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Zeolite-Promoted Oxidations of 1,1-Diarylethylenes

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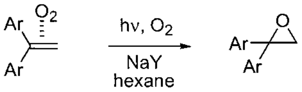
ABSTRACT



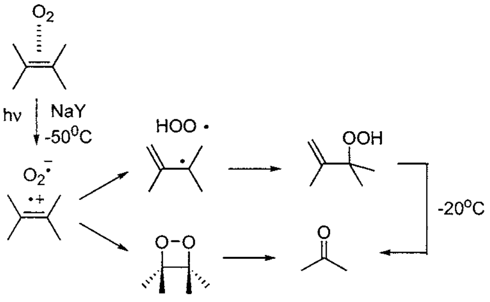
The intrazeolite photooxygenations of four diarylethylenes have been examined. Several intermediates, including an epoxide, have been identified by comparison to independently synthesized samples. Aldehyde intermediates were shown to undergo intrazeolite Norrish type I cleavages in competition with a novel new photooxygenation/autoxidation reaction.

Oxidations initiated by irradiation into oxygen/substrate charge transfer (CT)[1,2] bands are well-known reactions that have been extensively investigated.[3] Unfortunately, despite the economic and environmental appeal of using oxygen as a terminal oxidant, these reactions are of limited synthetic utility. The wavelength of light needed to initiate the oxidation also causes decomposition of the sensitive peroxide product. This problem has been recently and elegantly addressed by Frei and co-workers[4] who reported that incorporation of the oxygen/substrate charge transfer complex into the interior of a zeolite induces a dramatic red-shift of the CT band into a region where the peroxide product does not absorb. These intrazeolite photooxidations have been suggested to occur by a photochemically induced electron transfer followed by either collapse of the ion pair to a dioxetane or abstraction of an allylic hydrogen (Scheme 1).

More recently, intrazeolite photooxidations of 1,1-diaryl ethylenes that do not possess allylic hydrogens have been reported.[5] These reactions have been suggested to proceed, without any direct evidence, via epoxide intermediates. In addition, no agreement on the mechanism of formation or structures of the final products has been achieved. In this letter, we report a reinvestigation of the intrazeolite photooxygenations of diarylethylenes **1a** and **1b**, a comparison to the photooxygenation of diarylethylene, **1c**, and the first direct evidence for the intermediacy of an epoxide in these reactions. In addition, we suggest a mechanism that provides a rationale for all the experimental results, including novel wavelength dependences observed for the photooxygenations of **1a** and **1b** and the lack of a similar wavelength dependence for photooxygenation of **1c**.

The zeolite used in all of the experiments reported here is the honeycomblike Y zeolite characterized by four 7.4 Å windows tetrahedrally arranged around a 13 Å diameter supercage. The zeolite is prepared for reaction by heating under an oxygen atmosphere in a tube oven at 500 °C for

Scheme 1



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(2) Stevens, B. *Chem. Soc. Ann. Rep. A* **1974**, 29−47.

(3) Onodera, K.; Furusawa, G.-I.; Kojima, M.; Tsuchiya, M.; Aihara, S.; Akaba, R.; Sakuragi, H.; Tokumaru, K. *Tetrahedron* **1985**, *41*, 2215−2220 and references therein.

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24 h. The zeolite is then cooled and the 1,1-diarylethylene loaded by absorption from a hexane solution. In all cases, intercalation into the zeolite was 100% complete as determined by gas chromatographic monitoring of the hexane prior to irradiation. The reactions were conducted in oxygen-saturated solvent slurries by irradiation through appropriate filters. The products were either extracted with THF or CH_2Cl_2 from the intact zeolite or from solution after digestion of the zeolite with 10% HCl. The mass balances were greater than 90% in all cases. The products of the irradiations are depicted in Scheme 2 although the precise product ratios were very sensitive to the experimental conditions as shown in Table 1.

Scheme 2

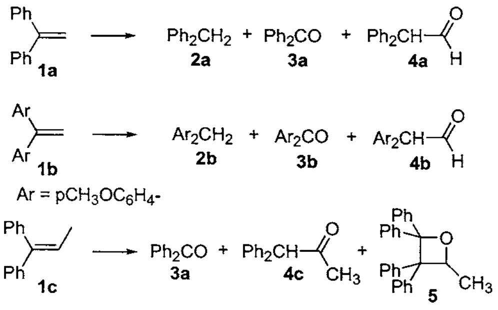


Table 1. Product Distributions in the Intrazeolite Photooxygenations of **1a**–**c**[a]

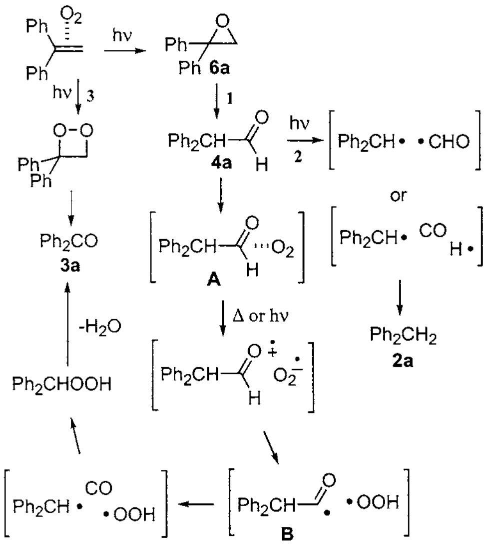
	⟨s⟩[b]	λ (nm)[c]	product ratios (%)				
			2	3	4	5	6
1a	0.27	>420		66	34		
	0.27	366		42	58		
	0.27	254	27	36	37		
	0.27[d]	>420		61	14		25
1b	0.27	>420		47	53		
	0.27	366	21	54	25		
	0.27	254	55 ± 3	34 ± 4	11 ± 6		
	0.27[e]	254	51	43	7		
1c	0.27[f]	>420		40 ± 2	59 ± 5		
	0.54	>420		49	51		
	0.27[f]	366		37 ± 2	62 ± 3		
	0.27	254		27	63	10	
	0.54	254		29	51	20	
	0.27[d]	>420		42	22		35

[a] All photooxygenations were conducted in hexane slurries except where noted. [b] Molecules per supercage. [c] Irradiation wavelength. [d] Conducted in NaY doped with pyridine ⟨s⟩ = 0.01. [e] Conducted in perfluorohexane slurry. [f] Trace amounts of another product tentatively assigned to $Ph_2C(CH_3)CHO$.

1,1-(4-Methoxyphenyl)ethane, previously suggested as a product of the intrazeolite oxidation of **1b**,[5a] was not formed in our system. In addition, this reduction product was unreactive under the reaction conditions and does not serve as a precursor to any of the observed products in Scheme 2. On the other hand, the previously reported[5a] effect of irradiation wavelength on the product ratios during photooxidations of **1a** and **1b** was corroborated in our studies. In particular, as the wavelength of irradiation decreased from 420 to 254 nm, the diarylmethanes, **2a** and **2b**, dramatically increased at the expense of the aldehydes, **4a** and **4b** (Table 1).

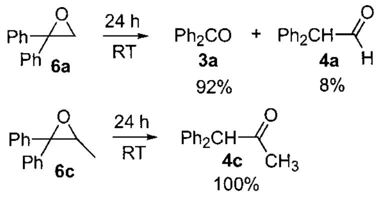
These results, and experiments described below that were designed to test the viability/competency of several of the potential intermediates, are consistent with the mechanism depicted in Scheme 3.

Scheme 3



The viability of epoxide **6** as a competent intermediate was demonstrated by irradiation of diarylethylenes **1a** and **1c** in zeolites that had been pretreated with pyridine to remove any residual Brönsted acid sites. At loading levels of 1 molecule of pyridine per every 100 supercages, substantial amounts of the epoxides, **6a** and **6c**, were isolated at the expense of **4a** and **4c**, respectively (Table 1). In addition, doping of non-pyridine-treated zeolite samples with independently synthesized samples of epoxides **6a** and **6c** resulted in thermal rearrangements to carbonyl compounds, **4a** and **4c**, respectively (Scheme 4). Presumably the carbonyl

Scheme 4



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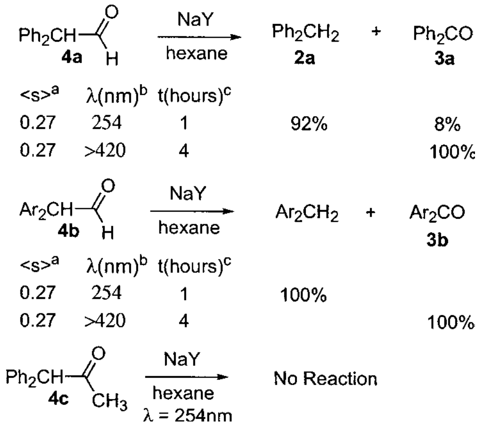
(5) (a) Lakshminarasimhan, P.; Thomas, K. J.; Johnston, L. J.; Ramamurthy, V. *Langmuir* **2000**, *16*, 9360–9367. (b) Kojima, M.; Nakajoh, M.; Matsubara, C.; Hashimoto, S. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1894–1901.

compounds are formed by acid-catalyzed openings of the epoxides followed by hydride shifts to the benzylic cationic centers (step 1 in Scheme 3).

The competencies of carbonyl compounds, **4a−c**, as precursors for the diarylmethanes, **2**, and phenones, **3**, were also verified by examining intrazeolite reactions of authentic samples (Scheme 5). These results prompt us to suggest that the diarylmethanes, **2a** and **2b**, are formed by Norrish type I cleavages of the aldehyde precursors as shown in Scheme 3 (step 2). A substantial body of literature precedent supports this suggestion. Decarbonylations of aliphatic[6] and α,*β*-unsaturated aldehydes are well-established reactions.[7] The absence of any cleavage product during intrazeolite photooxidation of **4c** also supports the suggestion of a Norrish type I mechanism; photodecarbonylation is only observed when the acyl radical has an adjacent stabilizing substituent present. The acetyl radical ($H_3C{-}^{\bullet}C{=}O$) formed in the cleavage of **4c** has a substantial activation barrier for loss of CO, and recombination to reform the ketone rather than decarbonylation is the anticipated and observed result. Finally, intrazeolite irradiation of **1b** in a perfluorohexane slurry (Table 1) was not accompanied by a reduced yield of **2b**, supporting the suggestion (Scheme 3) of an intramolecular hydrogen transfer of the aldehyde proton to the diarylmethyl radical intermediate rather than by hydrogen abstraction from the slurry solvent. Intrazeolite recombinations of radicals generated by Norrish type I cleavage reactions of dibenzyl ketones have previously been reported by Turro and co-workers.[8]

Scheme 5[a]



[a] Average number of molecules of starting material per supercage. [b]Irradiation wavelength. [c]Irradiation time

Examination of the results in Scheme 5 suggests that the previously reported[5a] dramatic wavelength dependence observed during intrazeolite photooxidations of **1a** and **1b** (Table 1) can be traced to the unusual behavior of aldehydes **4a** and **4b**; the diarylmethanes, **2**, dominate at short wavelengths, but the phenones, **3**, become increasingly important at long wavelengths. We suggest that at short wavelengths, Norrish type I cleavage is an important contributor to the photochemical behavior of **4a** and **4b**. However, at long wavelengths, a new reaction initiated by photochemically induced electron transfer in an aldehyde/oxygen charge-transfer complex (**A** in Scheme 3) becomes the predominant reaction pathway. Photochemically initiated oxidations of aldehydes are well-established reactions that exhibit quantum yields much greater than 1, consistent with a radical mechanism for this process.[9] This pathway to give phenone **3** can also be initiated thermally, albeit at a rate diminished in comparison to the photochemical reaction by approximately a factor of 4. Parenthetically, this thermal process is also responsible for the reduced yield of **4a** observed in the reaction of **6a** depicted in Scheme 4.

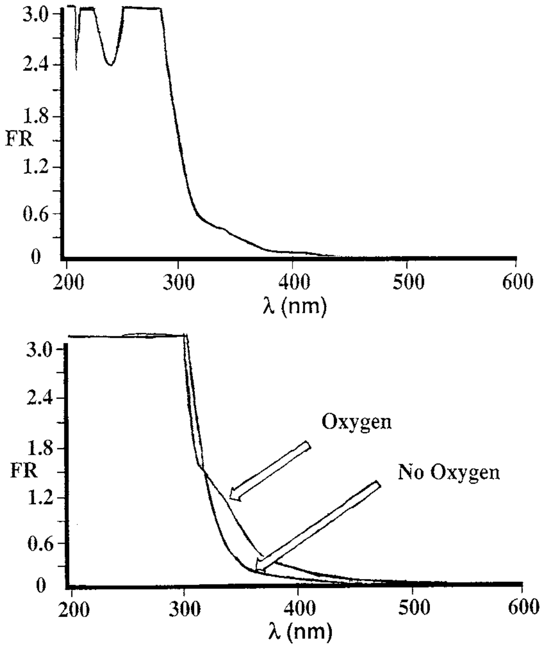


Figure 1. Diffuse reflectance UV−Vis Spectra of **4a** in the absence and presence of O_2. top; in the presence of O_2. bottom; a comparison.

The direct observation of the oxygen CT complex **A** by diffuse reflectance UV−vis spectroscopy (Figure 1) provides strong support for this aldehyde/oxygen CT-mediated pathway. In addition, thermal generation of an acyl radical has been implicated during the aldehyde-induced oxidation of olefins to epoxides in the presence of oxygen.[10] In these epoxidation reactions, the acyl radical is converted to an acyl

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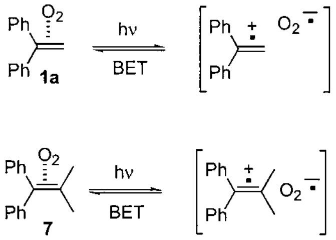
Scheme 6



peroxy radical by reaction with oxygen. The acyl radical in our reactions (**B** in Scheme 3) rapidly decarbonylate because of the incipient stability of the diarylmethyl radical.

The lack of reactivity of ketone **4c** by this oxygen CT-mediated oxidation is also consistent with the acyl radical pathway. However, this observation also requires a second pathway to form **3a** in the reaction of **1c** (Scheme 2). As an alternative, we suggest formation and decomposition of a dioxetane as shown in Scheme 3 (step 3), although at this point we cannot rigorously exclude contribution from Hock cleavage[11] of a transient allylic hydroperoxide.

Remarkably diarylethylene **7** is inert under these reaction conditions. It is tempting to suggest that back electron transfer (Scheme 6) in the photochemically generated superoxide/ethylene radical cation ion pair that precedes formation of the epoxide competitively inhibits its formation. If the thermodynamically more favorable BET in $\mathbf{1a}^{+\bullet}/O_2^{-\bullet}$ were in the Marcus inverted region, it would be slower than BET in $\mathbf{7}^{+\bullet}/O_2^{-\bullet}$ allowing epoxide formation to compete. In support of this speculation, literature precedent demonstrates that back electron-transfer rates often become slower with increasing driving force (i.e., they are indeed in the Marcus inverted region).[12]

Additional work to study these back electron transfer and other novel aspects of these intrazeolite photoxygenations are in progress and will be reported in due course.

Acknowledgment. We thank the National Science Foundation for their generous support of this research.

Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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