JOC Article

Ene Hydroperoxidation of Isobutenylarenes within Dye-Exchanged Zeolite Na–Y: Control of Site Selectivity by Cation–Arene Interactions

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The site selectivity in the singlet oxygen ene reaction of several deuterium-labeled isobutenylarenes depends on the position and the electronic nature of the aryl substitutents. For example, 1-(4-trifluoromethylphenyl)-2-methylpropene gives 82% *twin* selectivity whereas the isomeric 1-(2-trifluoromethylphenyl)-2-methylpropene gives 68% *twix* selectivity. If photooxygenation of these CF_3-substituted compounds is carried out in solution, the opposite selectivity trends are found. On the basis of DFT calculations, these results are rationalized in terms of oxygen–cation and cation–arene interactions.
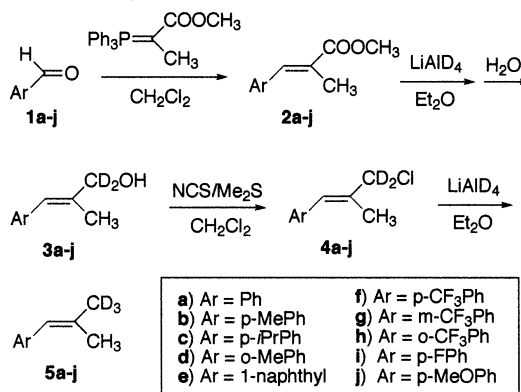
Introduction

The dye-sensitized intrazeolite photooxygenation of organic compounds has attracted recently considerable attention[1] due to the significant enhancement of product selectivity. For trisubstituted alkenes, the ene reaction is regioselective with preferential double-bond formation at the more substituted carbon of the double bond. In addition, the "*cis effect*" selectivity in the photooxygenation of trisubstituted alkenes does not operate within the zeolite.[2] On the other hand, the regioselectivity in the intrazeolite photooxygenation of electron poor alkenes is very close to that found in solution.[3]

Recently, we reported[4] that photooxygenation of isobutenylarenes within thionin-supported zeolite Na–Y is chemoselective, affording the ene allylic hydroperoxides as major or only products (Scheme 1). Although photooxygenation of these compounds in solution gives mainly oxygenated products arising from [4 + 2] or [2 + 2] addition to the arylalkene,[5] within zeolite Na-Y these products are minor or even absent. It was proposed[4] that Na^+ coordination to the aryl ring destabilizes the transition state for the formation of the zwitterionic intermediate, relative to the perepoxide intermediate; the zwitterionic intermediate[6] is the precursor of the Diels–Alder

SCHEME 1. Intrazeolite Photooxygenation of Isobutenylarenes
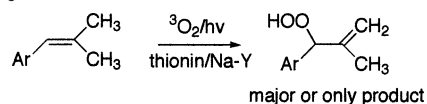
SCHEME 2. Synthesis of Labeled Alkenes 5a–j

or the [2 + 2] oxygenated products, while the perepoxide leads to the ene products.

Results

In this paper, we report a site-selectivity study of the ene reaction in the intrazeolite photooxygenation of the stereoselectively labeled 1-aryl-2-methylpropenes **5a–j**. The preparation of alkenes **5a–j** was accomplished in 93–99% purity for the E configuration following known literature procedures[2a,c] (Scheme 2). The only change is that instead of forming the labile allylic mesylates-d_2, the allylic alcohols-d_2 were transformed to the more stable

(1) (a) Ramamurthy, V.; Lakshminarasimhan, P. H.; Grey, C. P.; Johnston, L. J. *J. Chem. Soc., Chem. Commun.* **1998**, 2411–2418. (b) Zhou, W.; Clennan, E. L. *J. Am. Chem. Soc.* **1999**, *121*, 2915–2916. (c) Clennan, E. L.*Tetrahedron* **2000**, *56*, 9151–9179.

(2) (a) Stratakis, M.; Froudakis, G. *Org. Lett.* **2000**, *2*, 1369–1372. (b) Clennan, E. L.; Sram, J. P. *Tetrahedron* **2000**, *56*, 6945–6950. (c) Stratakis, M.; Nencka, R.; Rabalakos, C.; Adam. W.; Krebs, O. *J. Org. Chem.* **2002**, *67*, 8758–63.

(3) Clennan, E. L.; Sram, J. P.; Pace, A.; Vincer, K.; White, S. *J. Org. Chem.* **2002**, *67*, 3975–3978.

(4) Stratakis, M.; Rabalakos, C. *Tetrahedron Lett.* **2001**, *42*, 4545–4547.

(5) Frimmer, A. A.; Stephenson, L. M. In *Singlet Oxygen. Reactions, modes and products*, Frimer, A. A., Eds.; CRC Press: Boca Raton, 1985; pp 120–133.

(6) (a) Clennan, E. L. *Tetrahedron* **1991**, *47*, 1343–82. (b) Adam, W.; Prein M. *Acc. Chem. Res.* **1996**, *29*, 275–83.

TABLE 1. Site Selectivity in the Photooxygenation of Isobutenylarenes 5a–j
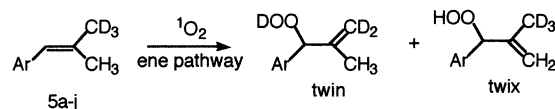
Substrate	Ar	Intrazeolite photooxidation (*twin/twix*)[a]	Photooxidation in solution[b] (*twin/twix*)[a]
5a		42/58	37/63
5b		43/57	45/55[d]
5c		45/55	42/58
5d		45/55	39/61
5e		61/39	18/82
5f		82/18	26/74[d]
5g		38/62	30/70
5h		32/68	77/23
5i		60/40	32/68[d]
5j		59/41	Not determined[e]

[a] The values were corrected for 100% *E* geometrical purity of the deuterium-labeled alkenylarenes. [b] Photooxygenation in CH_2Cl_2, with methylene blue as sensitizer. [c] The *twin/twix* selectivity is solvent dependent (ref 10). [d] Reference 11. [e] The reaction mixture was very complex, and the ene adduct was formed in <10% relative yield for the *twin/twix* selectivity to be determined accurately.

allylic chlorides-d_2 by reacting with *N*-chlorosuccinimide and dimethyl sulfide, according to a literature procedure.[7]

All arylalkenes afford upon photooxygenation within thionin-supported zeolite Na–Y, the ene allylic hydroperoxides[8] as the major or only products. In a typical experiment, 10 mg of the alkenylarene dissolved in 10 mL of hexane was added to a tube containing 1 g of dry thionin-supported Na–Y. The tube was irradiated at 0 °C for 4–5 min under a constant flow of oxygen. After extractive workup, the products were analyzed by ^{1}H NMR spectroscopy. It is remarkable that all substrates had been consumed after 5 min of irradiation, whereas the same amount of the alkenylarenes (~10 mg) in solution (CH_2Cl_2, with methylene blue as sensitizer) require reaction time of one to several hours to go to completion, and the product mixture is very complex as well. The mass balances, as estimated by GC using 2-phenylethanol or 2,6-di-*tert*-butyl-*p*-cresol as calibration compounds, were 86–94% except for **5e** (mass balance 78%).

(7) Grdina, M. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Org. Chem.* **1979**, *44*, 2936–2938.

(8) The allylic hydroperoxides were reduced with PPh_3 to the corresponding alcohols, whose spectral data are identical to the alcohols produced by 2-propenylmagnesium bromide addition to the arylaldehydes **1a–j**.
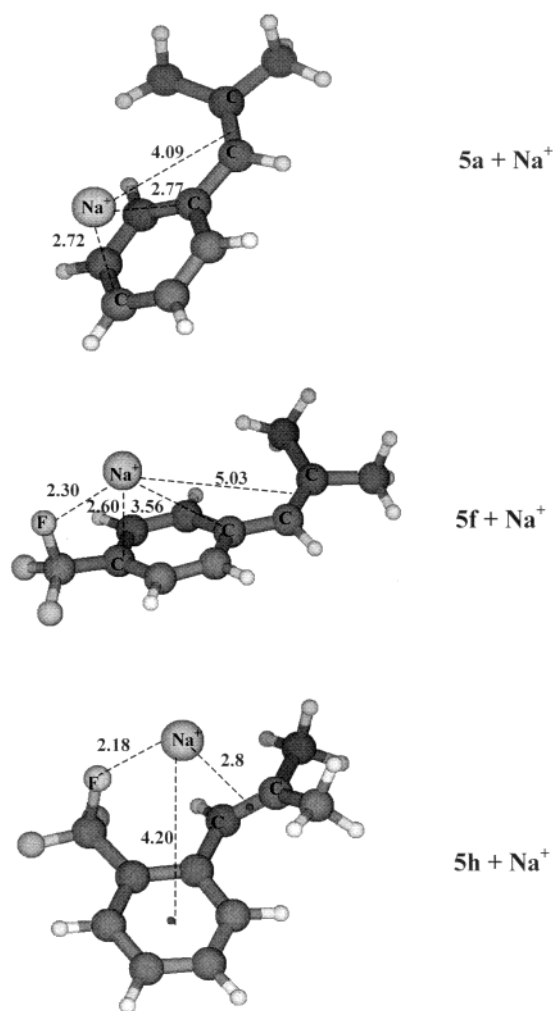
The intrazeolite photooxygenation results are presented in Table 1. For comparison, the site selectivity for the ene pathway in the photooxygenation of the same alkenes in solution is presented. In solution, the ene allylic hydroperoxides were formed as minor adducts, but we were able to either isolate them by column chromatography or calculate the ratio of *twin/twix*[9] selectivity from the crude reaction mixture, if the signals of the ene products in the region of 4.5−6.0 ppm were not overlapping with other absorptions. In the intrazeolite photooxygenation of substrates **5a−d**, where Ar = phenyl (**5a**), *p*-tolyl (**5b**), *p*-isopropylphenyl (**5c**), and *o*-tolyl (**5d**), the *twin/twix* methyl group reactivity is almost identical, with the *twix* methyl group being slightly more reactive. Similar *twin/twix* reactivities are found in solution. The preference for *twix* reactivity, if photooxygenation is carried in solution, has been rationalized[10] for the case of **5a** in terms of attractive oxygen−arene interactions during the formation of the intermediate perepoxide. For the *p*-CF₃-substituted styrene **5f**, however, very different selectivities were found in the zeolite compared to the solution.

Although in solution the *twix* reactivity is 74%, within Na-Y, it drops to 18%. Contrary to **5f**, for the *o*-CF₃ substituted styrene **5h**, the *twix* selectivity in solution is only 23%, while in Na-Y it increases to 68%. For the *m*-CF₃-substituted styrene **5g**, similar regioselectivities were found in solution and within Na-Y (*twin/twix* ~ 1/2). For alkenes **5e**, **5i**, and **5j**, where the substitutents are 1-naphthyl, *p*-fluoro, and *p*-methoxy, respectively, reactivities of approximately *twin/twix* = 60/40 are found within the zeolite, while in solution, the *twix* methyl group is more reactive.

Discussion

Before analyzing the intrazeolite regioselectivity results, we would like to present our theoretical calculations on the interaction of Na⁺ to some isobutenylarenes. Sodium cation is well-known to bind strongly to the π face of aromatics,[12] and this coordination is likely to affect the regioselectivity results in the photooxygenation of the isobutenylarenes within Na-Y. The theoretical treatment of the neutral and the sodium-bound molecules involved density functional theory (DFT)[13] with the three-parameter hybrid functional of Becke and the use of Lee−Yang−Parr correlation functional (B3LYP). The level of the calculations used herein was B3LYP/6-31G*. For **5a**, the cation binds on top and in the middle of the phenyl group at a distance of 4.088 Å from the middle of the alkene double bond (Chart 1). Also, the phenyl group

(9) For the terminology *twin* and *twix*, see: Adam, W.; Bottke, N.; Krebs, O. *J. Am. Chem. Soc.* **2000**, *122*, 6791−6792.

(10) Stratakis, M.; Orfanopoulos, M.; Foote, C. S. *J. Org. Chem.* **1998**, *63*, 1315−1318.

(11) Alberti, M.; Vougioukalakis, G.; Orfanopoulos, M. *Tetrahedron Lett.* **2003**, *44*, 903−905.

(12) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303−1324.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

CHART 1

5a + Na⁺

5f + Na⁺

5h + Na⁺

forms a dihedral angle of 29° with respect to the π system of the double bond. For alkene **5f**, in the lowest energy minimum structure the Na⁺ has shifted from the middle of the aryl ring to interact with the fluorine atoms.[14] The distance of the Na⁺ from the middle of the alkene double bond is 5.027 Å and 2.295 Å from the closest F atom (Chart 1). A second minimum less stable by 0.6 kcal/mol was also found in which the Na⁺ is located in the cone of the three fluorine atoms at a distance of 2.48 Å from each F (see the Supporting Information). For **5h**, the −CF₃ functionality shifts significantly the binding site. The Na⁺ is located at a distance of only 2.83 Å from the middle of the double bond (Chart 1). Finally, for substrates **5i** and **5j** where the substituents are *p*-fluoro and *p*-methoxy, respectively, the DFT calculations have shown that apart from the binding site of Na⁺ on the middle of the aryl ring, coordination to the heteroatoms is also significant. The minima in which the Na⁺ is bound to the heteroatoms are less stable by 1.5 kcal/mol for **5i**, and 1.2 kcal/mol for **5j**,[15] compared to the structures where the cation sits on top of the aryl ring (see the Supporting Information).

(14) The strong interaction of Na⁺ to fluorinated compounds within zeolite Na-Y is well known. For example see: Grey, C. P.; Poshni, F. I.; Gualtieri, A. F.; Norby, P.; Hanson, J. C.; Corbin, D. R. Lim, K. H.; Grey, C. P. *J. Am. Chem. Soc.* **1997**, *119*, 1981−1989.

SCHEME 3. Possible Transition States in the Intrazeolite Formation of the Ene Products for Alkenes 5a,f
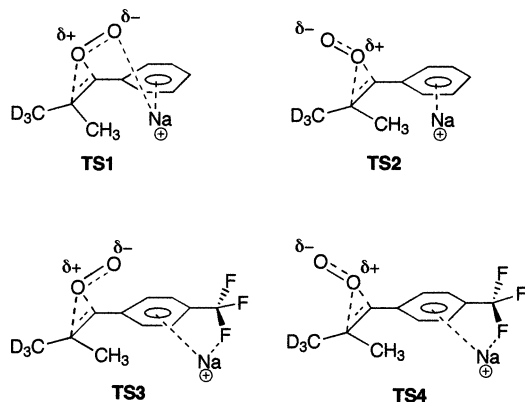
With the exception of the ortho-substituted substrate **5h**, all other alkenylarenes show a preference for *twix* allylic hydrogen atom abstraction if photooxygenation is carried out in solution. Favorable oxygen–arene interactions might be the driving force for this selectivity as postulated for the case of **5a**.[10] Within the zeolite Na-Y, however, we propose that the reactivity of the *twin* and *twix* methyl groups is controlled (i) by electrostatic interactions of Na$^+$ to the styrenes and (ii) by electrostatic interactions of the negatively charged oxygen of perepoxide to the Na$^+$.[16] Considering the nonsubstituted styrene **5a**, the relative higher stability of **TS1** (formation of the *twix* product) in Scheme 3, compared to the **TS2** (formation of the *twin* product), may arise from the favorable electrostatic interactions between the negatively charged oxygen of perepoxide and the cation. The same is expected to be true for styrenes **5b–d**. By placing a CF$_3$ substitutent at the para position in **5a** (substrate **5f**), interaction of Na$^+$ to the highly electronegative fluorine atoms shifts the binding site closer to the CF$_3$ functionality. The distance between the Na$^+$ and the double bond of the alkene is higher (Chart 1), therefore, than the stabilizing electrostatic interaction between the oxygen of the perepoxide and the cation less important (transition state **TS3** in Scheme 3). Thus, the reaction occurs preferentially at the *twin* methyl group via transition state **TS4**.

On going to the ortho-substituted CF$_3$-styrene **5h**, the binding of Na$^+$ to the fluorine atoms shifts the cation very close to the alkene double bond, thus favoring electrostatic interaction of the Na$^+$ to the perepoxide in which oxygen is directed toward the more substituted side of the alkene (68% *twix* selectivity). It is notable that the photooxygenation of **5h** in solution proceeds at a remarkably slow rate (less than 5% conversion after 30 min). Yet, we were able to integrate the appropriate peaks in the crude reaction mixture and found that the *twin* methyl group is 3–4 times more reactive compared to

the *twix* methyl group. This selectivity in solution, which is the opposite to that found for all other substrates in this study, could be rationalized considering the severe electronic repulsions of the fluorine atoms to the oxygen approaching the more substituted side of the alkene.

For substrates **5i** and **5j**, the substituents *p*-fluoro and *p*-methoxy compete with the phenyl ring for binding to the cation. We assume that the average binding site must be between the center of the arene and the F or O atoms, respectively, but not as shifted from the center of the aryl ring, as in the case of the *p*-CF$_3$-substituted styrene **5f**. In other words, the distance of the cation from the styrene double bond has increased, and formation of the perepoxide intermediate facing toward the more substituted side of the alkene is less favorable compared to **5a**, but more favorable compared to **5f**. Thus, intermediate values for the *twix* selectivity, between **5a** and **5f**, were found for **5i** and **5j**. In the case of the naphthyl-substituted compound **5e**, we postulate that coordination of Na$^+$ to the naphthalene moiety is also the driving force, for the reaction to occur preferentially, within Na-Y, at the *twin* position. Again, as proposed for **5i** and **5j**, the average binding site is expected to have shifted from the middle of the aryl ring which is next to the alkene double bond.

In conclusion, we have found that the site selectivity in the ene reaction of several isobutenylarenes within zeolite Na-Y can be correlated to the distance of the alkene double bond from the binding site of the Na$^+$ with the substrate. The longer the distance, the lower reactivity of the *twix* methyl group, due to the reduction of the favorable oxygen–cation interactions during the formation of the intermediate perepoxide in which oxygen is oriented toward the more substituted side of the alkene.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a 500 MHz instrument. Isomeric purities were determined by ^{1}H NMR, ^{13}C NMR, and GC on an HP-5 capillary column. All spectra reported herein were taken in CDCl$_3$. Preparation of the labeled alkenylarenes **5a**[10] and **5j**[17] has been described from earlier studies in our lab, while **5b** was a gift from Mrs. M. Alberti.[11]

The ^{1}H NMR data of the esters **2c–i** are as follows. **2c**: 7.68 (s, 1H), 7.36 (d, 2H, $J = 8.0$ Hz), 7.26 (d, 2H, $J = 8.0$ Hz), 3.82 (s, 3H), 2.94 (septet, 1H, $J = 7.0$ Hz), 2.14 (s, 3H), 1.27 (d, 6H, $J = 7.0$ Hz). **2d**: 7.76 (s, 1H), 7.20–7.23 (m, 4H), 3.84 (s, 3H), 2.29 (s, 3H), 1.97 (s, 3H). **2e**: 8.21 (s, 1H), 7.85–7.95 (m, 3H), 7.49–7.56 (m, 3H), 7.41 (d, 1H, $J = 7.1$ Hz), 3.81 (s, 3H), 2.08 (s, 3H). **2f**: 7.58 (s, 1H), 7.55 (d, 1H, $J = 8.0$ Hz), 7.45 (d, 1H, $J = 8.0$ Hz), 3.82 (s, 3H), 2.09 (s, 3H). **2g**: 7.69 (s, 1H), 7.63 (s, 1H), 7.47–7.59 (m, 3H), 3.84 (s, 3H), 2.12 (s, 3H). **2h**: 7.86 (s, 1H), 7.72 (d, 1H, $J = 7.8$ Hz), 7.57 (t, 1H, $J = 7.2$ Hz), 7.44 (t, 1H, $J = 7.2$ Hz), 7.33 (d, 1H, $J = 7.8$ Hz), 3.85 (s, 3H), 1.93 (s, 3H). **2i**: 7.64 (s, 1H), 7.37 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 5.7$ Hz), 7.08 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 8.5$ Hz), 3.82 (s, 3H), 2.10 (s, 3H).

The ^{1}H NMR data of the allylic alcohols-d_2 **3c–i** are as follows. **3c**: 7.23 (d, 2H, $J = 8.0$ Hz), 7.20 (d, 2H, $J = 8.0$ Hz), 6.50 (s, 1H), 2.91 (septet, 1H, $J = 7.0$ Hz), 1.93 (s, 3H), 1.64 (br s, 1H), 1.26 (d, 6H, $J = 7.0$ Hz). **3d**: 7.16–7.20 (m, 4H), 6.52 (s, 1H), 2.26 (s, 3H), 1.76 (s, 3H), 1.57 (br s, 1H). **3e**: 7.98 (m, 1H), 7.88 (m, 1H), 7.78 (d, 1H, $J = 8.0$ Hz), 7.46–7.52 (m, 3H), 7.35 (d, 1H, $J = 8.0$ Hz), 6.99 (s, 1H), 1.79 (s, 3H), 1.60 (br s, 1H). **3f**: 7.58 (d, 2H, $J = 8.2$ Hz), 7.37 (d, 2H, $J = 8.2$

(15) In agreement with the current results, almost isoenergetic minima for aryl versus methoxy binding were calculated for the Na$^+$ interaction to 4′-methoxyacetophenone. We thank Professor V. Ramamurthy for a prepublication copy of their work. Shailaja, J.; Lakshminarasimhan, P. H.; Pradhan, A.; Sunoj, R. B.; Jockusch, S.; Karthikeyan, S.; Uppili, S.; Chandrasekhar, J.; Turro, N. J.; Ramamurthy, V. *J. Phys. Chem. A* **2003**, *107*, in press.

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(17) Stratakis, M.; Hatzimarinaki, M.; Froudakis, G. E.; Orfanopoulos, M. *J. Org. Chem.* **2001**, *66*, 3682–3287.

Hz), 6.54 (s, 1H), 1.89 (s, 3H). **3g**: 7.52 (s, 1H), 7.44–7.51 (m, 3H), 6.56 (s, 1H), 1.89 (s, 3H). **3h**: 7.67 (d, 1H, $J = 7.8$ Hz), 7.51 (t, 1H, $J = 7.5$ Hz), 7.35 (t, 1H, $J = 7.5$ Hz), 7.32 (d, 1H, $J = 7.8$ Hz), 6. 71 (s, 1H), 1.73 (s, 3H), 1.66 (br s, 1H). **3i**: 7.23 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 5.7$ Hz), 7.02 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 8.5$ Hz), 6.48 (s, 1H), 1.86 (s, 3H).

The ^{1}H NMR data of the allylic chlorides-d_2 **4c–i** are as follows. **4c**: 7.24 (d, 2H, $J = 8.0$ Hz), 7.22 (d, 2H, $J = 8.0$ Hz), 6.58 (s, 1H), 2.93 (septet, 1H, $J = 7.0$ Hz), 2.02 (s, 3H), 1.28 (d, 6H, $J = 7.0$ Hz). **4d**: 7.16–7.20 (m, 4H), 6.60 (s, 1H), 2.26 (s, 3H), 1.84 (s, 3H). **4e**: 7.95 (m, 1H), 7.88 (m, 1H), 7.81 (d, 1H, $J = 8.0$ Hz), 7.47–7.54 (m, 3H), 7.35 (d, 1H, $J = 8.0$ Hz), 7.06 (s, 1H), 1.87 (s, 3H). **4f**: 7.59 (d, 2H, $J = 8.0$ Hz), 7.37 (d, 2H, $J = 8.2$ Hz), 6.61 (s, 1H), 1.98 (s, 3H). **4g**: 7.54 (s, 1H), 7.44–7.52 (m, 3H), 6.62 (s, 1H), 1.99 (s, 3H). **4h**: 7.68 (d, 1H, $J = 7.8$ Hz), 7.53 (t, 1H, $J = 7.5$ Hz), 7.38 (t, 1H, $J = 7.5$ Hz), 7.32 (d, 1H, $J = 7.8$ Hz), 6.78 (s, 1H), 1.82 (s, 3H). **4i**: 7.25 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 5.7$ Hz), 7.03 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 8.5$ Hz), 6.54 (s, 1H), 1.97 (s, 3H).

The spectroscopic data of the deuterated alkenes **5b–i** are as follows. **5b** (isomeric purity 98%): ^{1}H NMR 7.18 (br s, 4H), 6.30 (s, 1H), 2.40 (s, 3H), 1.92 (s, 3H); ^{13}C NMR 135.79, 135.28, 134.60, 128.71, 128.60, 124.96, 25.97 (septet, $J_{CD} = 19$ Hz), 21.08, 19.29; MS $m/z = 149$ (100, $m/z = 149$); HRMS calcd for $C_{11}H_{11}D_3$ 149.1283, found 149.1281. **5c** (isomeric purity 95%): ^{1}H NMR 7.19 (d, 2H, $J = 8.0$ Hz), 7.17 (d, 2H, $J = 8.0$ Hz), 6.25 (s, 1H), 2.90 (septet, 1H, $J = 7.0$ Hz), 1.87 (s, 3H), 1.26 (d, 6H, $J = 7.0$ Hz); ^{13}C NMR: 128.75, 128.65, 126.28, 126.04, 125.01, 33.76, 24.95 (septet, $J_{CD} = 19$ Hz), 24.05, 19.34; MS $m/z = 177$ (100, $m/z = 134$). **5d** (isomeric purity 99%): ^{1}H NMR 7.13–7.18 (m, 4H), 6.23 (s, 1H), 2.25 (s, 3H), 1.71 (s, 3H); ^{13}C NMR 137.88, 136.28, 134.84, 129.60, 129.40, 126.20, 125.22, 124.14, 25.18 (septet, $J_{CD} = 19$ Hz), 19.86, 19.12; MS $m/z = 149$ (100, $m/z = 149$); HRMS calcd for $C_{11}H_{11}D_3$ 149.1283, found 149.1281. **5e** (isomeric purity 96%): ^{1}H NMR 8.01 (d, 1H, $J = 5.9$ Hz), 7.86 (d, 1H, $J = 5.9$ Hz), 7.56 (d, 1H, $J = 8.2$ Hz), 7.45–7.50 (m, 3H), 7.32 (d, 1H, $J = 8.2$ Hz), 6.67 (s, 1H), 1.73 (s, 3H); ^{13}C NMR 136.77, 135.98, 133.55, 132.18, 128.27, 126.67, 126.61, 125.54, 125.29, 125.22, 122.95, 25.26 (septet, $J_{CD} = 19$ Hz), 19.50; MS $m/z = 185$ (100, $m/z = 167$); HRMS calcd for $C_{14}H_{11}D_3$ 185.1283, found 185.1280. **5f** (isomeric purity 93%): ^{1}H NMR 7.56 (d, 2H, $J = 8.2$ Hz), 7.32 (d, 2H, $J = 8.2$ Hz), 6.29 (s, 1H), 1.88 (s, 3H); ^{13}C NMR 142.30, 137.84, 128.88, 127.76 (q, $J_{CF} = 31.9$ Hz), 124.94 (q, $J_{CF} = 3.5$ Hz), 124.40 (q, $J_{CF} = 270$ Hz), 124.08, 26.03 (septet, $J_{CD} = 19$ Hz), 19.34; MS $m/z = 203$ (100, $m/z = 203$); HRMS calcd for $C_{11}H_8D_3F_3$ 203.1001, found 203.1000. **5g** (isomeric purity 98%): ^{1}H NMR 7.39–7.48 (m, 4H), 6.29 (s, 1H), 1.87 (s, 3H); ^{13}C NMR 139.39, 137.34, 131.93, 130.42 (q, $J_{CF} = 31.6$ Hz), 128.41, 125.38, (q, $J_{CF} = 3.2$ Hz), 124.32 (q, $J_{CF} = 271$ Hz), 123.92, 122.44 (q, $J_{CF} = 3.6$ Hz), 25.88 (septet, $J_{CD} = 19$ Hz), 19.22; MS $m/z = 203$ (100, $m/z = 203$). **5h** (isomeric purity 97%): ^{1}H NMR 7.65 (d, 1H, $J = 7.8$ Hz), 7.49 (t, 1H, $J = 7.5$ Hz), 7.32 (t, 1H, $J = 7.5$ Hz), 7.29 (d, 1H, $J = 7.8$ Hz), 6.43 (s, 1H), 1.71 (s, 3H); ^{13}C NMR 137.71, 137.21, 131.53, 131.13, 128.50 (q, $J_{CF} = 29.1$ Hz), 126.09, 125.56, (q, $J_{CF} = 5.4$ Hz), 124.37 (q, $J_{CF} = 272$ Hz), 122.76, 25.17 (septet, $J_{CD} = 19$ Hz), 19.19; MS $m/z = 203$ (100, $m/z = 203$); HRMS calcd for $C_{11}H_8D_3F_3$ 203.1001, found 203.0999. **5i** (isomeric purity 98%): ^{1}H NMR 7.20 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 5.9$ Hz), 7.03 (dd, 2H, $J_{HH} = 8.5$ Hz, $J_{HF} = 8.5$ Hz), 6.26 (s, 1H), 1.86 (s, 3H); ^{13}C NMR 161.06 (d, $J_{CF} = 243$ Hz), 135.25, 134.67 (d, $J_{CF} = 3.3$ Hz), 130.15 (d, $J_{CF} = 7.6$ Hz), 124.05, 114.80 (d, $J_{CF} = 21$ Hz), 25.81 (septet, $J_{CD} = 19$ Hz), 19.14; HRMS calcd for $C_{10}H_8D_3F$ 153.1033, found 153.1034.

Intrazeolite Photooxygenation. Preparation of thionin-supported zeolite Na-Y and the intrazeolite photooxygenation procedures are described in ref 2c. The ^{1}H NMR spectroscopic data of the ene allylic hydroperoxides, formed by the intrazeolite photooxygenation of the perprotio isobutenylarenes **5a–i** (d_0), are the following. Ene product from **5a**-d_0: 7.95 (s, 1H, OOH), 7.30–7.38 (m, 5H), 5.38 (s, 1H), 5.13 (br s, 1H), 5.08 (br s, 1H), 1.69 (s, 3H). Ene product from **5b**-d_0: 7.98 (s, 1H, OOH), 7. 25 (d, 2H, $J = 7.9$ Hz), 7.18 (d, 2H, $J = 7.9$ Hz), 5.35 (s, 1H), 5.13 (br s, 1H), 5.07 (br s, 1H), 2.36 (s, 3H), 1.70 (s, 3H). Ene product from **5c**-d_0: 7.97 (s, 1H, OOH), 7.28 (d, 2H, $J = 8.0$ Hz), 7.23 (d, 2H, $J = 8.0$ Hz), 5.36 (s, 1H), 5.14 (br s, 1H), 5.08 (br s, 1H), 2.92 (heptet, 1H, $J = 7.0$ Hz), 1.71 (s, 3H), 1.26 (d, 6H, $J = 7.0$ Hz). Ene product from **5d**-d_0: 8.12 (s, 1H, OOH), 7.37 (m, 1H), 5.19–7.25 (m, 3H), 5.61 (s, 1H), 5.12 (br s, 1H), 5.06 (br s, 1H), 1.74 (s, 3H). Ene product from **5e**-d_0: 8.21 (s, 1H, OOH), 8.14 (d, $J = 8.3$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 8.3$ Hz, 1H), 7.58 (d, $J = 7.1$ Hz, 1H), 7.48–7.55 (m, 3H), 6.15 (s, 1H), 5.21 (br s, 2H), 1.79 (s, 3H). Ene product from **5f**-d_0: 8.09 (s, 1H, OOH), 7.64 (d, $J = 8.1$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 5.44 (s, 1H), 5.12 (br s, 1H), 5.11 (br s, 1H), 1.70 (s, 3H). Ene product from **5g**-d_0: 8.46 (s, 1H, OOH), 7.63 (s, 1H), 7.60 (d, 1H, $J = 7.7$ Hz), 7.56 (d, 1H, $J = 7.7$ Hz), 7. 52 (t, 1H, $J = 7.7$ Hz), 5.44 (s, 1H), 5.14 (br s, 1H), 5.13 (br s, 1H), 1.71 (s, 3H). Ene product from **5h**-d_0: 8.13 (s, 1H, OOH), 7.68–7.73 (m, 2H), 7.62 (t, 1H, $J = 7.6$ Hz), 7.48 (t, 1H, $J = 7.5$ Hz), 5.82 (s, 1H), 5.12 (br s, 1H), 4.95 (br s, 1H), 1.79 (s, 3H). Ene product from **5i**-d_0: 8.05 (s, 1H, OOH), 7.33 (dd, $J_{H–H} = 8.0$ Hz, $J_{H–F} = 5.5$ Hz, 2H), 7.06 (dd, $J_{H–H} = 8.0$ Hz, $J_{H–F} = 8.0$ Hz, 2H), 5.36 (s, 1H), 5.13 (br s, 1H), 5.10 (br s, 1H), 1.69 (s, 3H). Ene product from **5j**-d_0: 7.99 (s, 1H, OOH), 7.29 (d, $J = 8.5$ Hz, 2H), 6.90 (d, $J = 8.5$ Hz, 2H), 5.33 (s, 1H), 5.14 (br s, 1H), 5.08 (br s, 1H), 3.81 (s, 3H), 1.70 (s, 3H).

Supporting Information Available: Fifteen ^{1}H NMR spectra of the labeled alkenylarenes and their intrazeolite photooxygenation reactions. Five calculated minima structures of Na$^+$ interaction to arenes **5f**, **5i**, and **5j** at the B3LYP/6-31G* level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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