10–1.23 (m, 4H), 0.90 (m, 2H). **2g**: 9.77 (d, 1H, J = 1.2 Hz), 2.42 (dt, 2H, J_1 = 7.0 Hz, J_2 = 1.2 Hz), 1.62–1.75 (m, 6H), 1.15–1.27 (m, 7H), 0.91 (m, 2H).

Preparation of the α,β-Unsaturated Esters (3a–g). In a one-necked flask were placed 80 mL of dry CH_2Cl_2 and 36.0 mmol of methyl(triphenylphosphoranylidene)propionate. Subsequently, 30.0 mmol of the appropriate aldehyde was added and the solution was stirred overnight. Most of the solvent was removed by evaporation and then 50 mL of hexane was added. The solid residue was washed with hexane (4 × 50 mL), the hexane was evaporated, and the oily residue was distilled at reduced pressure. The α,β-unsaturated esters were isolated in 60–80% yield and in >92% purity of the E diastereomer. The following are the ^1H NMR data of the esters **3a**–**g**. **3a**: 7.22–7.35 (m, 5H), 6.96 (t, 1H, J = 7.5 Hz), 3.76 (s, 3H), 3.56 (d, 2H, J = 7.5 Hz), 1.99 (s, 3H). **3b**: 7.21–7.34 (m, 5H), 6.84 (t, 1H, J = 7.5 Hz), 3.76 (s, 3H), 2.78 (t, 2H, J = 7.5 Hz), 2.52 (m, 2H), 1.81 (s, 3H). **3c**: 7.19–7.32 (m, 5H), 6.81 (t, 1H, J = 7.5 Hz), 3.77 (s, 3H), 2.67 (t, 2H, J = 8.0 Hz), 2.23 (m, 2H), 1.84 (s, 3H), 1.82 (m, 2H). **3d**: 7.19–7.32 (m, 5H), 6.78 (t, 1H, J = 7.0 Hz), 3.76 (s, 3H), 2.67 (t, 2H, J = 8.0 Hz), 2.23 (m, 2H), 1.85 (s, 3H), 1.68 (m, 2H), 1.52 (m, 2H). **3e**: 6.82 (t, 1H, J = 7.0 Hz), 3.76 (s, 3H), 2.09 (t, 2H, J = 7.0 Hz), 1.85 (s, 3H), 1.66–1.75 (m, 4H), 1.43 (m, 1H), 1.15–1.30 (m, 4H), 0.96 (m, 2H). **3f**: 6.78 (t, 1H, J = 7.0 Hz), 3.76 (s, 3H), 2.20 (m, 2H), 1.85 (s, 3H), 1.65–1.75 (m, 5H), 1.15–1.36 (m, 6H), 0.92 (m, 2H). **3g**: 6.78 (t, 1H, J = 7.0 Hz), 3.76 (s, 3H), 2.16 (m, 2H), 1.85 (s, 3H), 1.65–1.73 (m, 7H), 1.14–1.27 (m, 6H), 0.88 (m, 2H).

Reduction of α,β-Unsaturated Esters to the Allylic Alcohols-d_2 (4a–g). In a flame-dried, two-necked flask were added 15.0 mmol of $LiAlD_4$ and 15 mL of dry ether. The flask was cooled to 0 °C, and 5.0 mmol of anhydrous $AlCl_3$ was added in portions. The resulting slurry was stirred for an additional 20 min, followed by the dropwise addition of the α,β-unsaturated ester **3a**–**g** (25.0 mmol). The reaction mixture was stirred for 1–2 h and then treated with 2 mL of water. After extraction with ether, the deuterated allylic alcohols were isolated in 85–95% yield. The following are the ^1H NMR data of the alcohols **4b**–**g**. **4b**: 7.22–7.33 (m, 5H), 5.49 (t, 1H, J = 7.0 Hz), 2.70 (t, 2H, J = 8.0 Hz), 2.39 (m, 2H), 1.65 (s, 3H), 1.45 (br. s., 1H). **4c**: 7.20–7.32 (m, 5H), 5.46 (t, 1H, J = 7.0 Hz), 2.66 (t, 2H, J = 8.0 Hz), 2.11 (m, 2H), 1.73 (m, 2H), 1.68 (s, 3H), 1.45 (br. s., 1H). **4d**: 7.20–7.32 (m, 5H), 5.43 (t, 1H, J = 7.0 Hz), 2.65 (t, 2H, J = 8.0 Hz), 2.09 (m, 2H), 1.65 (s, 3H), 1.65 (m, 2H), 1.44 (m, 2H), 1.30 (br. s., 1H). **4e**: 5.46 (t, 1H, J = 7.5 Hz), 1.95 (t, 2H, J = 7.0 Hz), 1.65–1.75 (m, 5H), 1.68 (s, 3H), 1.15–1.35 (m, 5H), 0.91 (m, 2H). **4f**: 5.43 (t, 1H, J = 7.5 Hz), 2.06 (m, 2H), 1.65–1.75 (m, 6H), 1.69 (s, 3H), 1.15–1.28 (m, 6H), 0.91 (m, 2H). **4g**: 5.43 (t, 1H, J = 7.0 Hz), 2.02 (m, 2H), 1.65–1.74 (m, 6H), 1.69 (s, 3H), 1.38 (m, 2H), 1.14–1.27 (m, 6H), 0.89 (m, 2H).

Mesylation of the Allylic Alcohols-d_2 (5a–g). The allylic alcohols-d_2 **4a**–**g** (10.0 mmol) were placed into a flask charged with 30.0 mmol of dry triethylamine and 30 mL of dry dichloromethane. Subsequently, 11.0 mmol of methanesulfonyl chloride was added dropwise at 0 °C. Immediate precipitation of triethylammonium chloride was observed. After 25 min, the solids were removed by filtration, and the organic layer was washed with 5% HCl (until pH was acidic), then with saturated solution of $NaHCO_3$ (until pH was slightly basic), and finally with 50 mL of brine. Prolonged reaction time leads to the transformation of the initially formed mesylates to the corresponding allylic chlorides. The allylic mesylates do not persist and were used immediately in the next step without purification. The following are the ^1H NMR data of the mesylates **5a**–**g**. **5a**: 7.19–7.33 (m, 5H), 5.84 (t, 1H, J = 7.0 Hz), 3.44 (d, 2H, J = 7.0 Hz), 3.00 (s, 3H), 1.68 (s, 3H). **5b**: 7.21–7.34 (m, 5H), 5.68 (t, 1H, J = 7.0 Hz), 2.95 (s, 3H), 2.73 (t, 2H, J = 7.5 Hz), 2.44 (m, 2H), 1.70 (s, 3H). **5c**: 7.19–7.32 (m, 5H), 5.66 (t, 1H, J = 7.0 Hz), 3.02 (s, 3H), 2.65 (t, 2H, J = 8.0 Hz), 2.13 (m, 2H), 1.74 (m, 2H), 1.73 (s, 3H). **5d**: 7.17–7.30 (m, 5H), 5.62 (t, 1H, J = 7.0 Hz), 2.99 (s, 3H), 2.61 (t, 2H, J = 7.5 Hz), 2.10 (m, 2H), 1.72 (s, 3H), 1.65 (m, 2H), 1.43 (m, 2H). **5e**: 5.67 (t, 1H, J = 7.5 Hz), 3.02 (s, 3H), 1.98 (t, 2H, J = 7.0 Hz), 1.74 (s, 3H), 1.65–1.75 (m, 5H), 1.15–1.35 (m, 4H), 0.94 (m, 2H). **5f**: 5.63 (t, 1H, J = 7.0 Hz), 3.01 (s, 3H), 2.08 (m, 2H), 1.74 (s, 3H), 1.65–1.75 (m, 5H), 1.15–1.35 (m, 6H), 0.90 (m, 2H).

Preparation of the Alkenes-d_3 (6a–g). The crude mesylates **5a**–**g** (10.0 mmol) dissolved in 5 mL of dry ether were added dropwise at 0 °C to a flame-dried flask charged with a suspension of 4.0 mmol of $LiAlD_4$ and 10 mL of ether. The reaction mixture was stirred overnight, during which the mesylate had been transformed to the alkene-d_3. After treatment with 2 mL of water and extraction with ether, the alkenes **6a**–**g** were purified by flash silica gel chromatography with hexane as eluent. The purity of the *E*-alkenes varied between 90 and 95% and was calculated by comparison with the spectra of the corresponding undeuterated alkenes, prepared by Wittig reaction of isopropylidenetriphenylphosphorane with the aldehydes **2a**−**g**. The following are the spectral data of the deuterated alkenes **6a**−**g**. **6a** (*E* isomer 94%): ^{1}H NMR 7.17−7.31 (m, 5H), 5.35 (t, 1H, J = 7.5 Hz), 3.36 (d, 2H, J = 7.0 Hz), 1.74 (s, 3H); ^{13}C NMR 141.81, 132.37, 128.32, 128.28, 125.66, 123.20, 34.34, 24.70 (septet), 17.73; MS m/z = 149 (100, m/z = 149). **6b** (*E* isomer 94%): ^{1}H NMR 7.22−7.33 (m, 5H), 5.21 (t, 1H, J = 7.5 Hz), 2.67 (t, 2H, J = 8.0 Hz), 2.33 (m, 2H), 1.60 (s, 3H); ^{13}C NMR 142.40, 132.01, 128.43, 128.20, 125.64, 123.74, 36.15, 30.04, 24.79 (septet), 17.57; MS m/z = 163 (100, m/z = 72); HRMS calcd for $C_{12}H_{13}D_3$ 163.1440, found 163.1439. **6c** (*E* isomer 92%): ^{1}H NMR 7.19−7.32 (m, 5H), 5.18 (t, 1H, J = 7.0 Hz), 2.64 (t, 2H, J = 7.5 Hz), 2.05 (m, 2H), 1.69 (m, 2H), 1.62 (s, 3H);^{13}C NMR 142.70, 131.62, 128.41, 128.20, 125.56, 124.34, 35.50, 31.57, 27.62, 24.85 (septet), 17.65; MS m/z = 177 (100, m/z = 104); HRMS calcd for $C_{13}H_{15}D_3$ 177.1597, found 177.1599. **6d** (*E* isomer 95%): ^{1}H NMR 7.21−7.34 (m, 5H), 5.16 (t, 1H, J = 7.0 Hz), 2.66 (t, 2H, J = 7.5 Hz), 2.06 (m, 2H), 1.68 (m, 2H), 1.65 (s, 3H), 1.43 (m, 2H);^{13}C NMR 142.83, 131.25, 128.39, 128.21, 125.55, 124.63, 35.91, 31.13, 29.53, 27.85, 24.84 (septet), 17.61; MS m/z = 191 (100, m/z = 104); HRMS calcd for $C_{14}H_{17}D_3$ 191.1753, found 191.1754. **6e** (*E* isomer 92%): ^{1}H NMR 5.17 (t, 1H, J = 7.5 Hz), 1.88 (t, 2H, J = 7.0 Hz), 1.65−1.75 (m, 4H), 1.61 (s, 3H), 1.15−1.30 (m, 5H), 0.91 (m, 2H);^{13}C NMR 131.56, 123.45, 38.64, 35.91, 33.25, 26.68, 26.45, 24.95 (septet), 17.73; MS m/z = 155 (100, m/z = 55); HRMS calcd for $C_{11}H_{17}D_3$ 155.1753, found 155.1754. **6f** (*E* isomer 92%): ^{1}H NMR 5.13 (t, 1H, J = 7.0 Hz), 2.00 (m, 2H), 1.65−1.75 (m, 5H), 1.63 (s, 3H), 1.15−1.30 (m, 6H), 0.90 (m, 2H); ^{13}C NMR 130.82, 125.15, 37.64, 37.31, 33.37, 26.76, 26.43, 25.34, 24.84 (septet), 17.53; MS m/z = 169 (100, m/z = 55); HRMS calcd for $C_{12}H_{19}D_3$ 169.1910, found 169.1908. **6g** (*E* isomer 90%): ^{1}H NMR 5.14 (t, 1H, J = 7.0 Hz), 1.96 (m, 2H), 1.65−1.75 (m, 5H), 1.62 (s, 3H), 1.14−1.36 (m, 8H), 0.89 (m, 2H); ^{13}C NMR 130.94, 125.03, 37.69, 37.25, 33.47, 28.37, 27.19, 26.79, 26.48, 24.82 (septet), 17.58; MS m/z = 183 (100, m/z = 96); HRMS calcd for $C_{13}H_{21}D_3$ 183.2066, found 183.2070.

Preparation of Thionin-Supported Na−Y. In a flask charged with 2000 mL of deionized water was added 12 mg of thionin acetate, followed by 30 g of zeolite Na−Y (Degussa). After stirring for 3−4 h, the zeolite was removed by filtration, dried in the oven for 2 h at 90 °C, and then submitted to continuous extraction for 2 d. The purple solid was dried under vacuum (10 Torr) at 110−120 °C, until it turned light blue.

General Procedure for the Intrazeolite Photooxygenations. In a test tube were added 1.0 g of freshly dried thionin-supported zeolite Na−Y and 5 mL of dry hexane, which contained 10 μL of pyridine. After 5 min, another 5 mL of a solution of the alkene-d_3 (10 mg) in hexane was added. The tube was immediately photolyzed at 0 °C under a constant slow stream of oxygen gas for 1−2 min, followed by immediate addition 10 mL of moistened tetrahydrofuran. The slurry was stirred for 3 h, and then the solid was removed by filtration. The solvent was removed by rotary evaporation, and the ^{1}H NMR spectrum was taken directly on the crude reaction mixture. The product data is collected in Table 1. Further purification of the allylic hydroperoxides may be achieved by silica gel chromatography with chloroform as eluent. The following are the characteristic ^{1}H NMR data of the allylic hydroperoxides. Photooxygenation of **5a**: tertiary hydroperoxide [7.22−7.31 (m, 5H), 6.62 (d, 1H, J = 16 Hz), 6.32 (d, 1H, J = 16 Hz), 1.47 (s, 6H)]; secondary hydroperoxide [7.22−7.31 (m, 5H), 5.02 (s, 1H) 4.99 (s, 1H), 4.58 (t, 1H, J = 6.0 Hz), 2.93 (dd, 1H), 2.77 (dd, 1H), 1.79 (s, 3H)]. Photooxygenation of **5b**: tertiary hydroperoxide [7.21−7.35 (m, 5H), 5.89 (dt, 1H, J_1 = 16 Hz, J_2 = 7.0 Hz), 5.67 (d, 1H, J = 16 Hz), 3.44 (d, J = 7.0 Hz), 1.37 (s, 6H)]; secondary hydroperoxide [7.21−7.35 (m, 5H), 5.09 (s, 1H) 5.07 (s, 1H), 4.38 (t, J = 7.0 Hz), 2.70 (m, 2H), 1.94 (m, 2H), 1.78 (s, 3H)]. Photooxygenation of **5c**: tertiary hydroperoxide [7.18−7.32 (m, 5H), 5.74 (dt, 1H, J_1 = 15.5 Hz, J_2 = 7.0 Hz), 5.49 (d, 1H, J = 15.5 Hz), 2.76 (t, J = 7.0 Hz), 1.32 (s, 6H)]; secondary hydroperoxide [7.18−7.32 (m, 5H), 5.05 (s, 1H) 5.04 (s, 1H), 4.37 (t, J = 7.0 Hz), 2.42 (m, 2H), 1.76 (s, 3H)]. Photooxygenation of **5d**: tertiary hydroperoxide [7.19−7.32 (m, 5H), 5.75 (dt, 1H, J_1 = 15.5 Hz, J_2 = 8.0 Hz), 5.58 (d, 1H, J = 15.5 Hz), 2.65 (t, 2H, J = 8.0 Hz), 1.35 (s, 6H)]; secondary hydroperoxide [7.19−7.32 (m, 5H), 5.04 (s, 1H) 5.03 (s, 1H), 4.34 (t, J = 6.5 Hz), 2.64 (t, 2H, J = 7.5 Hz), 2.14 (m, 2H), 1.73 (s, 3H)]. Photooxygenation of **5e**: tertiary hydroperoxide [5.68 (dd, 1H, J_1 = 16 Hz, J_2 = 6.5 Hz), 5.50 (d, 1H, J = 16 Hz), 1.37 (s, 6H)]; secondary hydroperoxide [5.04 (s, 1H) 5.03 (s, 1H), 4.46 (t, J = 7.0 Hz), 1.75 (s, 3H)]. Photooxygenation of **5f**: tertiary hydroperoxide [5.71 (dt, 1H, J_1 = 15.5 Hz, J_2 = 7.0 Hz), 5.52 (d, 1H, J = 15.5 Hz), 1.98 (t, 2H, J = 7.0 Hz), 1.35 (s, 6H)]; secondary hydroperoxide [5.04 (s, 1H) 5.03 (s, 1H), 4.30 (t, J = 7.0 Hz)]. Photooxygenation of **5g**: tertiary hydroperoxide [5.73 (dt, 1H, J_1 = 16.0 Hz, J_2 = 7.0 Hz), 5.54 (d, 1H, J = 16.0 Hz), 1.95 (m, 2H), 1.34 (s, 6H)]; secondary hydroperoxide [5.04 (s, 1H) 5.03 (s, 1H), 4.34 (t, J = 7.0 Hz)].

1-Phenyl-3-methylbut-2-ene-4,4,4,3′,3′,3′-d_6 (6-d_6) was prepared by Wittig coupling of acetone-d_6 with the ylide produced from the phosphonium salt of 2-phenylethyl bromide. The alkene **6-d_6** was isolated in 65% yield after distillation and the ^{1}H NMR spectrum revealed negligible deuterium-scrambling at the geminal methyl groups: ^{1}H NMR 7.17−7.31 (m, 5H), 5.35 (t, 1H, J = 7.5 Hz), 3.36 (d, 2H, J = 7.0 Hz);^{13}C NMR 141.80, 132.26, 128.31, 128.27, 125.65, 123.22, 34.34, 24.77 (septet), 16.89 (septet); MS m/z = 152 (100, m/z = 134).

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Supporting Information Available: Twelve ^{1}H NMR spectra of compounds **6b**−**g** and some representative intrazeolite photooxygenation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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