

The oxa-di- π -methane rearrangement of β,γ -unsaturated ketones induced by the external heavy atom cation effect within a zeolite

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Photolyses of β,γ -unsaturated ketones **1** and **2** included in MY zeolites gave the oxa-di- π -methane products, which are believed to originate from the triplet state caused by heavy atom cations present within the supercage.

Recent application of zeolites in organic photochemistry,¹ and our interest in the chemistry of zeolites² and the photochemistry of β,γ -unsaturated ketones,³ has prompted us to investigate the photochemistry of these compounds within the supercages of zeolite Y. We report here the observation of a 1,2-acyl shift, or oxa-di- π -methane (ODPM) rearrangement, of bicyclo[2.2.1]hept-5-en-2-one (BHO) **1**[†] and bicyclo[2.2.2]oct-5-en-2-one (BOO) **2**[‡] included in heavy cation-exchanged zeolite Y.

The chemistry of β,γ -unsaturated ketones is well-known and many publications on this subject have been published during the last two decades.⁵ Upon direct irradiation, the majority of β,γ -unsaturated ketones undergo a singlet-mediated 1,3-acyl shift reaction to produce a rearranged β,γ -unsaturated ketone.⁶ Triplet-sensitized photolysis of these compounds, on the other hand, leads to the well known and synthetically useful ODPM rearrangement.⁷ Investigation of the extent of singlet-triplet interconversion of the excited guest molecule within a cage, channel or pore has been limited to the study of the photophysical processes of some aromatics and olefins,⁸ and photochemical reactions like photodimerization of acenaphthylene⁹ and photolysis of 2,3-diazabicyclo[2.2.2]oct-2-ene.¹⁰ We felt that the heavy cations present within the Y-type faujasite supercage could provide interesting results for the photochemistry of β,γ -unsaturated ketones. Because LiY and NaY were not effective for ODPM rearrangement, and KY did not show more than 15% activity for this reaction,[‡] we concentrated our experiments on CsY and TIY. It should be emphasized that the absence of triplet formation in LiY and NaY is consistent with their solution behaviour in which the intersystem crossing yields from singlet to triplet is reported to be near zero.¹¹ This led us to conclude that rearrangement in the supercages of LiY, NaY and mostly in KY is from the singlet excited state.[‡]

The Cs⁺ and Tl⁺ cations were exchanged into the NaY zeolite by mixing the powder with the appropriate 10% nitrate solution at 90 °C for 1 h. For each gram of zeolite, 10 ml of the cation nitrate solution was used. This cycle was repeated three times. The zeolite was filtered, washed thoroughly, and then held at 500 °C for 12 h. A typical procedure for the preparation of zeolite-guest complexes is provided below. Dry zeolite (2.1 g) and the ketone (30 mg)[§] were stirred in dry hexane (30 ml) for about 2 h under a dry nitrogen atmosphere. The complex was filtered and washed several times with dry hexane to remove any surface adsorbed materials. GC analysis of the filtrates showed that most of the ketone had been introduced into the cavities. The dry solid inclusion complexes were then placed in a quartz tube and photolyzed at 253.7 nm in a Rayonet photoreactor with five lamps for 10–35 h.[¶] The photolyses were carried out either in hexane slurry or in the solid state. The products were extracted by stirring the complex in 30 ml of dry Et₂O for *ca.* 12 h or dissolution of the zeolite framework with

Table 1 Photolyses results for BHO **1** under various conditions

Medium	Solution ^a		Slurry ^b		Solid	
	t/h	Yield (%)	t/h	Yield (%)	t/h	Yield (%)
Acetone	15	41				
CsY			10	21.4	25	39.2
CsY			15	24	30	40.4
CsY			20	27	35	41.9
TIY			10	33.6	25	55.5
TIY			15	34.3	30	57.8
TIY			20	35	35	61.1

^a Yield based on photolysis at 253.7 nm (quartz). Photolysis with a low pressure mercury lamp led to 70.4% of **3**. ^b Increasing the photolysis time to more than 20 h did not improve the results.

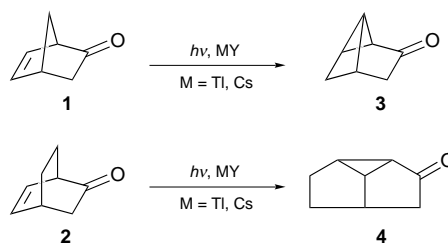
Table 2 Photolyses results for BOO **2** under various conditions

Medium	Solution ^a		Slurry ^b		Solid	
	t/h	Yield (%)	t/h	Yield (%)	t/h	Yield (%)
Acetone	15	37.3				
CsY			10	12.2	25	29.1
CsY			15	18.6	30	30.6
CsY			20	20.5	35	32.1
TIY			10	24.1	25	38.6
TIY			15	25.6	30	40.5
TIY			20	26.1	35	44.7

^a Yield based on photolysis at 253.7 nm (quartz). Photolysis with a low pressure mercury lamp led to 66.2% of **4**. ^b Increasing the photolysis time to more than 20 h did not improve the results.

1 M HCl. Mass balance in all cases was *ca.* 90%. Identification of products was made by GC (Perkin-Elmer 3920 gas chromatograph equipped with TCD detection and a packed column of 3% OV-17 on Chromosorb W) and comparison of retention times with those of authentic samples. The concentrations were determined by an internal standard procedure using cyclohexanone as the internal standard.^{||} The results are shown in Tables 1 and 2.

Photolyses of either the hexane slurry or the solid complexes led to the ODPM ketones **3** and **4** as the sole products (Scheme 1). Only traces of 1,3-acyl shift ketones could be detected as byproducts.



Scheme 1

Since intersystem crossing of β,γ -unsaturated ketones is usually slow following direct irradiation, population of the triplet excited state requires either to use of triplet energy sensitizers or the introduction of heavy atoms to decrease the barrier to the singlet–triplet transition (the heavy atom effect).¹² Because sensitization techniques have been difficult to apply in the crystalline state until now, the triplet state photochemistry of such compounds has not been studied in this medium, except for the remarkable work of Ramamurthy, who investigated the photolyses of Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ salts of a β,γ -unsaturated keto acid and found that there is a strong cation effect in the crystalline state but none in solution.¹³

The formation of the ODPM ketones under the effect of heavy cations within the Y zeolite in our system, particularly the 60% yield of the 1,2-acyl shift product in the presence of TIY, is strong support for the heavy atom cation effect in solid systems. The trends observed in the variation of the triplet yields with increasing mass, *i.e.* Li^+ , Na^+ < K^+ < Cs^+ < Tl^+ , is consistent with the expected spin-orbit coupling-induced triplet formation. The reason for the greater effect of heavy atom cations in the solid state than in the slurries might be attributed to the increased triplet lifetime of the ketone in the solid state, and the reduced diffusional mobility of the guest molecule toward the heavy cations when the channels are filled with solvent molecules. Such behaviour has been observed in the di- π -methane rearrangement of 11-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene within zeolite KY by the triplet–triplet energy transfer of several sensitizers to the guest molecule within the supercages.¹⁴

In conclusion, we believe that zeolite–guest complexes containing heavy cations can be considered as remarkable singlet–triplet transition matrices. Our results show it to be an efficient approach to energy transfer from a donor to an acceptor in the solid state. To the best of our knowledge, this is the first report of an ODPM rearrangement arising from an external heavy atom cation effect within a zeolite.

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Notes and References

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† This compound was prepared *via* oxidation of bicyclo[2.2.1]hept-5-en-2-ol using chromium oxide–pyridine in CH_2Cl_2 .

‡ The main rearrangement within the LiY, NaY and KY was 1,3-acyl shift with the formation of rearranged ketone.

§ A ketone : zeolite ratio of 1 : 70 gave the best results.

¶ Photolyses of either the hexane slurries or the dry solids with a low pressure mercury lamp were not efficient.

|| Ketones **3** and **4** were prepared according to the procedures mentioned in ref. 8(a) and were used after purification to establish the standard curves.

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