carboxylate: Optimized Conditions. Diethyl azodicarboxylate dried over 4-Å molecular sieves (191 mg, 1.1 mmol) was added to a solution of 3β-cholestanol (388 mg, 1.1 mmole), triphenylphosphine (288 mg, 1.1 mmol), and 2,6-lutidine (137 mg, 1.1 mmol) in dry distilled THF (10 mL) and stirred at room temperature. After 5 min purified[9] MCPBA (188 mg, 1.1 mmol) was added to the reaction mixture and stirring continued at room temperature for 5 h. After removal of the solvent, in vacuo, column chromatography (SiO_2; eluent petroleum spirit (40–60)/diethyl ether 98:2) of the crude reaction mixture gave the ester **2** (230 mg, 44%) as a colorless crystalline solid identical with an authentic sample (described below). Further elution with mixtures of petroleum ether and ether gave recovered 3β-cholestanol and then triphenylphosphine oxide (250 mg; 83%).

3α-Cholestanyl *m*-Chlorobenzoate: Preparation of an Authentic Sample. Diethyl azodicarboxylate (191 mg, 1.1 mmol) was added at room temperature to a stirred solution of 3β-cholestanol (388 mg, 1 mmol) and triphenylphosphine (288 mg, 1.1 mmol) in dry toluene (10 mL) resulting in a bright orange/red coloration. *m*-Chlorobenzoic acid (172 mg, 1.1 mmol) was then added and the mixture was stirred at room temperature for 5 h before evaporation and chromatography on silica gel. Elution with 2% ether in petroleum ether gave the ester **2** (444 mg, 83%) as a white crystalline solid with mp 108–109 °C (acetone): $[\alpha]^{27}{}_D$ +11.3° ($c = 1$ in $CHCl_3$); NMR 0.65 (s, 3 H), 5.25 (m, 1 H, width at $^1/_2$ height = 7 Hz), 7.2 (m, 2 H), 7.9 (m, 2 H); IR (Nujol) 1725 cm^{-1}; MS, *m/e* 526 (M^+), 370, 355, 230, 215. Anal. Calcd for $C_{34}H_{51}ClO_2$ (527.232): C, 77.45; H, 9.75; Cl, 6.72. Found: C, 77.25; H, 9.59; Cl, 6.80.

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Registry No. **1**, 17608-41-2; **2**, 117775-75-4; MCPBA, 937-14-4; $EtO_2CN{=}NCO_2Et$, 1972-28-7; Ph_3P, 603-35-0; Bu_3P, 998-40-3; $Ph_3P^+N(CO_2Et)N^-CO_2Et$, 58477-00-2; $Bu_3P^+N(CO_2Et)N^-CO_2Et$, 83053-10-5.

Intrazeolite Photochemistry. 5. Use of Zeolites in the Control of Photostationary Ratios in Sensitized Cis–Trans Isomerizations[1]

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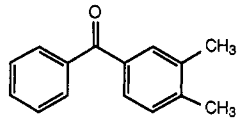
During the last few years a number of publications from our and other laboratories have examined the possibility of controlling the course of photochemical and photophysical processes by using zeolite supports.[3-12] This control usually reflects limitations in the mobility of and/or access to specific zeolite sites by the included molecule. We have now explored the use of the hydrophobic zeolite Silicalite to control the photostationary composition in sensitized cis–trans isomerizations. As a model system we have chosen the well-documented isomerization of stilbene.[13]

Silicalite (>99% SiO_2) belongs to a relatively new class of dealuminized zeolites with a framework structure consisting of five SiO_2 units.[14] The channel system consists of near-circular zig-zag channels cross-linked by elliptical straight channels. The diameter of the circular channels is 5.4 ± 0.2 Å and the cross section of the elliptical ones 5.75×5.15 Å^2.

The triplet sensitizer selected for our experiments was 3,4-dimethylbenzophenone (DMBP). Earlier work had shown that benzophenone includes very poorly on Silicalite;[4] thus, we expect that the substitution pattern in DMBP will exclude it from the channel structure and that only absorption on the surface of Silicalite is likely.



DMBP

Examination of stilbene models suggests that the cis isomer should not fit in the channels of Silicalite, while the diameter of the trans isomer is such that it should be readily included. In solution the triplet-sensitized isomerization of stilbene yields sensitizer-dependent photostationary ratios, which normally contain a moderate excess of the cis isomer.

Experimental Section

Silicalite, S-115, from Union Carbide has a particle size of ~1 μm and was calcined (500 °C for 24 h) and then allowed to equilibrate in air before use. We have noted significant fluctuation in the properties of different batches of Silicalite. While these differences were not evident in terms of particle size or composition (as determined by electron micrographs and X-ray fluorescence), inclusion in some cases led to the development of green-blue colors. We suspect that the color may reflect radical-ion generation; it was observed not only with stilbene but also with a variety of biphenyls. The lot number used in this study (966184061053-S-1) did not present this problem, while lot 961883060011-S-1 was particularly prone to color development. While in this paper we make no attempt to characterize the origin of these problems we simply want to bring them to the attention of potential users of Silicalite.

The substrates and sensitizer were incorporated on the Silicalite samples by using the same technique described earlier[3-5] (with isooctane as a solvent/carrier), and the dried samples were irradiated with the light from a Hanovia 200-W mercury–xenon lamp, filtered through a solution of stilbene (initially trans) in benzene, to minimize direct photolysis of the Silicalite-supported stilbene. The samples were supported on a rotating disk during the irradiation to ensure mixing of the sample and equivalent exposure to the light. This resulted in much longer irradiation times (0.25–210 h) than were required for solution or slurry experiments. The solid samples were then extracted for 12 h in a specially designed microsoxlet extractor with benzene as a solvent; we found that recovery with benzene was always better than 90%, while other solvents, such as diethyl ether, dichloromethane, or *n*-hexane, led to recoveries in the 30–70% range. The extract was then analyzed by gas chromatography on a Perkin-Elmer 8320

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[1] Issued as NRCC-29626.

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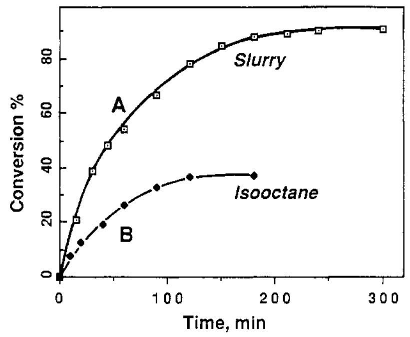

Figure 1. Cis to trans conversion upon irradiation of liquid samples of *cis*-stilbene and DMBP in isooctane with and without Silicalite. The DMBP/stilbene molar ratio was 1.7.

capillary instrument equipped with a 12-m BPI on vitreous silica column.

Results and Discussion

Addition of solid Silicalite to isooctane solutions of *cis*- or *trans*-stilbene followed by GC analysis of the liquid layer at various times showed that the cis isomer does not include significantly in this zeolite. In contrast, the trans isomer includes quite readily, as evidenced by the decrease of its concentration in the liquid phase. When Silicalite is present in a considerable excess, over 90% of the trans isomer can be included in around 20–30 min. Several tests of the maximum amount of *trans*-stilbene that the zeolite will accept led to saturation values of 80–90 mg of *trans*-stilbene per gram of Silicalite; of this about 80% was included in the first 3–4 h. When this is compared with the reported void value of 0.19 mL/g for this zeolite[14] (based on adsorption of small molecules such as *n*-hexane and methanol), it becomes clear that not all the void volume, but in fact, less than one half, is available for *trans*-stilbene inclusion. *trans*-Stilbene is a relatively large and somewhat rigid molecule, and this may limit its inclusion to only some regions of the Silicalite channel framework. It should also be noted that even for benzene the reported saturation volume (0.13 mL/g) is substantially less than the void volume of 0.19 mL/g.[14]

Irradiation of a slurry containing 20 mg of DMBP, 10 mg of *cis*-stilbene, 0.5 g of Silicalite, and 3 mL of isooctane led to conversion to trans in >90% yield. In effect the photostationary ratio approaches 100% trans at infinite time if an excess of the zeolite is present. Figure 1 shows a comparison of results in homogeneous solution and in a slurry. On the other hand, if the trans rather than cis isomer is used in the initial slurry, no isomerization takes place. We interpret these results in the following terms. The trans isomer is initially located in the channels of Silicalite, where it is not accessible to the sensitizer. It is important to note that since triplet energy transfer can only occur by the exchange mechanism, it requires that the donor and acceptor be in close proximity. On the other hand, the cis isomer is present in solution and in some surface sites where it is readily accessible to the triplet sensitizer. Energy transfer will of course lead to a mixture of cis and trans isomers; the former will remain readily accessible for future energy transfer events, while the latter move into the channel system and away from the sensitizer.

The same type of experiments can be carried out with solid samples. Extraction of the samples is nearly quantitative, with the sum of *cis*- and *trans*-stilbene yields usually exceeding 90% of the starting material. Starting with the cis isomer we have observed conversions of over 98%. Irradiation times using the same light source were typically about 5 times longer for the solid samples, probably reflecting a combination of less efficient coverage of the solid sample and light scattering effects. A typical conversion vs time plot is shown in Figure 2. The considerably larger scatter in this plot compared to those in solution or slurry most likely results from the difficulties associated with mixing of the solid samples during irradiation. Although the plot does not show a smooth build up as in solution, there is no obvious break that would indicate the initial isomerization of substrate-sensitizer near-neighbor pairs or rate-determining migration of the trans isomer into the channel structure.

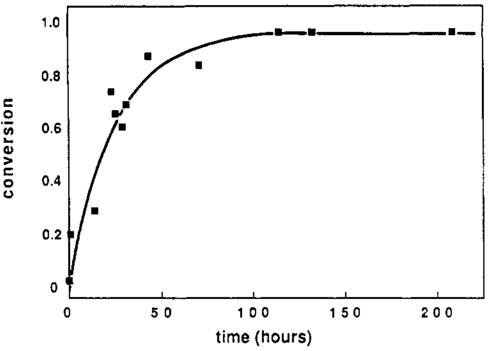

Figure 2. Cis to trans conversion upon irradiation of 400 mg of a solid sample containing initially 7.76 mg of *cis*-stilbene and 2.34 mg of DMBP.

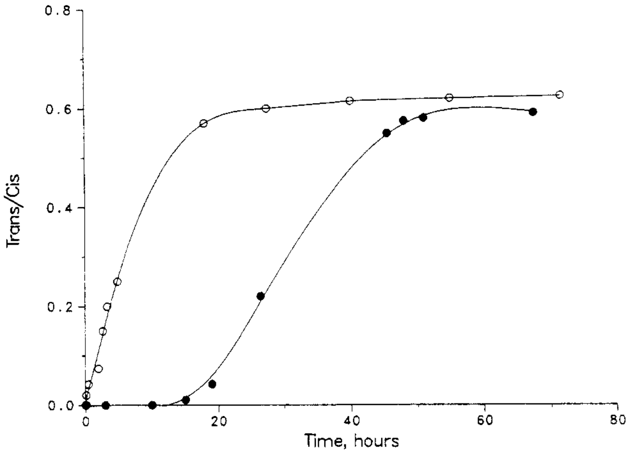

Figure 3. Evolution of the trans–cis stilbene ratio in solution as a function of irradiation time for samples containing 200 mg of DMBP and 500 mg of *cis*-stilbene in 20 mL of isooctane: (○) no Silicalite, (●) 5 g of Silicalite.

While the isomerization of stilbene is probably of no synthetic value in organic chemistry, the system does provide a good model in which possible applications of the method can be tested in a well-understood system. Naturally, applications such as the one described here are more attractive when they can be carried out in "wet systems", thus avoiding the preparation of solid inclusion samples. This has already been illustrated in Figure 1 for an example where an excess of Silicalite is present. In the presence of a stilbene excess the results are illustrated in Figure 3 in the form of the dependence of the trans/cis ratio in isooctane solution upon the irradiation time. We observe an initial indiction period, during which the liquid phase contains only cis isomer. During this period we observe a steady decrease of the total stilbene concentration, reflecting cis to trans isomerization followed by inclusion, which effectively removes the trans isomer from the solution. After the induction period (Figure 3), the isomerization becomes readily detectable and eventually levels off at the same photostationary ratio as in homogeneous solution, but in this case with only 7% of the stilbene remaining in solution. We believe that at this point the zeolite is saturated with the trans isomer, which can be recovered through extraction in a microsoxlet apparatus. Throughout the experiment essentially all the DMBP is present in solution, and this amount remains constant.

The applications of Silicalite described above bear of course some relation to recent applications of this zeolite for chromatographic purposes for which there are abundant examples.[15–17]

The ideas that are illustrated here with photochemical examples can have more general applications in the organic laboratory. In our own work we frequently require very pure samples of *cis*-stilbene and of *m*-terphenyl. The former usually contains some *trans*-stilbene, while *p*-terphenyl is a common impurity in *m*-terphenyl. In both cases the materials can be readily purified by stirring the solution (*m*-terphenyl) or neat material (*cis*-stilbene) with Silicalite.

Registry No. DMBP, 2571-39-3; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; silicalite, 7631-86-9.

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A Kinetic Study of the Reductive Cleavage of Diphenyl Ether by Sodium in Liquid Ammonia

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The chemical cleavage of the carbon–oxygen bond in ethers has received considerable attention in the recent literature.[1–4] In particular, the reductive cleavage of diphenyl ether has been studied under a variety of conditions. Both homogeneous and heterogeneous reductive media result in essentially quantitative cleavage of the starting material to yield phenol and benzene.[1,2] Thornton, Woolsey, and Bartak[1] have summarized the two most often suggested pathways to achieve cleavage. Both mechanisms involve formation of the radical anion as the first step. The first scheme is consistent with a first-order decomposition of the radical anion to the phenoxide ion and the phenyl radical as shown by eq 1 and 2. This scheme would be consistent with a second-order rate expression, first order with respect to each reactant. A second electron is used in the protonation process. In contrast, the second scheme

$$\mathrm{PhOPh} + e^- \rightleftarrows \mathrm{PhOPh}^{\bullet -} \qquad (1)$$

$$\mathrm{PhOPh}^{\bullet -} \rightarrow \mathrm{PhO}^- + \mathrm{Ph}^\bullet \qquad (2)$$

proposes formation of a dianion, either from consecutive electron addition (eq 1 and 3) or by disproportionation of the radical anion (eq 1 and 5). It is the dianion that subsequently cleaves to form the phenoxide ion and the phenyl ion (eq 4) that is then protonated. The rate expression for the second scheme should be consistent with a second-order dependence on the electron concentration with eq 3 representing the rate-determining step:

Table I. Kinetic Data for the Reaction of Diphenyl Ether with Sodium in Liquid Ammonia at −34 °C[10]

[Na], 10^{-4} M	[PhOPh], 10^{-3} M	k, 10^2 M^{-1} s^{-1}
4.1	6.6	5.0
4.1	0.95	4.4
4.2	2.1	4.3
5.2	1.9	3.5
8.4	1.6	2.4
10.3	1.2	1.9
3.8	2.1	4.3[a]
5.4	3.6	4.1[a]
3.1	1.5	7.3[a]
2.9	1.3	5.8[b]
9.5	35.0	3.3[c]

[a] NaCl added (9.9×10^{-4} to 4.7×10^{-2} M). [b] Cesium used as the metal. [c] 18-Crown-6 added.

$$\mathrm{PhOPh} + e^- \rightleftarrows \mathrm{PhOPh}^{\bullet -} \qquad (1)$$

$$\mathrm{PhOPh}^{\bullet -} + e^- \rightarrow \mathrm{PhOPh}^{2-} \qquad (3)$$

$$\mathrm{PhOPh}^{2-} \rightarrow \mathrm{PhO}^- + \mathrm{Ph}^- \qquad (4)$$

or, alternatively, with eq 5 representing the rate-determining step:

$$2\ \mathrm{PhOPh}^{\bullet -} \rightarrow \mathrm{PhOPh} + \mathrm{PhOPh}^{2-} \qquad (5)$$

$$\mathrm{PhOPh}^{2-} \rightarrow \mathrm{PhO}^- + \mathrm{Ph}^- \qquad (4)$$

If eq 1 is rate-determining in the second scheme, the rate expression would also be first-order with respect to the electron concentration.

In a recent publication, Thornton, Bartak, and Woolsey[1] reported an electrochemical study of the reduction of diphenyl ether in *N,N*-dimethylformamide (DMF). The cyclic voltammetry experiment at −17 °C exhibited only one reduction peak at potentials up to −3.0 V vs SCE, which was just before breakdown of either the solvent or the supporting electrolyte. On the reverse scan, no reoxidation peak was evident. These results are consistent with a one-electron reduction to form the radical anion followed by a very fast chemical cleavage reaction (eq 1–2). These findings support a previous study by Woolsey and coworkers,[2] who observed that Na-HMPA reductively cleaved diphenyl ether to form phenoxide and benzene. In both studies, the investigators indirectly detected the phenyl radical.[1,2]

We report a kinetic study of the reductive cleavage of diphenyl ether by Na in liquid ammonia at −34 °C. This study was undertaken to obtain the rate expression for the homogeneous reduction reaction.

The reaction was studied by the stopped-flow method since, under the conditions of this study, the reduction is too fast to follow by conventional methods. The experimental procedure has been described in detail elsewhere.[5,6] The disappearance of the ammoniated electron was followed optically by determining the absorption at 1000 nm as a function of time. For experiments run under pseudo-order conditions, plots of the natural log of the electron concentration versus time were found to be linear, indi-

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