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# Triplet photosensitization of myrcene and some dienes within zeolite Y through heavy atom effect

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**Abstract**

Myrecene undergoes successful triplet photosensitization within zeolite Y microreactor exchanged with $K^+$, $Cs^+$ and $Tl^+$ heavy cations. Norbornadiene, 5,5-diphenyl-1,3-cyclohexadiene and dicyclopentadiene under the same conditions afford the corresponding triplet products with higher yields and improved diastereoselectivity.

*Keywords:* Zeolite Y; Photoisomerization; Dienes chemistry; Heavy atom effect

## 1. Introduction

It is well known that intersystem crossing mostly violates the spin selection rules. Therefore, observation of efficient intersystem crossing to triplet states under direct irradiation in order to obtain products other than those arise from singlet states are not expected. However, this process can be intensified if: (a) the orbital transition involved possesses the character of a $p_x$ to $p_y$ orbital jump, and (b) the orbital transition is localized on a single atom. As a result, the selection rules (commonly termed El-Sayed's) have been deduced for intersystem crossing of carbonyl groups [1]. In the presence of ketones with proper triplet energies, many different organic molecules are known to absorb light and excitation to the corresponding triplet states occur efficiently. The consequence is the observation of products derived from triplet states. Although these processes enjoy many advantages, separation of sensitizer from reaction mixture is not easy and is time consuming.

A second important method for enhancing $S_0$ to $T_1$ absorption is heavy atom perturbation. The heavy atom may be directly affixed to the molecule being studied (internal heavy atom effect) or may be located in the solvent (external heavy atom effect) [2]. There are several reports about photophysical as well as photochemical processes arising from triplet states in the presence of heavy atoms [2]. The formation of similar products with comparable yields is promising. Furthermore, affixing heavy atom within a solid system makes the purification stage more convenient.

The singlet–triplet chemistry of conjugated and nonconjugated hydrocarbon dienes has been widely studied [3,4]. The singlet reactivity of these dienes, however, is different from the triplet state. As shown in Scheme 1, irradiation of myrcene (MRC), norbornadiene (NBD), dicyclopentadiene (DCP) and 5,5-diphenyl-1,3-cyclohexadiene (DCH) in the presence of organic sensitizers generate 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane [5], quadricyclene [6], pentacyclo[5,2,1,$0^{2.6}$,$0^{3.9}$,$0^{4.8}$] decane [7] and a mixture of *trans*-5,6-diphenylbicyclo[3,1,0]hex-2-ene (major product, 91%) and *trans*-4,5-diphenylbicyclo[3,1,0]hex-2-ene (minor product, 9%) [8], respectively. On the other hand, although different products are obtained from MRC [9] and DCH [8], no reaction occurs with DCP [7] and NBD [10] undergoes fragmentation to cyclopentadiene, acetylene and toluene under direct irradiation (Scheme 1). Study of a number of photophysical processes of some aromatic and nonaromatic olefins [11], and photochemical reactions like photolysis of 2,3-diazabicyclo[2.2.2]octa-2-ene [12], and Zimmerman photorearrangement of dibenzobarrelene and benzobarrelene [13] have been successfully achieved in the presence of different cations within the supercages of zeolite [14]. Pitchumani and Madhavan in their recent publication reported the inefficiency of $Tl^+$ and $Cs^+$ exchanged bentonites in promoting the triplet

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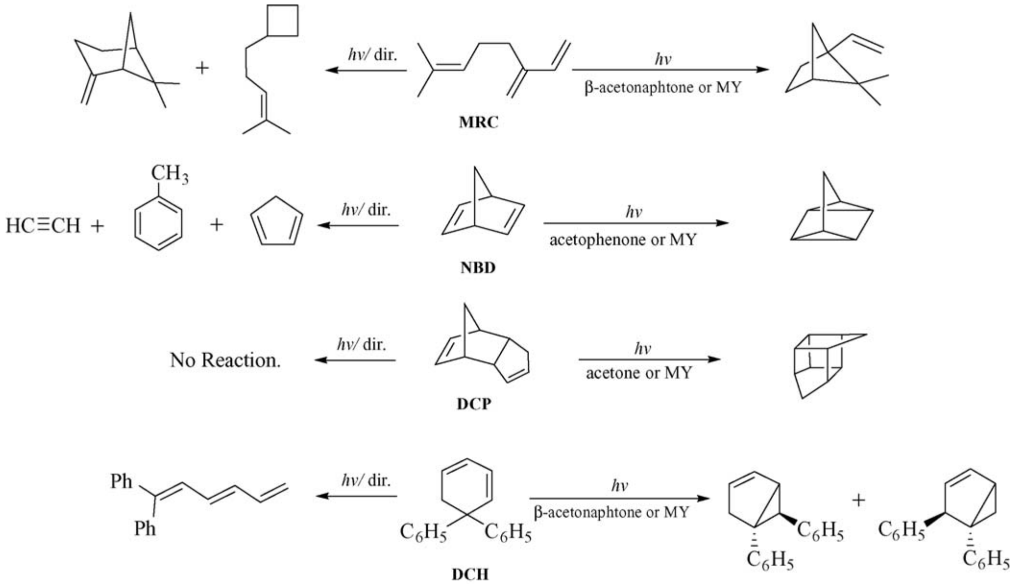

Scheme 1.

excitation of myrcene [15]. To the best of knowledge, since the photochemistry of MRC [5] within the zeolite supercages has not been studied before, we thought that successful photosensitization might be induced by the heavy atom cation within the zeolite Y. Although the internal [2 + 2]-cycloaddition of NBD and DCP in the presence of organic sensitizers have been reported previously [6,7], efficient achievements in the absence of sensitizers by using heavy atom exchanged zeolite could be a breakthrough in dienes photochemistry. Since Ramamurthy's work was based on di-π-methane rearrangement of dibenzobarrelene and benzobarrelene [13], we were prompted to experience rearrangement of DCH [8] in the presence of heavy atom included in zeolite Y. This could provide not only another evidence to explore a general method to produce triplets of dienes within the zeolite cavities, but also the enhancement of product diastereoselectivity arising from constraint environment of zeolite available to guest molecule could be tested.

## 2. Experimental

Myrcene, norbornadiene and metal nitrates were obtained from Merck and the liquids were distilled and dried before using. NaY zeolite was synthesized according to the reported procedure [16]. Monovalent cation-exchanged zeolites ($Li^+$, $K^+$, $Cs^+$ and $Tl^+$) were prepared by stirring 10 g of NaY with 100 ml of appropriate 10% nitrate aqueous solutions at 90 °C for 12 h. The slurries were filtered and washed thoroughly with distilled water for several times. The procedure was repeated for three times. The cation-exchanged zeolite was, then, kept in an oven at 500 °C overnight. The exchanged cation percentages of $Li^+$, $K^+$, $Cs^+$ and $Tl^+$ were determined by atomic absorption spectroscopy as 73, 87, 71 and 68, respectively. 5,5-Diphenyl-1,3-cyclohexadiene was prepared according to the procedure reported previously [8]. The procedure for diphenylacetaldehyde synthesis was modified by epoxidation of *trans*-stilbene and subsequent conversion to the desired aldehyde with $BF_3{\cdot}O(C_2H_5)_2$ in benzene in order to make the synthesis more efficient [17].

### 2.1. Diene loading in zeolite

Diene and activated MY with the ratio of 1:40 were stirred in 40 ml of dry hexane for 12 h. The solid was filtered and washed with hexane and, then, ether for several times in order to remove any adsorbed diene on the zeolite surface. The percentages of dienes included in zeolite Y were determined by GC analyses. The loading level (Table 1), i.e. the average number of zeolite supercages per guest molecule were calculated by the procedure reported previously [18,19].

### 2.2. Photolysis procedure

The dry solid was mixed with 100 ml of dry hexane and the slurry was irradiated in a proper vessel (see Tables 2 and 3 footnotes) using 450 W Hanovia medium pressure mercury lamp (which emits at different wavelengths including 2537 Å, consistent to $\lambda_{max}$ absorption of MRC, NBD, DCP and DCH) for appropriate period of time under argon atmosphere. The solid was then separated by filtration and washed with fresh hex-

Table 1
Loading level: the average number of zeolite supercages per guest molecule

| Reactants | MY | | | | |
|---|---|---|---|---|---|
| | LiY | NaY | KY | CsY | TlY |
| Myrcene (MRC) | 1.12 | 1.16 | 1.30 | 1.39 | 1.45 |
| Norbornadiene (NBD) | 0.97 | 1.02 | 1.14 | 1.26 | 1.30 |
| Dicyclopentadiene (DCP) | 1.35 | 1.47 | 1.96 | 2.38 | 2.56 |
| 5,5-Diphenyl-1,3-cyclohexadiene (DCH) | – | 1.28 | – | 1.41 | 1.50 |

Table 2
[2 + 2]-Photocycloaddition products of dienes MRC, NBD and DCP

| Reactant | Medium | Solution | | Slurry | |
|---|---|---|---|---|---|
| | | *t* (h) | Yield (%) | *t* (h) | Yield (%) |
| Myrcene[a] (MRC) | β-Acetonaphtone | 8 | 71 | | |
| | TlY | | | 8 | 92 |
| | CsY | | | | 85 |
| | KY | | | | 40 |
| | NaY, LiY | | | | <5 |
| Norbornadiene[b] (NBD) | Acetophenone | 3 | 72 | | |
| | TlY | | | 3 | 90 |
| | CsY | | | | 82 |
| | KY | | | | 83 |
| | NaY, LiY | | | | <5 |
| Dicyclopentadiene[b] (DCP) | Acetone | 10 | 33 | | |
| | TlY | | | 10 | 17 |
| | CY | | | | 13 |
| | KY | | | | 8 |
| | NaY, LiY | | | | <1 |

[a] Irradiation was carried out in pyrex vessel.
[b] Irradiation was carried out in quartz vessel.

ane for several times. The product was extracted by stirring the solid in 40 ml of dry ether for 15 h. Mass balance in all cases was ca.85%. Identification of products were made by GC (HP, 6890N, equipped with FID detector and HP-5 capillary column) analyses and comparison of retention times with those of authentic samples which were prepared in the presence of proper sensitizers (solution photolysis). The concentration of products was determined by using tetralin as internal standard.

## 3. Results and discussion

Following our previously reported oxa-di-π-methane rearrangement of bicyclic β,γ-unsaturated ketones [20], and our interest in utilizing the useful solid systems for achieving selective transformations in thermal and photochemical reactions [21], we are pleased to report the observation of photosensitization of the aforementioned dienes induced by the heavy atom cations of K$^+$, Cs$^+$ and Tl$^+$ within the microreactor of zeolite Y.

Results of [2 + 2]-photocycloaddition and di-π-methane rearrangement of dienes slurries in hexane (Scheme 1) within zeolite Y exchanged with Li$^+$, Na$^+$, Cs$^+$ and Tl$^+$ cations are presented in Tables 2 and 3. Inspection of the results exhibited in Tables 2 and 3 reveals that compared to the solution photolyses sensitized by organic sensitizers, the slurries of MRC, NBD and DCH have led to the identical products in higher yields in the presence of Cs$^+$ and Tl$^+$ cations. Particularly significant is DCH which has yielded a mixture of bicyclic products with improved diastereoselectivity in the presence of CsY and TlY (Table 3 and Scheme 1). It should be emphasized that the diastereoselectivity is similar to solution photolysis although with 4–5% improvement. From consideration of models, Swenton et al. have concluded that the bicyclic isomers arise from ring closure of a diradical intermediate from which the major isomer is produced predominantly due to steric factors [8]. A rationale preferable to the author for predomination of *trans*-5,6-bicyclic isomer may be attributed to the allowed process in the excited state versus the forbidden reaction to yield the minor *trans*-4,5-bicyclic isomer [8]. That similar trend is followed in slurry photolysis in this work with enhanced diastereoselectivity is not surprising since the constrained space of zeolite cavities directs the reaction toward the formation of dominant product with the least steric hindrance. Compared to Pitchumani's work which obtained 100% of triplet product with MRC in the presence of acetylnaphthalene, acetophenone and benzophenone sensitizers anchored on cationic and anionic clays in 20 h [15], our system which affords the same product with the same selectivity of 100% toward the formation of triplet product in 8 h seems remarkable. Such fascinating results have definitely arisen from the decreased mobility of diene within the zeolite, which in turn increases the energy transfer between substrate and heavy atom cation. Moreover, the main advantage of our system is the elimination of organic sensitizer, which is not only an important economical matter especially in industrial applications, but also is in harmony with green chemistry criteria in simplifying the reaction conditions. That DCP has

Table 3
Di-π-methane rearrangement product distribution of diene DCH[a]

| Medium | Solution | | Ratio | Slurry | | Ratio |
|---|---|---|---|---|---|---|
| | *t* (h) | Yield (%) | | *t* (h) | Yield (%) | |
| β-Acetonaphtone | 2 | 73 | 94:6 | | | |
| TlY | | | | 2 | 83 | 99:1 |
| CsY | | | | | 76 | 98:2 |
| NaY | | | | | <5 | |

[a] Irradiation was carried out in pyrex vessel.

afforded the corresponding cycloadduct with the minimum yield (see Table 2) is not surprising since loading level shows its lesser inclusion tendency within the cavities in comparison with other dienes (see Table 1). Another interesting result obtained in this study relates to NBD, which gives quadricyclene in 90% in the presence of TlY. As seen in Table 2, this reaction has produced quadricyclene more efficiently than the similar reaction sensitized by acetophenone. Moreover, the product is not contaminated with acetophenone, a substance, which its separation from product mixture is time consuming. With the exception of norbornadiene which shows similar activity in KY and CsY, the trend observed in the variation of the triplet yields with increasing masses, i.e. $Li^+ \sim Na^+ < K^+ < Cs^+ < Tl^+$ is consistent with the expected spin–orbit coupling induced by heavy atom [2].

Finally, as mentioned earlier, directing the chemical reactions from homogeneous states to heterogeneous media provides different advantages such as constrained space to molecules to affect the reaction diastereoselectivities and achievement of some desired properties like triplet energy transfer. Moreover, the solid support can be purified and reused. Perhaps, easier work-up in order to save time and chemicals and obtaining more pure products are of the more important gains.

## 4. Conclusion

In conclusion, obtaining such wonderful results provide a powerful evidence that zeolite–guest complex system containing an active atom in the vicinity of the molecule is a remarkable microreactor. This simple system provides a constrained space for the reaction to induce physical effect like heavy atom perturbation or chemical consequences to achieve diastereoselective synthesis, respectively.

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