

Photocyclization of α -(*o*-Ethylphenyl)acetophenone in Zeolites

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Received January 4, 1999

The diastereoselectivity in the photocyclization of α -(*o*-ethylphenyl)acetophenone (**1**) to 1-methyl-2-phenyl-2-indanol was studied in zeolites X and Y, and compared with that in isotropic solvents. The yields of E-diastereomer at the irradiation of **1** in protic solvents were higher than those in aprotic solvents. The ratios of E-diastereomer to Z-diastereomer in zeolites X and Y were much higher than those in isotropic solvents. The E/Z ratios at the irradiation of **1** in zeolites X were also found to be dependent on the cations present. As the cation size increased from Li⁺ to Cs⁺, the ratio decreased. However, any pattern in the E/Z ratios was not found in zeolites Y. The diastereoselectivity observed in the zeolites was interpreted by the conformational restriction imposed by the cavity size. An efficient oxidation of **1** in zeolites RbX and CsX was also observed.

Introduction

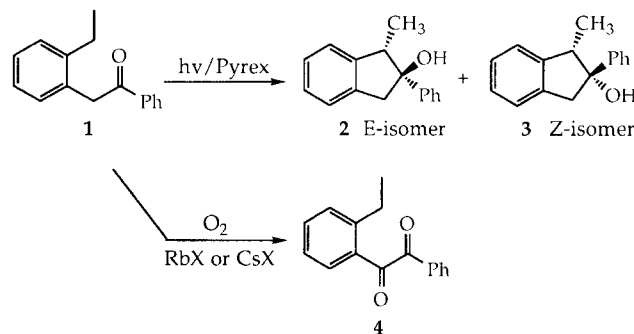
Much attention has been paid to studying the role of the organized and constrained media on the selectivity of organic photoreactions.¹ Zeolites are often employed as organized media.² Some deviations of product distribution from solution reactions are associated with the framework structure of zeolites and the counterions present within zeolites. Faujasite zeolites (types X and Y) are probably one of the most commonly employed materials. The faujasite family has a three-dimensional structure comprised of tetrahedrally arranged interconnecting supercages of about 13 Å internal diameter, which are connected to each other through 7-8 Å windows.³ Charge-compensating cations are present in the internal structure of the zeolites to occupy three different positions, and the free volume available for the substrates within the supercages depends on the number and nature of the cations.

The control of the stereochemistry on the Norrish-Yang cyclization via 1,4-biradical in zeolites has been extensively studied,⁴ but the photocyclization of ketones via 1,5-biradical in zeolites has not been explored. The modification of stereoselectivities in the product formation from 1,5-biradicals generated through δ -hydrogen abstraction by changing substituent and reaction medium has been recently investigated,^{5,6} and the observed selectivity was explained by the effect on the conformational equilibrium of the biradicals before cyclization. Zeolites with the reaction cavities of different geometries have important influences on the conformational flexibility of molecules. Therefore, this restriction may play a crucial role in controlling the selectivity in a chemical reaction. In this paper, we report the diastereoselective induction observed during the photocyclization of α -(*o*-ethylphenyl)acetophenone (**1**) adsorbed on cation-exchanged faujasite zeolites.

Results and Discussion

The irradiation of **1** (0.01 M) through a Pyrex filter resulted in the formation of two products, E-isomer (**2**) and Z-isomer

(**3**) of 1-methyl-2-phenyl-2-indanol (Scheme 1). The yields of **2** and **3** were measured by gas chromatography with the internal standard of *n*-hexadecane. The photoreaction in several solvent conditions was studied, and the results are summarized in Table 1. In 4-6 minute irradiations, the conversion yields of **2** and **3** in benzene were 6.2% and 93.8% in 36.4% conversion, and those in methanol were 40.6% and 59.4% in 15.5% conversion. The ratios of **2** to **3** were in good agreement with the previous results in benzene-*d*₆ and methanol-*d*₄.⁶ The increased yield of **2** in methanol-*d*₄ compared with that in benzene-*d*₆, thereby the lost selectivity, was previously

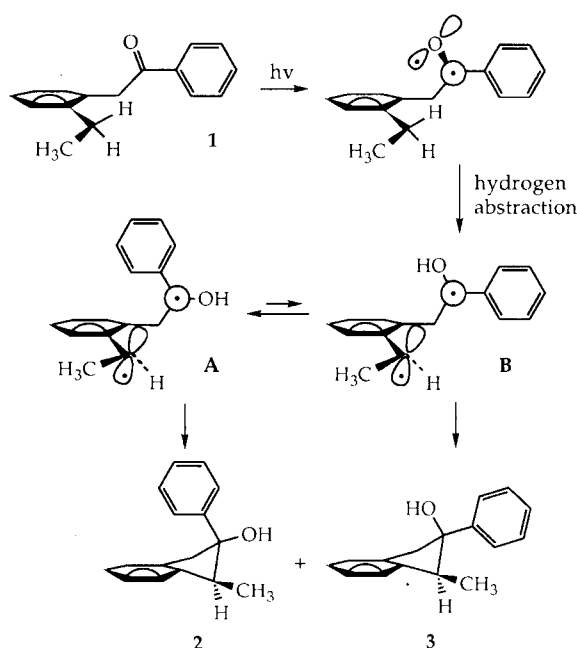


Scheme 1

Table 1. Product Distribution for Photoreaction of **1** in Some Solvents^a

medium	polarity ^b	conversion (%)	2/3
<i>n</i> -hexane	31.0	34.8	0.05
CCl ₄	32.4	41.1	0.05
benzene	34.3	36.4	0.07
CH ₂ Cl ₂	40.7	23.3	0.06
<i>tert</i> -BuOH	43.3	9.6	1.18
CH ₃ CN	45.6	14.1	0.36
2-PrOH	48.4	13.4	1.00
EtOH	51.9	14.5	0.94
MeOH	55.4	15.5	0.68
MeOH/H ₂ O ^c	58.3	10.3	0.60

^a Error limit of the analysis is $\pm 4.7\%$. ^b Numbers given represent empirical parameters of solvent polarity, $E_T(30)/(\text{kcal} \cdot \text{mol}^{-1})$ of the medium.⁷ ^c In 1 : 1 (v/v) mixture of MeOH and H₂O.



Scheme 2. The mechanism for the photocyclization reaction of **1**.

explained by the effect of hydrogen bonding on the conformational equilibrium in the 1,5-biradical (Scheme 2). When the hydroxyl group is solvated by hydrogen bonding, it is comparable in size to the phenyl group. Therefore, the rotamer **A**, which has higher energy in aprotic solvent, becomes nearly equal to the rotamer **B** in energy. The comparison of the **2/3** ratios in methanol, ethanol, 2-propanol, and *tert*-butanol revealed that the ratio gradually increased from methanol to *tert*-butanol, which supports the previous interpretation.⁶ The slightly higher **2/3** ratio (0.68) in methanol than that (0.60) in 1:1 mixture of methanol and water, the higher value (1.18) in *tert*-butanol than that (0.36) in acetonitrile despite the fact that *tert*-butanol is less polar,⁷ and the lower values (0.05–0.07) in less polar aprotic solvents (*n*-hexane, carbon tetrachloride, benzene, and dichloromethane) indicated that the effect of hydrogen bonding in determining the diastereoselectivity was more important than the polarity of the solvents.

The photoreaction of **1** in some cation-exchanged zeolites was studied. The compound **1** within zeolites X or Y was irradiated through a Pyrex filter. The conversions of 4.2%–14.7% were made within 15 minutes in the cases of LiX and LiY, and 30 minutes in the cases of CsX and CsY. On a control experiment, **1** was treated in the same procedure except the UV exposure. Under the experimental conditions for RbX and CsX, only a small amount of the starting material was recovered. Analysis of the mixture indicated that **1** adsorbed on the zeolites was transformed to an oxidized material (**4**). Some products found in the photolysis of **1** in RbX or CsX, with longer retention times in gas chromatography, were also monitored by photolyzing the purified **4**. Therefore, the photoproducts from **4** were not analyzed in this study. Material balances for the photoreaction of **1** on the zeolites, except RbX and CsX, were no less than 82.3%.

The results for the photolysis of **1** in zeolites X and Y are summarized in Tables 2 and 3. The **2/3** ratios in the zeolites

Table 2. Product Distribution for Photoreaction of **1** in Zeolites X^{a,b}

medium	vacant space within cage (Å ³)	conversion (%)	2/3
LiX	873	10.6	32.4
NaX	852	12.0	26.9
KX	800	11.3	7.3
RbX	770	4.2 ^c	1.9
CsX	732	5.4 ^c	1.9

^a Error limit of the analysis is $\pm 9.3\%$. ^b Occupancy number was kept at about 0.34. ^c A low conversion is due to the large contribution of thermal oxidation.

Table 3. Product Distribution for Photoreaction of **1** in Zeolites Y^{a,b}

medium	vacant space within cage (Å ³)	conversion (%)	2/3
LiY	834	11.1	5.4
NaY	827	14.7	12.7
KY	807	8.8	2.3
RbY	796	12.2	4.1
CsY	781	9.9	2.2

^a Error limit of the analysis is $\pm 3.9\%$. ^b Occupancy number was kept at about 0.30.

were found to be quite different from those in isotropic solvents. While the ratios were at the range of 0.05–1.18 in isotropic solvents, those were at the ranges of 1.9–32.4 in zeolites X and 2.2–12.7 in zeolites Y, respectively. It is also noteworthy that the **2/3** ratios in zeolites X were also dependent on the cations present within zeolite supercages. The ratio decreased as the cation size increased. For example, the **2/3** ratio was changed from 32.4 in LiX to 1.9 in CsX. However, any pattern in the **2/3** ratios was not found in zeolites Y. No notable pattern in zeolites Y has been previously observed in the photolysis of aryl alkyl ketones.^{4a,4c}

The variation of product distribution in zeolites X and Y has been interpreted by the micropolarity of supercages, the binding strength of cations, the size and shape of supercages, and the heavy atom effect of cations.⁸ Since the photocyclization occurs in the triplet mechanism,^{9,10} the effect of zeolites on the intersystem crossing from the singlet excited state is not expected to play an important role in the photoreaction. Therefore, the heavy atom effect does not seem to be effective.

As the micropolarity of zeolites decreased from LiX to CsX, the **2/3** ratio decreased (Table 2). Since the **2/3** ratio decreased from 0.36 to 0.07 as the polarity of isotropic solvent decreased from acetonitrile to benzene, the effect of the electrostatic field might work. However, the diastereoselectivity in isotropic solutions was much more significantly influenced by the conformational equilibrium of the biradicals than the polarity of the media.^{5,11} Moreover, quite a difference of the **2/3** ratios between in LiX (32.4) and in 1:1 mixture of methanol and water (0.60), although the polarity of both media was estimated to be similar,¹² indicated that the electrostatic field is not a significant factor. Since the effect of the electrostatic field is expected to work in both zeolites X and Y,^{4c,4d,12} the absence of cation effect on the

product distribution in zeolites Y is consistent with the interpretation.

It has been known that the carbonyl group of alkyl phenyl ketones makes electronic interaction with the cations present within the supercages.⁸ While the electronic interaction of the cations with **1** may influence the conformation of **1**, it is not expected to influence the distribution of the biradicals strongly.⁴ No pattern in the **2/3** ratio observed in zeolites Y, despite the fact that cation binding is greater with lighter atom due to higher charge per unit volume of the cation, supports the interpretation. Therefore, the effect is explained by the changes in the cage free volume upon cation exchange.

Since the E-diastereomer (**2**) has the phenyl and methyl groups on the same side, it is bulky and spherical in shape (Scheme 2). Therefore, **2** and its precursor biradical (**A**) are expected to fit within a single cage. On the other hand, the Z-diastereomer (**3**) is long and cylindrical. Considering the shape of the internal structure of the zeolites, **3** and its biradical (**B**) are expected to fit between two cages.^{4c,4d} When the cage can accommodate the intermediate, the formation of **2** will be favored. When the cage is not large enough to accommodate the intermediate, the formation of **3** will be favored. The increased formation of **2** in zeolites X and Y compared with that in isotropic solvents indicates that some constraints imposed by the supercages influence the conformational equilibrium of the biradicals to favor **A**. Since the largest Cs cation leaves the smallest free volume in the supercage, the conformational equilibrium of the biradicals is expected to shift toward **B** in CsX and CsY compared with that in LiX and LiY. Therefore, the photoreaction in CsX and CsY resulted in the more favorable formation of **3** than in LiX and LiY. The number of mobile cations per supercage is about 4 for zeolites X, and the number of mobile cations is less than one per supercage for zeolites Y.³ Therefore, a much larger decrease in cage free volume by exchanging the cations occurs in zeolites X than in zeolites Y. The diastereoselectivity controlled by the size of the cage is then expected to be higher in zeolites X than in zeolites Y, which was observed in our experimental results (Tables 2 and 3).

Control experiments indicated that the oxidation of **1** via a dark process occurred in zeolites RbX and CsX (Scheme 1). The structure of the product was elucidated on the basis of their spectroscopic properties. The mass spectrum (EI) of **4** exhibits the weak molecular ion peak at m/e 238 and two strong fragment peaks at m/e 133 and 105. The characteristic stretchings at 1678 and 1599 cm^{-1} in its IR spectrum and two carbonyl peaks at 197.17 and 195.19 ppm in its ^{13}C NMR spectrum suggest the structure of the product to be **4**. The maximum absorption wavelength (257 nm, *n*-heptane) in the UV spectrum is consistent with the assignment. The extent of the oxidation reaction occurred during the sample handling for the photolysis in zeolites increased with the increased cation size in zeolites X,¹³ and most of the starting material was oxidized in RbX and CsX. However, no oxidation was observed in zeolites Y. Although the oxidation of organic compounds has been extensively studied,¹⁴ the observed oxidation in the zeolites may be characterized by

its simplicity and mild conditions.¹⁵ We are in the process of examining the nature of oxidizing sites and expanding the systems that can be subjected to mild oxidation within zeolites.

Experimental Section

Materials and instruments. Compounds **1**, **2**, and **3** were prepared as described previously.¹⁶ Molecular sieves 13X and sodium Y zeolite were purchased from Aldrich Chemical Co. and used as received. Solvents for spectroscopic measurements were in spectroscopic grade and used as received. Other solvents were purified by refluxing over phosphorus pentoxide (or sodium) followed by distillation. ^1H NMR and ^{13}C NMR spectra were obtained at 300 MHz on a AMX Bruker spectrometer. Chemical shifts (δ) are reported as parts per million downfield from tetramethylsilane used as an internal standard. Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum 2000. Mass spectra (MS) were obtained on a Hewlett-Packard 5890-JMS AX505WA double focusing magnetic sector mass spectrometer. Gas chromatographic analyses were carried out with a Donam System 6200 gas chromatograph with 30 m HP-1 capillary columns.

Irradiation of **1 in isotropic solvents.** After 10 minutes of nitrogen purging, **1** (4.7 mg) in a solvent (2 mL) was irradiated through a cylindrical Pyrex glass filter with a 450-watt Hanovia medium-pressure mercury lamp for 4-6 minutes. After a known amount of *n*-hexadecane was added, the mixture was analyzed by gas chromatography to exhibit two products. The conditions for the measurements were as follows: column diameter, 0.25 mm; film thickness, 0.25 mm; oven temperature, initially 100 $^\circ\text{C}$ (5 min), elevated at 3 $^\circ\text{C}/\text{min}$ to 150 $^\circ\text{C}$ (20 min) and at 5 $^\circ\text{C}/\text{min}$ to 250 $^\circ\text{C}$. Retention times (min) were 24 for *n*-hexadecane, 40 for **2**, 42 for **3**, and 44 for **1**.

Preparation of zeolites X and Y. The cation of interest was exchanged according to the method described previously.¹⁷ Exchange levels for each zeolite were as follows: LiX, 84.5%; KX, 89.5%; RbX, 70.7%; CsX, 67.4%; LiY, 65.7%; KY, 98.3%; RbY, 74.5%; and CsY, 63.3%.

Irradiation of **1 in zeolites.** Zeolites were activated at 470 $^\circ\text{C}$ for 13 hours prior to use.¹⁸ After cooled in a desiccator, a pre-weighed amount (100-190 mg) of the zeolites were added to 5 mg of **1** in 5 mL of *n*-hexane. The resulting mixture was stirred for 12 hours. The loading levels are estimated to be at the occupancy number of 0.30-0.34 molecule per supercage. Gas chromatographic analysis of the resulting solution showed that **1** had been completely introduced into the cavities. The zeolites were washed with *n*-hexane several times, and the solvent was removed by blowing a stream of nitrogen over the sample. The solid inclusion complexes in a Pyrex tube were degassed (1×10^{-2} mmHg) on a vacuum line and flushed with dry nitrogen at least five cycles.¹⁹ The solid powders were irradiated through a cylindrical Pyrex glass filter with a 450-watt Hanovia medium-pressure mercury lamp for 15-30 minutes. The irradiation was carried out in continuously

rotated cells to ensure uniform exposure to the light source. After dissolving the zeolite framework by stirring it in aqueous HCl solution (0.8 N, 20 mL) for 30 minutes, the reaction mixture was extracted with dichloromethane (3×20 mL). The combined organic layer was dried over sodium sulfate, filtered, and concentrated. A known amount of *n*-hexadecane was added, and the resulting mixture was dissolved in dichloromethane and subjected to GC analysis. The conversion was estimated by measuring the disappearance of **1**. For zeolites X except RbX and CsX, the material balances were found to be no less than 91.6%. For zeolites Y, the material balances were no less than 82.3%. Control experiments established that the products were stable in the acidic extraction conditions.

Oxidation of **1 within zeolites.** The compound **1** (20 mg) and RbX (0.78 g) in *n*-hexane (10 mL) were stirred for 12 hours. After the evaporation of the solvent, the powders were put in air for 48 hours. The same extraction procedure described in the irradiation within zeolites afforded **4**. Gas chromatographic analysis indicated the complete conversion to **4**. ¹H NMR (CDCl₃, 300 MHz) δ 8.00-7.22 (9H, m, aromatic H), 3.11 (2H, q, *J* = 7.4 Hz), 1.31 (3H, t, *J* = 7.5 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 197.17, 195.19, 147.96, 135.14, 134.38, 133.68, 133.53, 131.80, 131.42, 130.37, 129.44, 126.39, 27.90, 15.87; IR (CHCl₃) 3020, 2975, 2935, 2875, 1678, 1599, 1572, 1450 cm⁻¹; MS (EI) *m/e* (%) 238 (M⁺, 2), 133 (100), 105 (23), 103 (4), 77 (14), 55 (1).

Acknowledgment. This research was financially supported by Korean Ministry of Education through Research Fund (BSRI-98-3448) and Korea Science and Engineering Foundation (981-0303-018-2, 98-0501-09-01-3).

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