

Intramolecular Photocycloaddition of 3-(3-Butenyl)cyclohex-2-enone and 3-(2-Propenoxy)cyclohex-2-enone in Zeolites

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The effects of zeolites on the intramolecular [2+2] photocycloadditions of 3-(3-butenyl)cyclohex-2-enone (**1a**) and 3-(2-propenoxy)cyclohex-2-enone (**1b**) were investigated. When **1a** adsorbed in cation-exchanged zeolites X and Y was irradiated through a Pyrex filter, the products from the 1,6-ring closure biradical increased compared to the results from the photoreaction in homogeneous solutions. In the intramolecular 1,5-ring closure photocycloaddition of **1a** and **1b**, the products from the *cis*-fused intermediates increased in zeolites X and Y. The regiochemical and stereochemical outcomes of the photocycloadditions in the zeolites were interpreted by the binding of the guest molecules with the cations in the supercages.

Introduction

Photochemistry in organized assemblies has attracted considerable attention during the last two decades because of their potential use for controlling photophysical and photochemical behavior of organic molecules.¹ Zeolites have been found to be very convenient hosts.^{2,3} Besides a passive role of zeolites defining the shape, size, and flexibility, the interaction between the walls and the guest molecules influences the course of photochemical and photophysical events.³ Among the zeolites studied in photochemical investigations, zeolites X and Y have been probably used most frequently. The structure of the zeolites consists of an inscribed sphere (supercage) with a diameter of *ca.* 13 Å, which is connected tetrahedrally to four other supercages through *ca.* 8 Å pores.¹ Charge-compensating cations are present in the internal structure of the zeolites to occupy three different positions.

The [2+2] photocycloaddition of enone to alkene is one of the most widely used photochemical reactions. The structures of the products in many photoreactions of cyclic enones suggest that they are mainly derived from biradical intermediates in which a five-membered ring has been formed. In some cases, however, two reaction pathways, by way of 1,5-ring closure (crossed) and 1,6-ring closure (parallel), are competing. Although the photoreaction has been extensively used, the mechanism has not been well understood.⁴ The biradical nature of a key intermediate is well established,⁵ but the existence of triplet exciplex is still controversial. Several factors in modifying the regioselectivity and stereoselectivity, such as chain length,⁶ substituents of the system,^{7,8} and incorporation of the conjugated double bond into a ring,⁸ have been reported. In addition to the factors, reaction medium seems to be another factor in controlling the regiochemistry and stereochemistry. Therefore, we studied the effects of zeolites on the outcomes of the intramolecular [2+2] photocycloaddition of 3-(3-butenyl)cyclohex-2-enone (**1a**) and 3-(2-propenoxy)cyclohex-2-enone (**1b**).

Experimental Section

Materials and instruments. Enones **1a** and **1b** were synthesized and purified by chromatography on silica.^{8,9} Molecular sieves 13X, sodium Y zeolite, lithium nitrate, potassium nitrate, rubidium nitrate, and cesium nitrate 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 ¹³C NMR spectra were obtained at 300 MHz and/or 500 MHz on AMX Bruker spectrometers. 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 or a Nicolet 205 FT-IR Spectrum 2000. Inductively coupled plasma atomic emission analyses were performed with a Shimadzu ICPS-1000IV spectrometer. Inductively coupled plasma mass analyses were performed with a VG PQ2-turbo spectrometer. 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 or a HP 6890 gas chromatograph with 30 m HP-1 capillary columns.

Irradiation of 1b in benzene. After 10 minutes of nitrogen purging, a solution of **1b** (8.5 mg) in benzene (5 mL) was irradiated through a cylindrical Pyrex glass filter with a 450-watt Hanovia medium-pressure mercury lamp for 30 minutes. The reaction mixture was analyzed by gas chromatography to exhibit two components in the conversion of 18.6%. The yields of **2b** and **3b** on the basis of the consumed **1b** were estimated to be 4.3% and 65.5%, respectively. For a preparative scale reaction, a solution of **1b** (484.5 mg) in benzene (16 mL) was irradiated for 37 hours. The reaction mixture was partially separated by a silica gel column chromatography eluting with *n*-hexane and ethyl acetate mixtures of increasing polarity. **2b**: ¹H NMR (CDCl₃, 300 MHz)

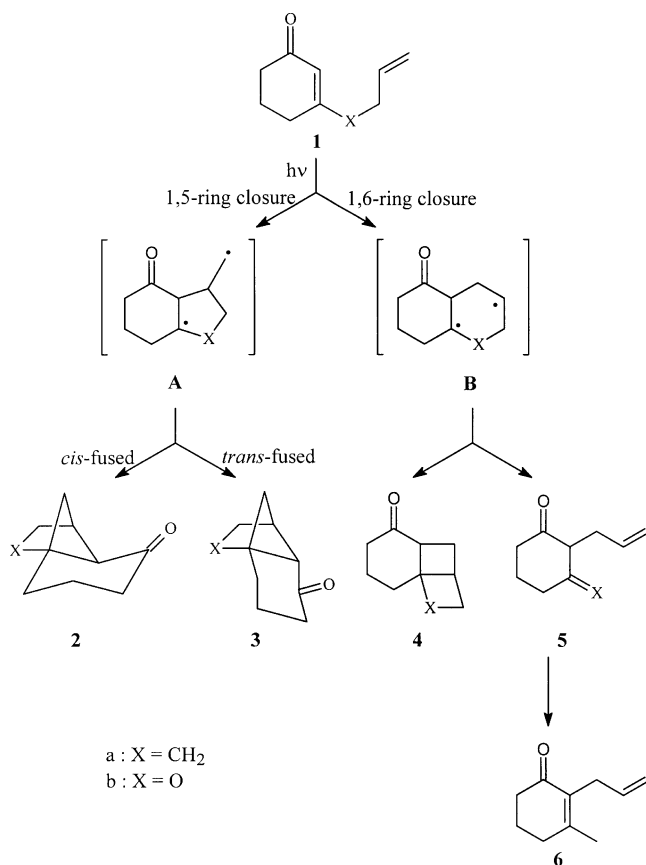
δ 3.87 (d, H_a , $J=6.2$ Hz), 3.83 (dd, H_b , $J=6.3$ Hz), 3.27 (dd, H_c , $J=3.1$ Hz), 2.43 (d, H_d , $J=9.3$ Hz), 2.40-1.85 (m, 5H), 1.89 (dd, H_f , $J=8.2, 3.2$ Hz), 1.65 (m, 1H), 1.35 (dd, H_e , $J=9.3, 8.2$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 209.65, 91.45, 70.07, 60.88, 40.70, 40.15, 37.95, 26.36, 22.76; IR (CHCl_3) 3010, 2955, 2893, 1709, 1235 cm^{-1} ; MS (EI) m/e (%) 152 (M^+ , 7), 124 (22), 96 (100), 82 (44), 67 (30).

Preparation of zeolites X and Y. The cation of interest was exchanged from zeolites NaX or NaY with the appropriate nitrate solution.¹⁰ For each gram of the zeolite, 100 mL of 0.1 M nitrate solution was added, and the resulting mixture was stirred at 80 °C for 24 hours. This was repeated three times. After filtration, the white powders were washed thoroughly with distilled water (100 mL per gram of zeolite), dried at 120 °C, and calcinated at 500 °C for 24 hours. Cation exchange levels were measured by the inductively coupled plasma atomic emission analysis or the inductively coupled plasma mass analysis. Exchange levels for individual 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. Prior to use, zeolites were activated at 470 °C for 13 hours.¹¹ Activated zeolites were cooled to room temperature in a desiccator and used immediately. In a typical preparation,¹² 250 mg of the zeolite and 2.5-5 mg of 1 in 5 mL *n*-hexane (loading level: occupancy number of 0.1-0.2 molecule per supercage) were stirred for about 12 hours. Gas chromatographic analysis of the resulting solution indicated that 1 was not in the hexane layer. The zeolites were washed with *n*-hexane several times, and the solvent was removed by blowing a stream of nitrogen over the sample. The resulting solid sample in a Pyrex tube was degassed (2×10^{-2} mmHg) on a vacuum line and flushed with dry nitrogen at least three cycles. The solid powders were irradiated through a cylindrical Pyrex glass filter with a 450-watt Hanovia medium-pressure mercury lamp. The irradiation cells were continuously agitated to ensure uniform irradiation. After the photolysis of 1a, the reaction mixture was extracted by stirring the sample in diethyl ether (40 mL) overnight. In the case of 1b, ethyl acetate (80 mL) was used. After filtration, the solution was reduced to about 1 mL, and analyzed by gas chromatography with the internal standard of *n*-decane. The temperature of the analyses was in the range of 60 °C and 150 °C. Material balances were found to be no less than 82%.

Results and Discussion

The irradiation of 1a in benzene (0.007 M) through a Pyrex filter resulted in the formation of four products 2a-5a in 15% conversion (Scheme 1).¹³ The ratio of 2a-5a, as measured by gas chromatography, was estimated to be 19.4%, 43.5%, 31.4%, and 5.7%, respectively, which are in good agreement with the previous result.⁸ Other aprotic solvents could be used, but no significant effect due to the solvent polarity was observed (Table 1). In contrast to the previous study that reported the exclusive formation of 3b,⁹ the irradi-



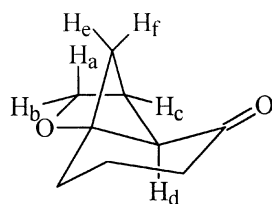
Scheme 1

ation of 1b in benzene (0.01 M) afforded two products at the ratio of 5.9 : 94.1 in 19% conversion as estimated by gas chromatography. Spectroscopic data of 3b were in agreement with those in the literature.⁹ The minor product was assigned to be 2b by spectroscopic data analyses. The mass spectrum of the minor product exhibits the molecular ion peak at m/e 152. The IR (1709 cm^{-1} for unconjugated carbonyl group) and ^1H NMR spectra (no olefinic proton signal) do not exhibit any signal for olefinic bond. The ^{13}C NMR spectrum of 2b is also similar to that of 3b. These indicate

Table 1. Product Distribution for Photoreaction of 1 in Homogeneous Solutions^a

Solvent	1a ^b		1b ^c
	4a+5a+6a ^d	2a	2b
	2a+3a+4a+5a+6a	2a+3a	2b+3b
benzene	0.37	0.31	0.06
CH_2Cl_2	0.35	0.29	0.06
2-PrOH	0.37	0.31	0.07
EtOH	0.38	0.30	0.06
CH_3CN	0.38	0.29	0.06
$\text{MeOH}/\text{H}_2\text{O}^e$	0.58	0.29	0.07

^aNumbers reported are the average of at least two measurements. Error limit of the analysis is $\pm 4\%$. ^b0.007 M solutions of 1a were irradiated within 15% conversion. ^c0.01 M solutions of 1b within 19% conversion. ^d6a was observed in $\text{MeOH}/\text{H}_2\text{O}$. ^eIn 1:1 mixture of MeOH and H_2O .



2b
Figure 1

that it is a tricyclic isomer of **3b**. Its ^1H NMR spectrum exhibits a similar pattern with that of the endo form of a tricyclic compound from 3-allylamino-2-cyclohexen-1-one.¹⁴ The stereochemistry of **2b** was firmly confirmed by examining the coupling between endo H_d and endo H_c (Figure 1). A large long-range coupling constant ($J=9.3$ Hz), which has been known to occur only if two protons are in W configuration,¹⁵ is obtained in **2b**, but not in **3b**. In the irradiation of **1b** in aprotic solvents such as dichloromethane and acetonitrile, the ratio of **2b/2b-3b** remained constant within experimental errors (Table 1).

The results of the photolysis of **1** in zeolites X and Y are summarized in Table 2. The irradiation of **1a** in zeolites X and Y afforded **2a-6a**. Control experiments suggested that polar acidic environments of the zeolites increase the formation of **6a** by the incidental shift of double bond of **5a**.^{8,13} The product distribution was found to be affected by the inclusion in zeolites X and Y. In the photolysis of **1a** in benzene, 37% of the products were derived from the 1,6-ring closure biradical **B_a** (**4a-5a**). When **1a** was included in zeolites X and Y, the yields of **4a-6a** from **B_a** increased. The product ratio was also dependent on the nature of the cations present within zeolite supercages. The yields of **4a-6a** in both X- and Y-type faujasites increased as the cation size decreased (light-atom effect). For examples, the ratio of **4a-6a/2a-6a** changed from 0.73 in LiX to 0.41 in CsX, and from 0.73 in LiY to 0.46 in CsY. Another phenomenon

Table 2. Product Distribution for Photoreaction of **1** in Zeolites X and Y^a

Medium	1a ^b		1b ^c
	4a+5a+6a	2a	2b
	2a+3a+4a+5a+6a	2a+3a	2b+3b
LiX	0.73	0.36	0.25
NaX	0.70	0.52	0.39
KX	0.63	0.43	0.37
RbX	0.53	0.38	0.32
CsX	0.41	0.23	0.19
LiY	0.73	0.33	0.30
NaY	0.76	0.54	0.60
KY	0.62	0.45	0.48
RbY	0.56	0.40	0.32
CsY	0.46	0.31	0.18

^aNumbers reported are the average of at least two measurements. Error limit of the analysis is $\pm 3\%$. ^bAbout 10-25% conversion was made for 1.5 hour irradiation. ^cAbout 11-31% conversion for 25 hours.

observed was that the ratio of **2a/2a-3a** varied with different cations in the supercages, while the ratio remained similar regardless of the medium polarity of homogeneous solutions. With the exception of LiX and LiY, the ratio decreased from light atom-exchanged zeolites to heavy atom-exchanged zeolites. The deviations in the cases of Li-exchanged zeolites have been previously observed in some photoreactions such as the photolysis of α -alkyldibenzyl ketones¹⁶ and in photophysical study for the electric field/micropolarity within the faujasite supercage.¹⁷

The irradiation of **1b** in cation-exchanged zeolites through a Pyrex filter exclusively gave rise to the 1,5-ring closure products (**2b** and **3b**), which was also observed in benzene (Tables 1 and 2). The photoreaction of **1b** was found to be much slower than that of **1a**. About 10-25% conversion of **1a** in zeolites X and Y was made for about 1.5 hour irradiation, and 11-31% conversion of **1b** for 25 hour irradiation. The favorable formation of the 1,5-ring closure products and the slower reaction rate due to oxygen substitution have been studied previously,¹⁸ and may be explained by the larger reversion rate of the internally oxa-substituted 1,4-biradical intermediate **B_b** than the externally oxa-substituted 1,4-biradical intermediate **A_b** due to spin-orbit coupling.¹⁹ The irradiation of **1b** in zeolites X and Y afforded more **2b** than in benzene (Table 2). The stereoselectivity was also found to be dependent on the nature of the cations in the zeolites. While the ratio of **2b/2b-3b** remained constant in homogeneous conditions, the ratio in the zeolites also increased as the cation size decreased with the exceptions of LiX and LiY. For examples, the ratio of **2b/2b-3b** changed from 0.39 in NaX to 0.19 in CsX, and from 0.60 in NaY to 0.18 in CsY.

In the intramolecular photocycloaddition of enone and alkene, the regiochemistry is determined by the stability of biradical intermediates, thereby the relative efficiencies to cyclobutane adducts and to the starting materials.⁴ While the major pathway in the photolysis of **1a** in benzene was the one involving **A_a**, the yields of the products from **B_a** increased in the zeolites (Scheme 1). The stereochemistry of the products in the intramolecular 1,5-ring closure photocycloaddition is controlled by the stability of 1,4-biradical intermediates. Since the *cis*-fused 1,4-biradical intermediate would be expected to be severely hindered, the product (**3**) from the *trans*-fused intermediate would be favored in homogeneous solutions.¹⁴ However, more favorable formation of **2** from the *cis*-fused intermediate was observed in zeolites X and Y.

The effects of zeolites on the regiochemistry and stereochemistry have been interpreted by cage size, micropolarity of cage, and/or binding strength of cation.^{3,20} Since the sizes of the supercages are bigger than those of 1,4-biradical intermediates, the effect of cage size does not seem to be a major factor. The ratio of **2/2-3** in the zeolites became closer to that in various homogeneous solutions as the charge density of the cation within cage decreased (from Li-exchanged zeolites to Cs-exchanged zeolites). Since the ratios were similar regardless of the solvent polarity of homogeneous solutions,

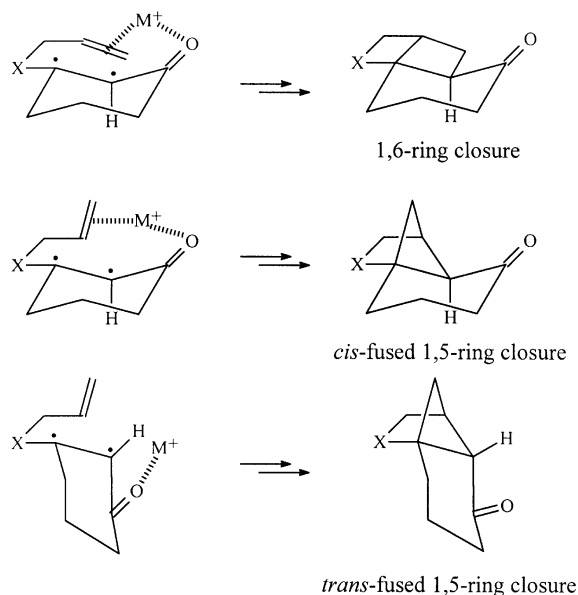


Figure 2. Conformations showing the electronic interaction between the cation and the guest molecule.

the variation in the ratio of **2/2-3** in zeolites X and Y can not be explained by the micropolarity of cage.¹³ Moreover, the regiochemistry (**4a-6a/2a-6a**) observed in the photolysis of **1a** in the zeolites was not correlated with the micropolarity of cage. Therefore, the effect may be due to the difference in the binding strength of the cations with the guest molecules. In other words, the carbonyl group and olefinic bond of the guest molecules may make electronic interaction²¹ with the cations present within the supercages to make a configuration in favoring the formation of **4a-6a** and **2**.

Since the stabilization of the guests at site close to the cation is expected if the light-atom effects observed are due to the electronic interaction between the cation and **1**, the IR spectra of **1a** in several media were compared. Since a trace of water adsorbed in zeolite made it difficult to compare the C–O stretching vibration, we compared the C–C stretching vibration. The C–C stretching vibration of **1a** remained similar regardless of the solvent polarity: 1625 cm⁻¹ in dichloromethane, 1624 cm⁻¹ in methanol, and 1624 cm⁻¹ in 0.1 M LiNO₃/methanol solution. However, a remarkable change was observed in LiX. The C–C stretching frequency of **1a** in LiX was found to be 1591 cm⁻¹, which was red-shifted by 33 cm⁻¹ compared to that in methanol. Because the micropolarity of LiX is estimated to be between those of methanol and LiNO₃/methanol,⁵ the red shift strongly suggests the interaction of the guest molecule and the cations in LiX. This shift is in accordance with the results observed in a conjugated olefin system tightly bound to the surface of zeolite.²²

The chelations of the carbonyl oxygen and olefinic bond to cation to conformationally control the photobehavior of molecules included in zeolites X and Y can be visualized as shown in Figure 2. The configuration of the enone with the interaction of the olefinic bond and the cation can make the 1,6-ring closure more favorable than the 1,5-ring closure. This explains the increased yield of **4a-6a** in the zeolites.

Since cation binding is expected to be greater with lighter atom due to higher charge per unit volume of the cation,^{3,23} the yield of **4a-6a** decreases from LiX and LiY to CsX and CsY. When the enone interacting with the cation undergoes the 1,5-ring closure, the formation of the *cis*-fused intermediate is more favorable than that of the *trans*-fused intermediate due to the chelation (Figure 2). Therefore, the increased ratio of **2/2-3** in the zeolites was observed. Changes of photobehavior due to the guest-cation interaction have been previously observed in the photoreactions of alkyl phenyl ketones, α -alkylbenzoin ethers, and α -alkyldeoxybenzoins.^{11,24}

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