Asymmetric induction in an intramolecular [2+2] photocycloaddition within chirally modified zeolite supercages

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ABSTRACT

Photoirradiation of 1-cyano-2-(5-methyl-2-oxa-4-hexenyl)naphthalene, included in NaY zeolites along with chiral inductors, such as diethyl tartrate or phenylalaninol, gives an intramolecular [2+2] photocycloadduct with a maximum 15% ee. The degree of enantioselectivity was found to depend on the Si/Al ratio, the nature of the cations in the zeolites, the structure of the chiral inductors, and the molar ratio of substrate and chiral inductors.

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1. Introduction

Investigation of asymmetric photoreactions is important not only from the perspective of enantioselective organic synthesis, but also in terms of mechanisms of chiral recognition of photoexcited transient species.[1] Thus far, a variety of asymmetric media and nanocavities have been employed for enantiodifferentiation in photoreactions.[2] Zeolites have been used to provide nanometer-sized reaction cages for photoreactions,[3] and as media to conduct enantioselective photoreactions.[4–8] For example, enantioselective hydrogen abstraction of carbonyl compounds,[5] Norrish–Yang photocyclization,[6] photorearrangements,[7] and photoisomerization[8] have been performed by using chirally modified zeolites. Although [2+2] photocycloadditions of alkenes,[9,10] a synthetically useful reaction for the construction of polycyclic compounds containing cyclobutane rings, within zeolites have been examined,[11] chiral induction in these processes taking place within zeolite cavities has not been described.

In our current effort, we observed that intramolecular [2+2] photocycloaddition of a 1-cyano-2-alkenylnaphthalene derivative taking place within zeolites modified by chiral compounds proceeds with a modest degree of enantioselectivity. Herein, the results of this study are described.

2. Results and discussion

Chirally modified zeolites were prepared by using the following procedure. NaY, NaX zeolites, and Mordenite, dried at 410–430 °C for 12 h, were added to cyclohexane solutions containing the chiral compounds shown in Chart 1. After stirring for 3 h at room temperature and filtration, the zeolites including chiral inductors were

added to cyclohexane solutions of 1-cyano-2-(5-methyl-2-oxa-4-hexenyl)naphthalene **1** and the suspensions were stirred for 3 h. Filtration gave zeolites containing the chiral inductors and **1**. ^{1}H NMR and liquid chromatography showed that the chiral inductors and **1** were not present in the above filtrates and that treatment of the generated zeolites with acetonitrile led to quantitative removal of **1** and the chiral inductors.
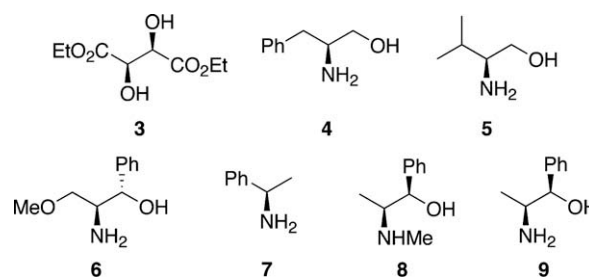

Chart 1. Structure of chiral inductors.

Stirred suspensions, containing the prepared zeolites, in cyclohexane in Pyrex tubes were irradiated by using a high-pressure mercury lamp for 3 h (Scheme 1). Filtration and extraction of organic compounds from the precipitates by washing with acetonitrile and concentration in vacuo of the acetonitrile solution gave mixtures, from which **2** was separated by high-performance liquid chromatography (HPLC) equipped with an achiral gel permeation chromatography (GPC) column. Determination of the enantiomeric excess of intramolecular [2+2] photocycloadduct **2** was accomplished by using HPLC with a chiral column (Fig. 1). The separated enantiomers were analyzed by circular dichroism (CD) spectrometry, which demonstrated that they display opposite Cotton effects. The enantiomeric excesses (ees) were obtained by integration of HPLC peaks and by comparisons with those of a racemic mixture

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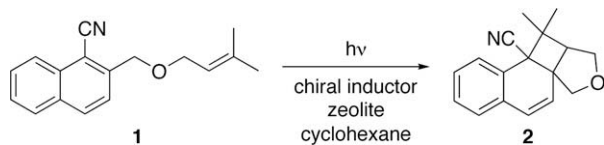
Scheme 1. Intramoleuclar [2+2] photocycloaddition of **1** within chirality modified zeolite supercages.
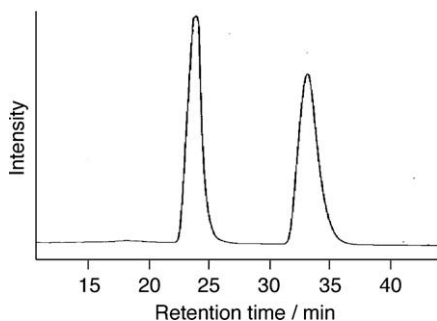

Figure 1. HPLC chart indicating resolution of entantiomers from racemic **2** with a chiral OJ column.

of **2**, prepared by photoirradiation of **1** in the absence of a chiral source.

The results (Table 1) demonstrate that the degree of enantiose-lectivity associated with intramolecular photocycloaddition of **1** depends on the type of zeolite and the chiral inductor used.[12] Irra-diation of a cyclohexane slurry of compound **1** adsorbed on dry NaY zeolite (Si/Al = 5.6) along with L-(+)-diethyl tartrate **3** gives photoproduct **2** with an enantiomeric excess of 10%. The major enantiomer of the photocycloadduct **2** is reversed when D-(−)-diethyl tartrate was used. Enantiomeric excesses (ees) of **2** of up to 12–15% were generated when NaY zeolite (Si/Al = 4.8) along with the enantiomerically pure amino alcohols **4** and **5** were employed. Photoreactions of **1** in NaX zeolite, containing (1S,2S)-(+)-**6** gave an ee of **2** above 11%. Finally, the use of (R)-(+)-α-phen-ylethylamine **7** as a chiral inductor for photoreactions of **1** gives **2** with a low ee and when Mordenite was employed nearly racemic **2** is generated.

The extent of ee observed in this process is also dependent on the Si/Al ratio, the molar ratio of **1**, the chiral inductor, and the nat-ure of alkali metal cations in the zeolite. The effect of the molar ra-tio of chiral inductor and substrate is displayed in the data given in Table 2. The amount of L-(+)-diethyl tartrate **3** varied in the range of 3–45 mg and a fixed (5 mg) amount of substrate **1** was used. The

Table 1
Enantiomeric excesses in intramolecular [2+2] photocycloaddition of **1** within chirally modified zeolite supercages

Entry	Chiral inductor	ee (%)[a]			
		NaY (5.6[b])	NaY (4.8[b])	NaX	Mordenite
1	L-(+)-Diethyl tartrate **3**	10	1	1	<1
2	L-Phenylalaninol **4**	2	15*	2	<1
3	(S)-(+)-2-Amino-3-methyl-1-butanol **5**	<1	13*	<1	<1
4	(1S,2S)-(+)-2-Amino-3-methoxy-1-phenyl-1-propanol **6**	<1	1*	12*	<1
5	(R)-(+)-α-Phenylethylamine **7**	<1	3	<1	<1

[a] The designation * indicates that the major enantiomer from the chiral HPLC column (OJ) is the first peak. The absolute configuration of the enantiomers was not determined.
[b] Si/Al ratio.

Table 2
Effects of the amount of L-(+)-diethyl tartrate **3** and cations in zeolite in the intramolecular [2+2] photocycloaddition of **1**[a]

Entry	Cation in zeolite	Amount of L-(+)-diethyl tartrate **3** (mg)	Conversion (%)	ee (%)
1	Na⁺	3	54	<1
2	Na⁺	6	40	10
3	Na⁺	11	13	4
4	Na⁺	18	5	1
5	Na⁺	27	6	<1
6	Na⁺	45	3	nd[b]
7	Li+	6	59	1
8	K⁺	6	51	3
9	Rb⁺	6	12	<1
10	Cs⁺	6	23	<1

[a] Photoreactions were carried out in cyclohexane slurry containing Y-type zeolite (5.6) and **1** (5 mg).
[b] Not determined.

highest ee (10%) is obtained when 5 mg of **1** and 6 mg of **3** are used while higher ratios of **3** cause dramatic decreases in both the con-version and enantioselectivity.

The nature of metal cations in the zeolite supercage also influ-ences this process. Metal cations in zeolites can be exchanged by using the ionic exchange method. Among the five alkali metal cat-ions probed, the highest ee (10%) was obtained in photoreactions carried out in a zeolite containing sodium.

We expected that interactions between the substrate and chiral inductors would be greater when the zeolites containing the sub-strate and chiral inductor are present in the solid state without sol-vent. However, irradiation of solid state materials led to the formation of **2** with low ee (Table 3).

We have already described the fact that photocycloaddition of **1** in the solution phase gives **2** in a reversible manner.[13] Photoirradi-ation of racemic **2** and L-(+)-diethyl tartrate **3** adsorbed on NaY zeolite led to recovery of racemic **2** and photocycloreversion prod-uct **1**. Based on this result, which indicates the photocycloreversion is not an enantioselective process, we conclude that the enantiodif-ferentiation seen in the photoreactions of **1** is a consequence of chi-ral induction in the photocycloaddition process.

The pore size of NaY and NaX zeolites is about 7.4 Å, and their cavity size is about 13 Å. Since maximum widths of the substrates and chiral compounds are about 6.5 **1**, 6.0 **2**, 3.6 **3**, 4.3 **4**, 4.4 **5**, 5.2 **6**, 4.4 **7**, 4.4 **8**, and 4.4 **9** Å, respectively, molecular sizes that are small enough to pass through the pore and to be included in the nanocavities. The included molecules might interact with the sur-face of the cavities by using their aromatic rings, amino, and car-bonyl groups. If the substrate **1** is included within a cavity in which chiral inductors have already been adsorbed, enantiodiffer-entiation may occur in the process of photocycloaddition because the substrate **1** is located in a chiral environment. From supercage concentration of NaY and NaX zeolites, estimated to be approxi-mately 6×10^{-4} mol/g,[3e] the occupancies of **1** and chiral inductors under the experimental conditions are calculated to be 11% and 16–28%, respectively. These values and molecular sizes indicate

Table 3
Photoreaction of **1** in a chirally modified zeolite in solid state[a]

Entry	Chiral inductor	Conversion (%)	ee (%)
1	L-(+)-Diethyl tartrate **3**	49	5
2	L-Phenylalaninol **4**	55	<1
3	(1R,2S)-(−)-Ephedrine **8**	10	1
4	(1R,2S)-(−)-Norephedrine **9**	44	<1

[a] NaY zeolite (5.6) was used.

that there is enough possibility for **1** to encounter with a chiral inductor in the same cavity.

The effects of the Si/Al ratio on this process appear to be associated with a change in the number of Brönsted acidic sites.[14] A decrease in the Si/Al ratio allows protonation of the substrate and the chiral inductor to take place more extensively. The degree of protonation may affect the enantiodifferentiation process. Since Mordenite has a one-dimensional micropore, it is not suitable for promoting effective interactions between the substrate and chiral compounds. The effect of the molar ratio of substrate and chiral inductors is likely a result of supercage crowding. An increase in the amount of chiral inductor makes the zeolite supercage highly crowded and thus unlikely to adsorb substrate and/or to separate the reaction sites of the intramolecular photocycloaddition. The supercage crowding causes decreasing conversion and also ee. The effects of cations are attributable to their size, which alters the spacial volume of the supercage and the interaction between substrate and chiral inductor, and to the softness, which affects the cation–π interaction between chiral inductor and zeolite surface. Finally, the fact that the conversion of the photoreaction is lower when Rb^+ and Cs^+ are used as the cation is probably due to a heavy atom effect which lowers the excited singlet lifetime of **1** by enhancing the rate of intersystem crossing leading to an unreactive excited triplet state.

3. Conclusion

Asymmetric induction in the intramolecular [2+2] photocycloaddition of **1** by its incorporation in chirally modified zeolites has been observed. Photoreactions of **1** in NaY zeolites containing coadsorbed chiral inductors gave rise to photoproduct **2** with ee values as high as 15%. The extent of ee was found to depend on the Si/Al ratio, the nature of the alkali metal cation in the zeolites, the structure of the chiral inductors, and the molar ratio of substrate and the chiral inductors. It was demonstrated that nanocavities in chirally modified zeolites can be used for the development of enantioselective [2+2] photocycloaddition reactions. Further design of effective asymmetric interaction in zeolites is required for the improvement of ee.

4. Experimental

4.1. General

NaY zeolites (JRC-Z-Y5.6, JRC-Z-Y4.8) were obtained from The Catalysis Society of Japan as reference catalysts. NaX zeolite (F-9) was donated from Tosoh Corporation. Substrate **1** was synthesized by using the reported procedure.[13c] Cyclohexane was distilled from sodium. ^1H NMR (300 MHz) was recorded on Varian Mercury 300 spectrometer. HPLC separation was done by Jasco Megapak GEL 201C (GPC, eluent: $CHCl_3$) equipped with Jasco PU-986 pump and Shodex RI-72 refractometry. Resolution of enantiomers was performed by Daicel Chemical Industries, LTD., chiral OJ column, equipped with Jasco PU-980 pump, UV-970 UV/Vis detector, and CD-2095 plus CD detector.

4.2. Preparation of chirally modified zeolites and their photoreactions

After NaY, NaX zeolites and Mordenite were dried at 410–430 °C for 12 h, the zeolites (300 mg) were added to cyclohexane solutions (50 mL) containing chiral compounds (6 mg) shown in Scheme 1, and were stirred for 3 h at room temperature. After filtration, the zeolites were washed with excess cyclohexane to remove the compounds adsorbed on the surface of zeolites.

Afterwards, the solid was dried in vacuo at 60–70 °C for 12 h. Then the zeolites including chiral inductors were added to cyclohexane solution (50 mL) of 1-cyano-2-(5-methyl-2-oxa-4-hexenyl)naphthalene (**1**, 5 mg), and the suspensions were stirred for 3 h at room temperature. Final filtration and drying in vacuo at 60–70 °C for 12 h gave zeolites carrying chiral inductors and substrate **1**. It was confirmed by using ^1H NMR and liquid chromatography that the chiral inductors and the substrate did not remain in each filtrate. It was also confirmed that the extraction of organic compounds from the zeolites in which substrate **1** and the chiral inductors were adsorbed, by washing with acetonitrile, recovered both compounds quantitatively.

Suspensions containing the prepared zeolites carrying chiral inductors and **1**, in cyclohexane (5 mL) in Pyrex tubes were irradiated by a high-pressure mercury lamp with continuous stirring by a magnetic stirrer for 3 h. Filtration and extraction of organic compounds from the solid by stirring in acetonitrile for 3 h and evaporation gave a crude mixture containing intramolecular photocycloadduct **2**. Compound **2** was separated from the crude mixture by HPLC (GPC). Resolution of the enantiomers of **2** was achieved by HPLC with a chiral column OJ. Each fraction was subjected to circular dichroism (CD) spectra, and it was confirmed that the CD spectra of each fraction were mirror images of one another. Characterization of the products was done by ^1H NMR, and the enantiomeric excesses (ees) were obtained from integrals of HPLC traces by comparison of the racemic mixture of compound **2**, prepared by the photoirradiation of **1** without any chiral source.

4.3. Ion exchange in zeolites

A mixture of NaY zeolite (25 g), lithium nitrate (50 g), and distilled H_2O (500 mL) was refluxed for 24 h. The solid was collected by filtration, washed with distilled H_2O, and then dried at 400 °C for 12 h. This procedure was repeated three times. Potassium-, rubidium-, and cesium-included zeolites were prepared in this manner by using potassium, rubidium, and cesium nitrates.

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12. Conversion of **1**, in the data listed in Table 1, is approximately 30–50%. The photoreaction of **1** under these conditions gave exclusively **2**.

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