

Regioselective Photodimerization of Enones in Zeolites

George Lem, Nikolas A. Kaprinidis, and David I. Schuster*

Department of Chemistry, New York University
New York, New York 10003

Naresh D. Ghatlia and Nicholas J. Turro*

Department of Chemistry, Columbia University
New York, New York 10027

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Regioselectivity and stereoselectivity in organic photochemistry continue to be topics of great interest. In recent years, such selectivity has been achieved to a considerable extent in photochemical processes carried out in constrained media.¹⁻⁶ Of particular interest are the remarkable results obtained in zeolites. Zeolites have recently been shown to exert a significant influence on the unimolecular photoreactivity of included guest molecules, as in Norrish Type I and Type II photoreactions.⁷ In the area of bimolecular photoprocesses, zeolites have been shown to influence the course of [2 + 2] photodimerization of acenaphthylene,⁸ but no such studies have been reported for [2 + 2] photocycloaddition reactions of enones, a reaction of recognized mechanistic importance.⁹ In an initial foray in this area, the effects of zeolites on photodimerizations of cyclopentenone (1) and cyclohexenone (2) have been investigated. Little control over the regiochemistry of such reactions is attainable when they are carried out in isotropic solvents.^{10,11} In this report, we show that a relatively high degree of regioselectivity in enone photodimerization can be achieved in zeolites, due to size constriction effects in the supercages of X- and Y-type faujasites as well as the complexing ability of the charge-compensating cation of the zeolite on included guests.

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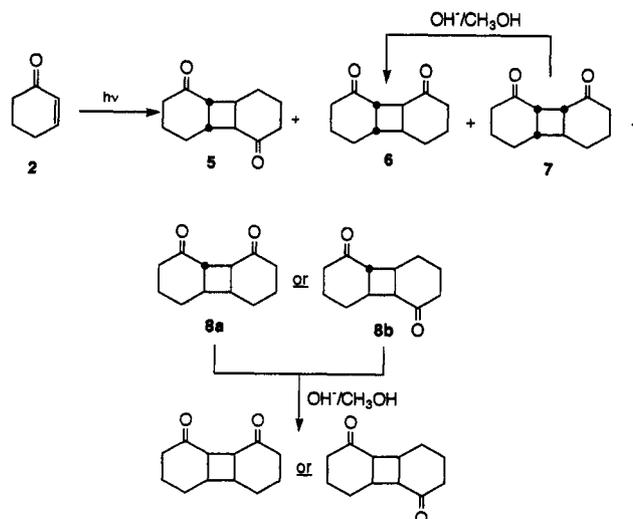
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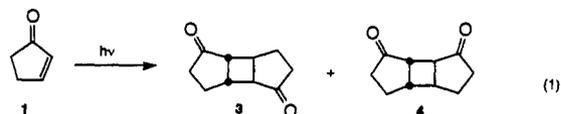
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Scheme I



The photodimerizations of cyclopentenone (CP) and cyclohexenone (CH) in solution have been extensively studied and are fairly well understood.^{9,12} In the case of cyclopentenone, head-to-tail (HT) and head-to-head (HH) dimers 3 and 4 are formed from interaction of a CP triplet excited state and a CP ground state (eq 1).¹⁰ In both polar and nonpolar solvents, the major



dimer formed is HT (3). Similarly, photodimerization of CH in solution occurs via a triplet excited state to give two major [2 + 2] dimers, whose stereochemistry has been suggested to be *cis-anti-cis* HT (5) and HH (6);¹¹ these structures have recently been confirmed using X-ray crystallography.¹³ In addition, two minor unidentified products 7 and 8 were detected in hexane, methanol, acetonitrile, and benzene photolysates.¹¹ Both of these dimers have now been shown to possess a *trans* 6/4 ring junction. Although 7 could not be isolated in pure form, treatment with base converted 7 into 6, according to gas chromatographic analysis, demonstrating that 7 is the *trans*-fused HH dimer shown in Scheme I. Dimer 8 was isolated using column chromatography and has 12 distinct peaks in its ¹³C NMR spectra, in contrast to the six peaks shown by the symmetrical dimers 5 and 6. Upon base-catalyzed epimerization, 8 is converted into a new CH cyclodimer, which must be either the *cis-syn-cis* HH or *cis-syn-cis* HT dimer. Thus, 8 must have one of the alternative *trans*-fused HH or HT dimeric structures 8a and 8b shown in Scheme I. Photodimerization of CH in nonpolar solvents gives predominantly the HT photodimer, but the regioselectivity switches in favor of the HH photodimer (ratio 1.6:1) in polar solvents.¹¹

The dimer ratios from irradiation of cyclopentenone included in dry MX and MY faujasites, using the output of a 450-W medium-pressure lamp filtered through a potassium chromate solution, are given in Table I.¹⁴ Typically, when 5 mg of enone in 100 mg of dry zeolite is irradiated for 1.25 h in a continuously

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(14) Exchange levels of the zeolites as measured by atomic absorption spectroscopy are as follows: LiX = 46%, NaX = 100%, KX = 64%, CsX = 37%, LiY = 64%, NaY = 100%, KY = 84%, CsY = 62%. Since cations within the supercages are easily exchangeable, the low exchange levels of some of the zeolites arise from inaccessible cation sites which are not exposed to organic guests. We are grateful to Dr. V. Ramamurthy at Du Pont for this data.

Table I. Product Ratio from Photodimerization of 2-Cyclopentenone in Zeolites and in Solution^a

medium	ratio 3/4	medium	ratio 3/4
LiX	0.93 ● 0.06	KY	0.68 ± 0.04
NaX	0.60 ± 0.05	CsY	0.79 + 0.02
KX	0.80 ± 0.03	NaA	9.4
CsX	0.50	benzene	3.64 ● 0.07
LiY	1.36 ± 0.01	methanol	1.66 ± 0.02
NaY	1.21 ± 0.14		

^a Product yields were measured at 10–50% conversion by gas chromatography, except in the case of NaA where the conversion was ca. 95%. Products were removed from zeolites by treatment with 1 N HCl, followed by extraction into CH₂Cl₂; all dimers were acid stable (for experimental details see ref 15). Loading in all cases was 5% by weight. Solution photolyses were performed at enone concentrations of 1 M. Product ratios are tabulated with standard mean error from two or more independent experiments; except in the cases of CsX and NaA where only single experiments were performed. For the exchange levels of the zeolites, see ref 14.

Table II. Product Ratios from the Photodimerization of 2-Cyclohexenone in Zeolites and in Solution^a

medium	ratio 5/6	ratio $\frac{7+8}{5+6+7+8}$
LiX	0.26 ± 0.01	0.30 ● 0.01
NaX	0.13 ● 0.02	0.23 ± 0.02
KX	0.16 ± 0.01	0.09 ± 0.01
CsX	0.11 ± 0.02	not determined
LiY	0.46 ± 0.10	0.61 ± 0.01
NaY	0.46 ± 0.03	0.50 ± 0.02
KY	0.08 ± 0.01	0.07 ● 0.02
CsY	0.09 ± 0.01	not determined
NaA	1.16 ± 0.28	0.16 ± 0.02
benzene	1.95 ± 0.02	0.26 ± 0.01
methanol	0.63 ± 0.02	0.14 ● 0.01

^a Product yields were measured at 6–40% conversion by gas chromatography, except in the case of NaA where the conversion was ca. 95%. For other experimental details, see Table I.

agitated tube, the conversion of enone to dimers ranges from 5 to 40%. Dimers are analyzed by gas chromatography after treatment of the zeolites with HCl and extraction with methylene chloride. The dimers were shown to be stable under these conditions.¹⁵ It can be seen that there is an increase in the formation of the HH relative to the HT dimer in both X- and Y-type faujasites as the size of the counterion increases and the available space in the faujasite cavity decreases. The effect is larger in the X-type faujasites, which have a higher proportion of counterions and hence less available space in the cavities than in the MY zeolites. The regioselectivity in favor of the HH isomer is most pronounced, in the cases of NaX and CsX, where the formation of the HH isomer is favored by a factor of 2 over the HT regioisomer. Such a result has never been achieved in solution photodimerizations of CP.¹⁰

In the case of CH photodimerization in faujasites, carried out as above, the HH dimer is consistently preferred over the HT dimer in KY, CsY, CsX, KX, and NaX (Table II). In most of the zeolites, the *trans*-fused dimers 7 and 8 are formed in amounts comparable with the yields in solution, but in zeolites NaY and LiY they are the major dimers. It was shown that the product ratios in NaX and NaY do not change perceptibly as a function of irradiation time. In NaY, the proportion of *trans*-fused dimers

(15) A 0.2 M solution of cyclohexenone in pentane was photolyzed for 10 min, corresponding to a 5% conversion of the starting material. The dimer ratios were then checked by gas chromatography. Following evaporation of pentane, the mixture of cyclohexenone photodimers was redissolved in 1 mL of CH₂Cl₂ and 1 mL of 1 N HCl and sonicated for 15 min. The organic layer was separated, dried over MgSO₄, and analyzed by gas chromatography. No new products nor a difference in the dimer ratios were observed relative to the photolysate before acid treatment.

7 and 8 is 0.53 and 0.48 after irradiation for 45 and 75 min, corresponding to 48% and 66% conversion of starting material, respectively. The time course was studied more completely in NaX. For example, the fraction of *trans*-fused dimers is 0.17 and 0.19 after irradiations of 30 min and 4.5 h, corresponding to 7% and 19% conversions of starting material, respectively. Thus, the enhanced yields of the *trans*-fused photodimers in the zeolites do not seem to be due to secondary photoreactions. Dimer ratios also do not change when dimers are allowed to remain within the zeolite for up to 24 h after irradiation before workup compared with immediate workup following irradiation. In addition, no isomerization of the pure dimer 6 was observed when it was included within NaY¹⁶ and left in the dark for 24 h.

In the photodimerization of CP, the greatest reversal in regiochemistry from HT to HH is observed in CsX, the faujasite with the smallest supercage volume and the weakest electrostatic interaction of the ion.⁷ Similarly, the results from the photodimerization of CH in zeolites indicate a preference for the more compact and more polar HH regioisomer in the zeolites with smaller cage volume such as KY, CsY, and CsX. An interesting trend is also observed in the photodimerizations of CP and CH in the X faujasites, where the HT/HH ratios of dimers are similar in the NaX and CsX cases although the relative free volumes of the faujasite cages are quite different.^{7b} We suggest that the complexing effect of the charge-compensating cation and the size constriction factor in the NaX supercage probably play a role in controlling regiochemistry. In zeolites such as CsX, the size constriction factor of the supercage is probably the dominant factor in controlling the HT/HH ratios. Chelation of the carbonyl oxygen to conformationally control the photobehavior of molecules included in zeolite matrices has been proposed to explain the results in Norrish Type I and II photoreactions of benzoin alkyl ethers and alkyl deoxybenzoin in zeolites.¹⁷ Chelation by Na cations was also postulated to be responsible for the enhanced regioselectivity in the photodimerization of cyclohexenone derivatives intercalated within clay layers.^{4b}

As a control experiment, the photodimerization of cyclopentenone and cyclohexenone was carried out on zeolite NaA, which contains 2-Å pores, rendering the internal cavity of the zeolite inaccessible to most organic guest molecules.^{7b} As can be seen in Tables I and II, the HT/HH dimer ratios on photodimerization of CP and CH on the external zeolite surface of NaA are completely different from those for dimers formed within the faujasite supercage. Hence, the observed regiochemical selectivities for the photodimerization of CP and CH in zeolites X and Y must be a consequence of enone molecules included within the faujasite supercavity.

The results presented above demonstrate that zeolites can play an important role in determining regio- and stereoselectivity in enone photocycloadditions.^{9,12}

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(16) A mixture composed of 5 mg of dimer 6 dissolved in 1 mL of pentane and 100 mg of NaY was allowed to stand in a sealed sample tube. At 30 min intervals the supernate was checked by gas chromatography for residual dimer 6 not loaded into the zeolite. After 1.5 h, all of 6 appeared to be loaded into the faujasite, after which the supernate was decanted, and the zeolite was then washed twice with pentane. The zeolite was then dried with a gentle stream of Ar gas for 15 min, sealed and left in the dark for 24 h. The zeolite sample was then treated with 1 N HCl, extracted with CH₂Cl₂, and checked for isomerized dimers by gas chromatography.

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