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Confined Space-Controlled Hydroperoxidation of Trisubstituted Alkenes Adsorbed on Pentasil Zeolites

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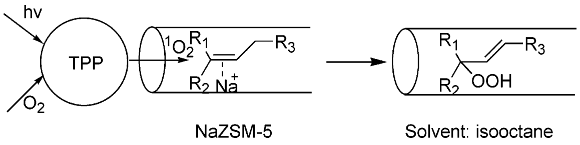

Photosensitized oxidation of trialkylalkenes 2-methyl-2-pentene (**1**), 1-methylcyclohexene (**2**), *trans*-3-methyl-2-pentene (**3**), *cis*-3-methyl-2-pentene (**4**), and 2-methyl-2-butene (**5**) included in the internal framework of Na-ZSM-5 zeolites was investigated. The zeolite samples having adsorbed the alkenes were suspended in isooctane, and the sensitizer, tetraphenylporphyrin (TPP), was dissolved in the solution. Singlet oxygen produced in the solution diffused into the internal framework of the zeolites and reacted with alkenes. For all the substrates studied, the ene-type allylic hydroperoxides were obtained in a highly regioselective manner. The regiochemistry for **1**−**4** in favor of the allylic hydrogen abstraction from the largest substituents is in contrast to their photooxidation within the dye-supported zeolite Na−Y, where the secondary hydroperoxides are preferentially produced. The tight confinement of the alkenes within the narrow channels of the ZSM-5 zeolites is likely to be responsible for this selectivity.

Introduction

The reaction of singlet oxygen ($^1O_2$) with alkenes containing allylic hydrogens has attracted much attention because the allylic hydroperoxide products are important building blocks for synthetic organic chemistry.[1−7] This reaction was first introduced by Schenck[8] in the late 1940s, and is often referred to as the "ene" or Schenck reaction.[6,7] A large number of experimental and theoretical studies have established a mechanism for this reaction involving the perepoxide intermediate, and the effects of the substituents in alkenes on the direction of the approach of singlet oxygen to the stereogenic faces of the substrate molecules have been thoroughly investigated.[6,7] However, the potential synthetic use of this reaction is suppressed by the fact that reaction with substrates containing several distinct allylic hydrogens generally produces several distinct products, and the selectivity of the reaction is poor. To gain the selectivity in the reaction, various efforts have been made in the past decades, and remarkable regio- and stereocontrol has been obtained.[9−12] For example, Adam and coworkers[9] successfully utilized hydrogen bonding to control the facial diastereoselectivity of the ene reactions in a series of allylic alcohols and amines. On the other hand,

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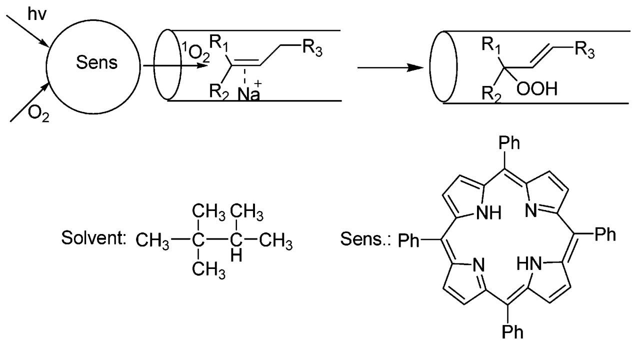
several research groups have employed organized and constrained media to enhance the selectivity in the hydroperoxidation of alkenes.[10−12] In particular, Ramamurthy,[10] Clennan,[11] Stratakis,[12] and their co-workers have used the dye-supported Y-type zeolites as media for selective oxidation of alkenes. They demonstrated that for trisubstituted alkenes the ene reaction within these intrazeolites is regioselective with preferential double-bond formation at the more substituted carbon of the double bond and the "*cis* effect" selectivity in solution does not operate within zeolites. For the photoxygenation of 1-methylcycloalkenes,[10c] in contrast to the reaction in solution, even an anti "*cis* effect" selectivity was found in the intrazeolites. Ramamurthy[10] and Clennan[11] proposed, respectively, that the metal cation comlexation to the alkene and the electrostatic interaction of the cation with the pendant oxygen in the perepoxide intermediate are responsible to the regiochemistry of the intrazeolite photooxidation.

Although the photooxidation of the alkenes within Y-zeolites has been extensively investigated, curiously the ene reaction conducted within the internal framework of pentasil zeolites was scarcely studied.[13,14] Here, we report the photooxidation of trisubstituted alkenes 2-methyl-2-pentene (**1**), 1-methylcyclohexene (**2**), *trans*-3-methyl-2-pentene (**3**), *cis*-3-methyl-2-pentene (**4**), and 2-methyl-2-butene (**5**) within ZSM-5 zeolite, a member of the pentasil zeolite family. The internal surface of ZSM-5 consists of two types of pore systems (channels):[15] one is sinusoidal with a near-circular cross-section of ca. 5.5 Å, and the other is straight and perpendicular to the sinusoidal channels. The straight channels are roughly elliptical with dimensions of ca. 5.2 × 5.8 Å. These channels of ZSM-5 can allow the absorption of benzene and other molecules of similar molecular size but prevent molecules that possess a larger size/shape from being sorbed into the internal framework. In the present work, tetraphenylporphyrin (TPP) and isooctane were selected as the photosensitizer and solvent, respectively. We trapped the alkenes in the channels of ZSM-5 zeolite and dissolved the sensitizer in the solvent. The zeolite sample was suspended in the solution (Scheme 1). The choice of the sensitizer and solvent was motivated by the desire that they were prevented from being sorbed into the ZSM-5 channels due to their size and shape characteristics.[16] Thus, the internal framework of the zeolite was "dry," and the substrate was protected from being extracted to the solution during photolysis. Singlet oxygen was generated in the solution and diffused into the zeolite channels to react with the alkene. We found that in addition to the cation complexation to the alkene and to the pendant oxygen of the perepoxide, the narrow internal confined space of ZSM-5 channels also play a crucial role in the control of the direction of the pendant oxygen, and a remarkable selectivity of the hydroperoxidation is observed. In many cases, the ene product distribution is significantly different both from those in Na−Y zeolites and in solutions. In this sense, the photosensitized oxidation of alkenes within ZSM-5 is complementary with that in Y-type zeolites. Therefore, one can choose Y-type or ZSM-5 zeolites as reaction media to direct the selectivity in alkene photooxidation toward the desired products.

SCHEME 1. Schematic Presentation of the Reaction System



Results and Discussion

General Methods. We used the ZSM-5 with a different Si/Al ratio as the reactive media: a "low" Al content (Si/Al = 55) and a "high" Al content (Si/Al = 25). All of the zeolites were sodium cation exchanged forms. Inclusion of **1**−**5** within the zeolites was achieved by using dichloromethane as the solvent. The powder of ZSM-5 having adsorbed the substrate was collected by filtration of the solvent, dried under nitrogen, and then washed with isooctane to remove the substrate adsorbed on the external surface of ZSM-5. The loading level was kept at ca. 17 mg of substrate on 1 g of ZSM-5. The sample prepared above was suspended in isooctane. The sensitizer, TPP, was dissolved in the solution. The suspension was saturated with oxygen by bubbling the gas during photolysis. A 450-W medium-press Hanovia Hg lamp was used as the light source, and a glass filter was employed to cut off the light with wavelength < 400 nm. Generally, after 30 min of photolysis the conversion of the starting material was near 100%. Similar conversion was obtained in isooctane in the absence of ZSM-5 zeolite after the same irradiation period. After photolysis, the ZSM-5 powder was separated from the solvent by filtration. The hydroperoxide products were extracted with dichloromethane. For ease of analysis, the produced hydroperoxides were converted to the corresponding alcohols

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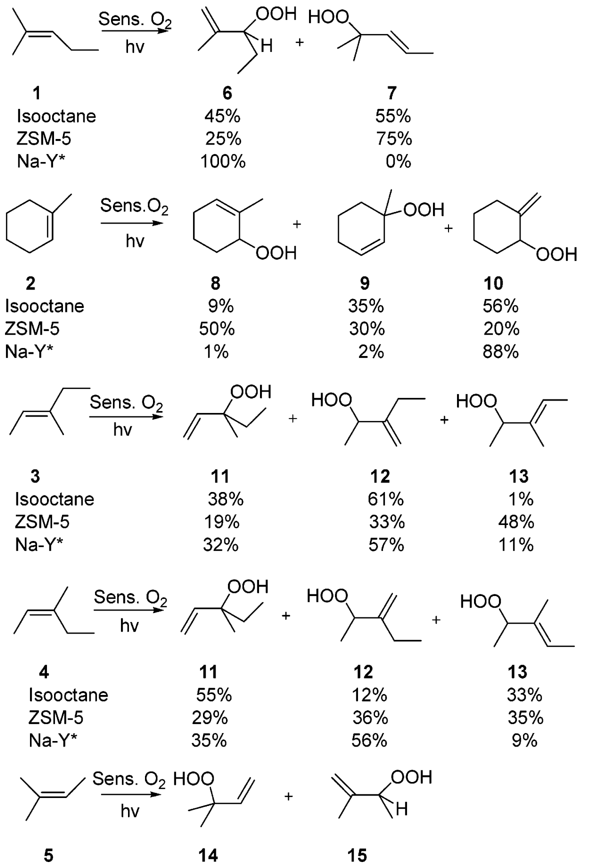
(16) The kinetic diameter of isooctane is >6.2 Å based on the fact that for neopentane the kinetic diameter is 6.2 Å. Thus, it cannot be sorbed into the ZSM-5 internal framework; see: Turro, N. J.; Wan, P. *J. Am. Chem. Soc.* **1985**, *107*, 678−682. TPP has a greater kinetic diameter compared with isooctane.

SCHEME 2. Product Distributions in Photosensitized Oxidation of Alkenes[a]



1	6	7
Isooctane	45%	55%
ZSM-5	25%	75%
Na-Y*	100%	0%

2	8	9	10
Isooctane	9%	35%	56%
ZSM-5	50%	30%	20%
Na-Y*	1%	2%	88%

3	11	12	13
Isooctane	38%	61%	1%
ZSM-5	19%	33%	48%
Na-Y*	32%	57%	11%

4	11	12	13
Isooctane	55%	12%	33%
ZSM-5	29%	36%	35%
Na-Y*	35%	56%	9%

5	14	15
Isooctane	49%	51%
ZSM-5	30%	70%
Na-Y*	28%	72%

[a] Key: *the product distributions for the reactions within Na−Y are quoted from refs 10a−c and 11b,c.

by reaction with triphenylphosphine. The oxidation products were analyzed by gas chromatography and identified by ^{1}HNMR and mass spectroscopies. Material balance in general was greater than 95%.

Photosensitized Oxidation of 1. Reaction of **1** with singlet oxygen gives secondary (**6**) and tertiary (**7**) allylic hydroperoxides as shown in Scheme 2. The product distributions for the reactions carried out in isooctane solution, within ZSM-5 zeolite and within thionin-supported Na−Y zeolite are also shown in Scheme 2. The hydroperoxidation of **1** in solution and within dye-doped Na−Y has been extensively examined.[6,7] In solution, nearly equal amounts of secondary and tertiary hydroperoxides were obtained. This product distribution has been rationalized on the basis of the fact that singlet oxygen attacks the alkene from the top and doubly substituted side of the double bond (*cis* effect). In such an approach, the formed perepoxide is stabilized by secondary interactions between the pendant oxygen and allylic hydrogens, which are situated parallel to the π-orbital (Figure 1a). Thus, both the methyl and methylene hydrogens can be placed in an appropriate geometry for abstraction, and **6** and **7** are formed in a nearly equal amount. Within thionin-supported Na−Y, **6** was exclusively produced. In 1996, Ramamurthy and coworkers[10a] attributed this dramatically enhanced regioselectivity to complexation of the alkene to a sodium cation in the interior of the zeolite (Figure 1b). This complexation would compel the sterically demanding allylic methyl group to rotate to the face approached by singlet oxygen, thereby preventing access to the allylic hydrogens on the methylene carbon. As a result, no tertiary hydroperoxide could be generated. In 1999, Clennan and co-workers[11b] proposed that sodium cation complexed to the pendant oxygen in the perepoxide rather than to the double bond (Figure 2). Markovnikov directing effects (as a result of greater charge buildup on the carbon framework) and the preferential formation of the perepoxide with the pendant oxygen on the least substituted side of the double bond (Figure 2, perepoxide a) were responsible to the observed regiochemistry. Seemly, a combination of ideas proposed by Ramamurthy and Clennan can account for the regioselectivity during the oxidation within dye-supported Na−Y zeolite.[6,17]

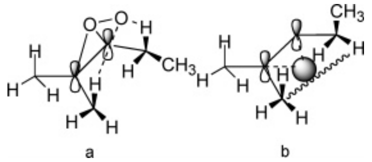


FIGURE 1. Perepoxide intermediate and Ramamurthy's model for oxidation of alkenes within Na−Y zeolite.

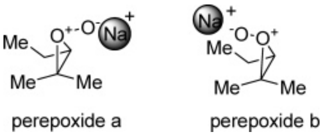


FIGURE 2. Clennan model for oxidation of alkenes within Na−Y zeolite.

Surprisingly, the regioselectivity in the photooxidation of **1** within ZSM-5 is in dramatic contrast to its photooxidation within dye-supported Na−Y. The isolated yield of **6** + **7** was greater than 95% based on the consumption of the starting material, and the main product is the tertiary (**7**) rather than the secondary (**6**) hydroperoxide. To ascertain that the selectivity is not due to any experimental artifacts, we performed the following control experiment. First, we carried out the photooxidation of **1** in isooctane by using TPP as the sensitizer. Then we added ZSM-5 to the solution. Analysis of the hydroperoxides in the solution showed that almost all of the hydroperoxides were adsorbed into the zeolite. After separation of the ZSM-5 powder from the solvent by filtration, the hydroperoxides were extracted again by dichloromethane, and analysis (after reduction by triphenyl phosphine) by gas chromatography revealed that they could be quantatively recovered. Thus, the hydroperoxides were stable and had no unusual affinity for zeolite interior.

We tentatively attribute the change in regioselectivity, as the photooxidation is moved from the interior of Na−Y to the ZSM-5, to the tight confinement of **1** in the ZSM-5 channels. As mentioned above, within Na−Y the sodium cation complexes with alkene and the pendant oxygen

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[17] Clennan, E. L. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York; Vol. 9, 2003.

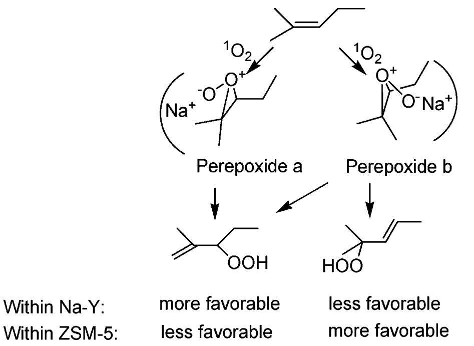

FIGURE 3. Na^+- and zeolite-directing regioselectivity in the photooxidation of 2-methyl-2-pentene.

in the perepoxide, and the pendant oxygen is preferentially on the least substituted side of the double bond (Figure 3, perepoxide a). Thus, **6** is exclusively produced. In contrast, within ZSM-5 the narrow space of the channel would force the perepoxide to orient with the pendant oxygen on the largest group (ethyl) substituted side of the double bond (perepoxide b), because the perepoxide in such conformation is more compact compared with perepoxide a. As a result, the abstraction of the allylic hydrogen from the ethyl is possible. We have estimated the molecular dimensions of perepoxides a and b[18] and compared them with the size of Na−ZSM-5 channel. First, we used a molecular dynamics annealing process to obtain a rough lowest energy conformation for perepoxide a (or perepoxide b), which was followed by a molecular mechanics energy minimization. Then we defined a cylinder that can accommodate the perepoxide in such conformation and has minimum dimensions. The length of the smallest cylinder is assigned to the length of the longest axis of the perepoxide. We believe that the perepoxide will orient with the long axis aligned with the ZSM-5 channel, so that the double bond and the pendant oxygen can interact with the sodium cation on the zeolite channel wall. The dimensions of the perepoxides were determined based on the assumption that the internulear length in the molecule is equivalent.[19] The calculated width pluses 1 Å to account for the size of the exterior hydrogen atom.[20] The obtained widths and lengths for perepoxides a and b are given in Table 1. Evidently, the data determined in this way are somewhat arbitrary. However, they give a relative ranking that is adequate for the present purposes. The kinetic width of the channels in Na−ZSM-5 are estimated to be 5.5 Å.[21] Obviously, while perepoxide b can enter the internal surface of the zeolite, perepoxide a is too large to fit into the channels.

Photosensitized Oxidation of 2. As observed in the case of **1**, the photosensitized oxidation of **2** differed significantly when included in ZSM-5 zeolite compared to those in homogeneous solutions and within dye-supported Na−Y zeolite (Scheme 2). In isooctane solution, the oxidation afforded the endocyclic (**8** and **9**) and exocyclic (**10**) ene allylic hydroperoxides with nearly equal amounts. However, within Na−Y, the photooxygenation is highly regioselective with almost exclusive formation of **10**.[10a] This regiochemistry has been interpreted by Ramamurthy,[10] Clennan,[11] and Stratakis[12] on the basis of cation complexing to the alkene and the pendant oxygen on the least substituted side of the endocyclic double bond (Figure 4, perepoxide a). In contrast, within the interior of ZSM-5, the endocyclic ene allylic hydroperoxides (**8** + **9**) are the predominant products. Mass balance in this reaction was excellent (greater than 95%). This observation is again consistent with the proposal that the confined space of ZSM-5 channels forces the perepoxide to orient with the pendant oxygen directed toward the largest group substituted side of the endocyclic double bond (Figure 4, perepoxide b). As in the case of **1**, we assume that the perepoxide will orient with the double bond aligned with the zeolite channel due to the interaction of the cation on the channel wall with the alkene and the pendant oxygen. Calculation showed that indeed perepoxide b has smaller width than perepoxide a (Table 1), and can fit into the ZSM-5 channels, while perepoxide a cannot be accommodated into the internal surface of the zeolite.

Photosensitized Oxidation of 3 and 4. The evidence that the confined space of the ZSM-5 channels compels the pendant oxygen in the perepoxide to direct toward the largest group substituted side of the alkene is further strengthened by the intrazeolite photooxidation of **3** and **4**. The oxidation of **3** in isooctane almost exclusively resulted in **11** and **12**, and only a trace of **13** was produced (Scheme 2). Again, this observation can be well-rationalized in terms of *cis*-effect. In the intrazeolite photooxygenations, the *cis*-effect is significantly diminished. Within Na−Y, although the main products were originated from the hydrogen abstraction from the two *cis*-methyl (**11** and **12**), considerable amount of **13** was generated.[11c] Within ZSM-5, the change of the regioselectivity is even more significant, and **13** becomes the main product. Evidently, the photooxygenation both within Na−Y and ZSM-5 favors the allylic hydrogen abstraction from the ethyl group. For this substrate, the notation that the pendant oxygen in the perepoxide intermediate directs to the least substituted side of the double bond is the same as the presentation that the pendant oxygen is on the largest group substituted side. Thus, the direction of the effects of the Na−Y and ZSM-5 media on the regioselectivity is the same. The calculated molecular dimensions for the perepoxide with pendant oxygen on the largest group substituted side of the double bond (perepoxide b) and for that with pendant oxygen on the *cis*-dimethyl side (perepoxide a) are given in Table 1. Clearly, only perepoxide b can be formed within ZSM-5 channels.

In contrast, the effects of the Na−Y and ZSM-5 media on the regioselectivity in the photooxygenation of **4**, the isomer of **3**, are significantly different. While the photooxidation within Na−Y afforded the hydroperoxide generated from the abstraction of hydrogen in the *trans*-

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[18] Calculations were performed using ChemBats3D-Pro, Cambridgesoft Corp., Cambridge, MA. Details are given in the Experimental Section.

[19] Morkin, T. L.; Turro, N. J.; Kleinman, M. H.; Brindle, C. S.; Kramer, W. H.; Gould, I. R. *J. Am. Chem. Soc.* **2003**, *125*, 14917−14924.

[20] 1 Å was chosen as a rough compromise between the hydrogen covalent (0.4) and van der Waals radii (1.1−1.3 Å). See: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry* 3rd ed.; Interscience: New York, 1972; pp 116−119.

[21] Olson, D. H.; Kokotallo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, *85*, 2238−2243.

TABLE 1. Dimensions of the Perepoxide Intermediates

substrate	1		2		3		4		5	
perepoxide	a	b	a	b	a	b	a	b	a	b
dimensions (length (Å) × width (Å))	7.4 × 5.6	8.0 × 4.8	6.6 × 6.1	6.8 × 5.3	6.7 × 6.7	6.1 × 5.4	6.6 × 6.3	6.0 × 5.4	6.2 × 4.9	6.1 × 5.1

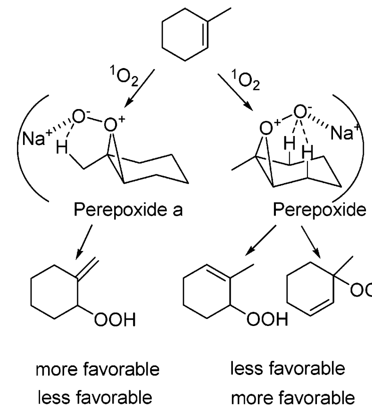

FIGURE 4. Na$^+$- and zeolite-directing regioselectivity in the photooxidation of 1-methylcyclohexene.

methyl (**12**) as the main product,[10c] the internal surface of ZSM-5 enhances the formation of **13**, and **11** + **13** dominate the products. Again, these regioselectivities clearly show that within Na−Y the pendant oxygen of the perepoxide directs toward the least substituted side of the double bond (perepoxide a), while in ZSM-5 the pendant oxygen is on the largest group substituted side of the alkene (perepoxide b). Indeed, the calculated dimensions of the perepoxides (Table 1) indicate that only perepoxide b can be accommodated into the ZSM-5 channels.

Photosensitized Oxidation of 5. The above argument on the regiochemistry of the photooxidation of alkenes within the interior of ZSM-5 suggests that such regioselectivity for the substrates without a large substituent would be absent. Experiments show that this is indeed the case for **5**. The photooxidation of **5** in isooctane gave **14** and **15** with equal amounts, while the product ratios both within Na−Y[10b] and ZSM-5 were in favor of the secondary hydroperoxide, **15**. For this alkene, the calculated dimensions of the perepoxides are given in Table 1. Evidently, all the two diastereomers of the perepoxide can be accommodated within the ZSM-5 channels; thus, the character of photooxidation is almost identical with that in Na−Y zeolite.

Effects of Al Contents on Product Distribution. As mentioned above, we used the ZSM-5 zeolites with a different Si/Al ratio as the reaction media: low Al content (Si/Al = 55) and high Al content (Si/Al = 25). We found that for all the substrates at the loading levels used in the present work the products and their distributions are independent of the Al content. This is readily understood by consideration of the character of ZSM-5 zeolite. It has been established that there exist hydrophilic centers in the internal surface of pentasils, the most common of which are hydroxyl groups or cations associated with a tetrahedrally coordinated aluminum, and the remaining regions in the internal surface are hydrophobic.[22] Within a zeolite alkene molecules are adsorbed to the surface near Al atoms due to the interaction between the π-electron density of the substrate and the cation of the zeolite.[10,23] Based on the unit cell composition ($Na_xSi_{96-x}Al_xO_{192}$) of Na−ZSM-5 zeolite,[13,22b] the concentration of Al is calculated to be ca. 6.3×10^{-4} and 2.3×10^{-4} M per gram of zeolite with a Si/Al value of 25 and 55, respectively. The loading level of the substrates employed in the present study is ca. 2.1×10^{-4} M per gram of zeolite. Thus, both for high and low Al content samples every substrate molecule may associate with a cation near an Al atom and the complexation of the cation to the alkene and to the pendant oxygen can operate in the manners described above. Thus, the Al content shows no effect on the product distributions.

Conclusions

The product distributions for the photosensitized oxidation of **1**−**4** adsorbed within ZSM-5 zeolites are significantly different from those in homogeneous solutions and within Na−Y zeolites. Within dye-supported Na−Y zeolites, the "*cis* effect" selectivity in solution does not operate, and for the oxidation of 1-methylcycloalkenes even an anti "*cis* effect" selectivity was observed. This has been interpreted in terms of the complexation of the cation to the alkene and to the pendant oxygen of the perepoxide and the orientation of the pendant oxygen to the least substituted side of the double bond. In contrast, within ZSM-5 zeolites the constrained space of the zeolite channels compels the pendant oxygen to direct toward the largest group substituted side of the double bond, thus forming a more compact intermediate. As a result, the oxidation proceeds with preferential formation of the products derived from the hydrogen abstraction from the largest group. The oxidation within ZSM-5 zeolites is complementary with that in Y-type zeolites. Thus, one can choose either ZSM-5 or Y-type zeolites as reaction media to direct the selectivity in the photosensitized oxidation of alkene toward the desired products.

Experimental Section

General Procedure for the Intrazeolite Photooxygenations. Alkenes **1**−**5** and the solvents isooctane and dichloromethane were spectra grade. ZSM-5 zeolites with Si/Al = 25 and 55 were sodium-exchanged forms and were baked at 550 °C for 10 h prior to use. For a typical photooxygenation experiment, an activated zeolite sample was added to the substrate solution in dichloromethane and stirred at room temperature for 1 h. The zeolite sample having absorbed the substrate was collected by filtration of the solvent, dried under nitrogen, and washed with isooctane to remove the substrate absorbed on the external surface of the zeolite. The sample

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was subsequently suspended in isooctane in a Pyrex tube. To the tube was added a known amount of the sensitizer (TPP) solution in isooctane. This suspension was bubbled by a constant stream of oxygen during irradiation. A 450-W medium-press Hanovia Hg lamp was used as the light source, and a glass filter was employed to cut off the light with wavelength <400 nm. The filter thus ensured the absence of direct excitation of the alkene substrate. After irradiation, the zeolite was collected by filtration and stirred in each 20 mL of dichloromethane for three times. The extracted products were analyzed by their ^{1}HNMR spectra. The products were then converted into the corresponding alcohols by the reaction with triphenylphosphine and analyzed by gas chromatography−mass spectroscopy on a GC−MS spectrometer and by comparison with authentic samples. For preparative samples, the corresponding alcohols obtained from the reaction with triphenylphosphine were isolated by column chromatography on silica eluting with dichloromethane and identified by their spectral properties.

6. ^{1}HNMR (400 MHz, CD_3CN) δ: 9.23 (s, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 4.14 (t, 1H), 1.68 (s, 3H), 1.54 (m, 2H), 0.86 (t, 3H). MS of its corresponding alcohol: *m/e* 43, 71, 85, 100 (M^+).

7. ^{1}HNMR (400 MHz, CD_3CN) δ: 8.74 (s, 1H), 5.66 (m, 1H), 5.56 (d, 1H), 1.69 (d, 3H), 1.24 (s, 6H). MS of its corresponding alcohol: *m/e* 43, 67, 85, 100 (M^+).

8. ^{1}HNMR (400 MHz, CD_3CN) δ: 9.35 (s, 1H), 5.68 (br s, 1H), 4.18 (br s, 1H), 1.73 (s, 3H), 1.20−1.95 (m, 6H). MS of its corresponding alcohol: *m/e* 55, 69, 84, 97, 112 (M^+).

9. ^{1}HNMR (400 MHz, CD_3CN) δ: 8.76 (s, 1H), 5.88 (m, 1H), 5.53 (d, 1H), 1.23 (s, 3H), 1.20−1.95 (m, 6H). MS of its corresponding alcohol: *m/e* 55, 79, 84, 97, 112 (M^+).

10. ^{1}HNMR (400 MHz, CD_3CN) δ: 9.28 (s, 1H), 4.85 (d, 2H), 4.29 (t, 1H), 1.2−1.95 (m, 8H). MS of its corresponding alcohol: *m/e* 55, 69, 79, 84, 97, 112 (M^+), 113 (M + 1).

11. ^{1}HNMR (400 MHz, CD_3CN) δ: 8.76 (s, 1H), 5.90 (q, 1H), 5.17 (d, 1H), 5.14 (d, 1H), 0.80−1.56 (m, 8H). MS of its corresponding alcohol: *m/e* 43, 55, 67, 71, 85.

12. ^{1}HNMR (400 MHz, CD_3CN) δ: 9.23 (s, 1H), 5.00 (s, 1H), 4.91 (s, 1H), 4.41 (q, 1H), 0.80−1.56 (m, 8H). MS of its corresponding alcohol: *m/e* 43, 55, 67, 71, 85.

13. ^{1}HNMR (400 MHz, CD_3CN) δ: 9.09 (s, 1H), 5.48 (q, 1H), 4.30 (q, 1H), 0.80−1.56 (m, 9H). MS of its corresponding alcohol: *m/e* 43, 55, 67, 71, 85, 100 (M^+).

14. ^{1}HNMR (400 MHz, CD_3CN) δ: 8.88 (s, 1H), 5.97 (q, 1H), 5.19 (d, 1H), 5.11 (q, 1H), 1.26 (s, 6H). MS of its corresponding alcohol: *m/e* 43, 59, 71, 86 (M^+),

15. ^{1}HNMR (400 MHz, CD_3CN) δ: 9.25 (s, 1H), 4.92 (d, 2H), 4.39 (q, 1H), 1.72 (s, 3H), 1.18 (d, 3H). MS of its corresponding alcohol: *m/e* 43, 71, 86 (M^+).

Calculation of the Dimensions of the Perepoxides. The dimensions of the smallest cylinder that can accommodate the most reasonable conformation of a perepoxide were estimated by first performing a molecular dynamics annealing calculation on the perepoxide using MM2 in program ChemBats3D-Pro, from CambridgeSoft. The cooling rate was 1 kcal/atom/ps, and the final temperature was 300 K. An additional molecular mechanics optimization was performed to a minimum rms gradient of 0.1. The relevant axes were then determined by visual inspection. Equivalent atomic center-to-center distances were measured graphically, and 1.0 Å was added to this distance to take into account the dimensions of the exterior hydrogen atoms. Repeated calculations of this type gave dimensions that were reproducible to ca. 0.15 Å.

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