Communications

The Effects of Media on the Intramolecular Photocycloaddition of 3-(3-Butenyl)cyclohex-2-enone

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Although the [2+2] photocycloaddition of enone to alkene is one of the most widely used photochemical reactions, several aspects on the mechanism and the factors in controlling the regiochemistry have not been understood.[1] The biradical nature of a key intermediate in the photoreaction is well-established,[2] but the existence of triplet exciplex is still controversial. In the intramolecular [2-2] photocycloaddition, two reaction pathways, by way of 1,5 (crossed) closure and 1,6 (parallel) closure, are competing. Several factors in modifying the regioselectivity, such as chain length,[3] substituents of the system,[4,5] and incorporation of the conjugated double bond into a ring,[5] have been reported, although the mechanistic bases of the factors are not well-understood. In addition to these, reaction medium seems to be another factor in controlling the regiochemistry, which may have more applicability in synthesis. Therefore, we studied the effects of various solvents and zeolites on the intramolecular [2+2] photocycloaddition of 3-(3-butenyl) cyclohex-2-enone (1). The important role of the organized and constrained media on photoreaction has been recognized.[6] However, controlling the photochemistry of enones by zeolites as media has been investigated recently.[7]

3-(3-Butenyl)cyclohex-2-enone (1) was prepared by Grignard reaction of 3-butenylmagnesium bromide on 3-ethoxy-2-cyclohexenone.[5] The irradiation of 1 (7.43 × 10⁻³ M) in benzene under a nitrogen atmosphere with a 450-watt Hanovia medium-pressure mercury lamp through a Pyrex filter resulted in the formation of four products 2-5 in 15% conversion (Scheme 1). The yields of 2-5, as measured by gas chromatography with the internal standard of n-decane, were

estimated to be 19.4%, 43.5%, 31.4%, and 5.7%, respectively, which are in accordance with the previous results that were obtained with a Uranium filter.[5,8] The irradiation of 1 in dichloromethane or acetonitrile under the same conditions gave the same products, and the distributions of 2-5 were similar to that in benzene (Table 1). On the other hand, the intramolecular photocycloaddition of 1 in 1:1 mixture of methanol and water notably increased the products (4-6) via the 1,4-biradical intermediate B derived from 1,6-ring closure (Scheme 1). However, the addition of any cations to the solution did not change the product ratio within experimental error. Although the effect in the mixture of methanol and water is not immediately obvious, these results indicated no effect of the medium polarity on the photoreaction, which is consistent with the mechanism including the biradical intermediates.[1,2]

The photoreactions of 1 in cation-exchanged zeolites were studied. Various zeolites were prepared by the ion exchange reactions of NaX, NaY, and NaA with appropriate nitrate
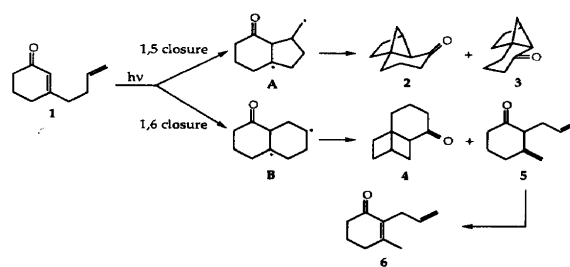
Scheme 1.

Table 1. Product Distribution (%) for Photoreaction of **1** in Various Media[a]

Medium	from intermediate **A**		from intermediate **B**			2+3:4+5+6
	2	**3**	**4**	**5**	**6**	
benzene	19.4	43.5	31.4	5.7	–	62.9:37.1
CH_2Cl_2	18.7	45.9	28.6	6.8	–	64.6:35.4
CH_3CN	17.7	43.9	32.4	6.0	–	61.6:38.4
$MeOH/H_2O$[b]	12.1	30.0	48.3	2.9	6.7	42.1:57.9
0.10M $LiNO_3$[b]	12.1	29.5	48.7	2.8	6.9	41.6:58.4
0.10M $NaNO_3$[b]	12.4	29.5	49.0	2.5	6.6	41.9:58.1
0.10M KNO_3[b]	12.1	30.2	48.1	2.7	6.9	42.3:57.7
0.10M $RbNO_3$[b]	11.9	29.9	48.7	2.8	6.7	41.8:58.2
0.10M $CsNO_3$[b]	12.2	30.8	49.7	–	7.3	43.0:57.0

[a]Number reported are the average of at least two measurements. Error limit of the analysis is ±2%. [b]In methanol-water (1:1) mixture.

Table 2. Product Distribution (%) for Photoreaction of **1** in Zeolites X and Y[a]

Medium	from intermediate **A**		from intermediate **B**			2+3:4+5+6
	2	**3**	**4**	**5**	**6**	
LiX	9.8	17.6	51.7	4.6	16.3	27.4:72.6
NaX	15.6	14.6	49.6	3.1	17.1	30.2:69.8
KX	15.9	21.3	46.1	3.2	13.5	37.2:62.8
RbX	17.8	29.4	40.3	2.6	9.9	47.2:52.8
CsX	13.3	45.8	28.1	12.3	12.3	59.1:40.9
LiY	9.0	18.3	54.2	7.0	7.0	27.3:72.7
KY	13.2	11.3	57.1	3.2	3.2	24.5:75.5
RbY	17.1	21.1	47.4	3.0	3.0	38.2:61.8
CsY	17.3	26.3	38.8	–	–	43.6:56.4

[a]Number reported are the average of at least two measurements. Error limit of the analysis is ±3%.

solutions.[9,10] The inclusion of the starting material within zeolites X and Y was achieved by using *n*-hexane as a solvent. In all cases the loading level was kept low, which corresponded to the occupancy number of 0.1-0.2 molecule per supercage. All irradiations were conducted on solvent-free solid samples. After **1** within zeolites X or Y was irradiated in continuously agitated tube for about 1.5 hours (10-25% conversion), the reaction mixture was extracted with diethyl ether. Material balances were no less than 87% in the photolyses on zeolites X and Y. This ensured that no unidentified product was trapped in zeolite framework. On a control experiment **1** was treated in the same procedure except the UV exposure. Only the starting material was recovered, which indicated that none of the products derived from the photolysis of **1** adsorbed on the zeolites was formed through a thermal reaction.

The results of the photolyses of **1** in cation-exchanged zeolites X and Y are summarized in Table 2. The product distributions in zeolites were found to be quite different from that in benzene. When **1** was included in zeolites X or Y, the yields of the products derived from the 1,4-biradical **B** increased. Significant amounts of **6** were also observed. The compound (**6**) seems to be formed through incidental shift of the double bond of **5**, which was reported to occur slowly at room temperature.[5] Since the rearrangement reaction was found to be faster when adsorbed on silica or heated in refluxing methanol (38.9% conversion for 3 hours), the formation of **6** may be due to polar acidic environment of zeolites. The product ratios were also dependent on the nature of the cations present within zeolite supercages. The yields of **4-6** increased as the cation size decreased (light-atom effect). For examples, the ratio of **2+3** and **4+5+6** changed from 27.4:72.6 in LiX to 59.1:40.9 in CsX, and from 27.3:72.7 in LiY to 53.9:46.1 in CsY (Table 2). Control experiments with zeolites A, which contain smaller pores (~4 Å), resulted in low material balances (<30%) and quite different ratios of **2+3** and **4+5+6**.[6,11] On the external surfaces of LiA and NaA, the ratios in the solid-state photoreaction mixtures were 51.7:48.3 and 60.2: 39.8, respectively. These indicated that the adsorption on the internal surfaces occurred in the cases of zeolites X and Y.

Since the triplet mechanism of the photocycloaddition has been well-established,[1] the heavy-atom effect on the inter-

system crossing of singlet excited state does not seem to be effective.[12] The increased yields of **4-6** in decreased cation sizes can not be explained by the effect of electrostatic field because no effect of the polarity was observed in isotropic solvents and different product distributions in solutions and zeolites were obtained. For example, the ratios of **2+3** and **4+5+6** in 1:1 mixture of methanol and water and LiX were quite different, although the polarity of both media was estimated to be similar.[13] Therefore, the light-atom effect may be interpreted as the electronic interaction between the cation and **1**,[14] which stabilizes the guests at site close to the cation. This was supported by the IR spectrum of **1** adsorbed in LiX. The frequency of the C=C stretching of **1** in LiX was 1591 cm^{-1} that was red-shifted by 33 cm^{-1} compared to those in methanol and in 0.10 M $LiNO_3$ methanol solution. Similar results were observed in conjugated olefin systems tightly bound to the surface of zeolites.[15] However, it is not obvious how the interaction, thus the restriction of conformational and/or transitional movement, influences the competition between the formations of **2+3** and **4+5+6** (formation of biradicals, formation of the products, and/or biradical reversion).[2] It is interesting to note that the cations in zeolites influenced the reaction but the cations in isotropic solvents did not influence the reaction. In the photoreaction of a β,γ-unsaturated ketone, the lack of the cation effect in aqueous solution was also observed, while significant effects of the cations in crystals and zeolites were observed.[16] The effects of media on the regioselectivity and stereoselectivity of several intramolecular [2+2] photocycloadditions are under investigation in our laboratories.

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8. ¹H NMR and IR spectra for all of the reactant and products were compared with those in literature.

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Synthesis of Machinable Optical Monolith of Forsterite-PMMA Organic-Inorganic Nanocomposite through a New Synthetic Strategy

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Many experimenters were attracted by the sol-gel method. because it could be a good synthetic tool for preparing their sample in an exotic morphology such as thin film.[1] preformed monolith.[2] uniformly sized particles.[3] or highly porous monolith.[4] Therefore. in some sense. the method should be considered to have very high processability. But. considering the usefulness of the final products in a practical application. a weak point of the method should also be dealt. The problem is that the mechanical properties of the sample prepared by the method are very poor. During the drying process. shrinkage occurs in an unacceptably large extent.[5] If hastily dried, the sample develops cracks.[6] The monolith experiences warping which render the method useless in preparing a sample in exact dimension.[7] From the reason. the maximum dimension acceptable is ~1 mm thick for a monolith, and ~1 μm for a thin film. Most of all, the sol-gel product has very poor mechanical strength. and is not machinable at all. Without an additional heat treatment. the product disintegrates in polar solvents. and readily breaks by small stress.

These problems had been tackled by various ways. Drying Control Chemical Agents (DCCA) were used to get a crack-free monolith.[8] Solvent was removed in its critical state to get a shrinkage- and crack-free monolith.[9] But. still the mechanical properties of the products were poor. Recently. in an effort to circumvent these problems. a new kind of approach came up as a promising synthetic tool. Rather than to prepare simply the inorganic sol-gel product. the method was modified to produce nano-structured organic-inorganic composite materials. This new kind of organic-inorganic composite was refered as a CERAMER (CERAmic+polyMER)[10] or ORMOCER (ORganically MOd-