Remarkable Product Selectivity During Photo-Fries and Photo-Claisen Rearrangements within Zeolites

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Shape selectivity consists in often subtle matching of size and shape of reactants, transition states, and/or products with the size and shape of pores, cages, and pore volumes of the intracrystalline zeolite phase.[1] We provide below examples of how this feature can be a useful tool in controlling product distribution in a photochemical reaction.[2] The reactions we have chosen to investigate are photo-Fries rearrangement of phenyl acetate and phenyl benzoate and photo-Claisen rearrangement of allyl phenyl ether (Scheme 1). We have chosen these reactions for the following reasons: (a) These reactions have been extensively investigated in isotropic solution media.[3−5] (b) Attempts have been made earlier to control product distribution within various ordered media with varied success.[6] (c) The products of the Fries reaction, hydroxyacetophenones and hydroxybenzophenones, are used in the manufacture of pharmaceuticals. For example, the para selective rearrangement of phenyl acetate is a key step in the Hoechst−Celanese process for the manufacture of 4-acetaminophenol.[7] (d) Fries rearrangements of aryl esters are often carried out on an industrial scale with conventional catalysts such as AlCl$_3$ and mineral acids like HF and H$_2$SO$_4$. In such reactions, selectivity is poor and the catalyst used generates a large amount of toxic waste products. A combination of zeolite as a medium and light as the reagent offer a new approach towards "clean chemistry". (e) The goal of achieving selectively a single isomer within zeolites by thermal Fries reaction has not been realized.[8]

The internal structure of the two types of zeolites (faujasites X and Y and pentasils ZSM-5 and ZSM-11) that we have utilized as media in this study vary in size and shape. Differences in product selectivity obtained in this study between faujasites and pentasils as the media reveal a powerful message.

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(2) As far as we know, there is only one example of shape selectivity in photochemical reactions known in the literature and this is provided by Turro and co-workers: (a) Turro, N. J.; Lei, X.; Cheng, C. C.; Abrams, L.; Corbin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 5824. (b) Turro, N. J. *Pure Appl. Chem.* **1986**, *58*, 1219. (c) Turro, N. J.; Cheng, C. C.; Abrams, L.; Corbin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 2449.

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Scheme 1
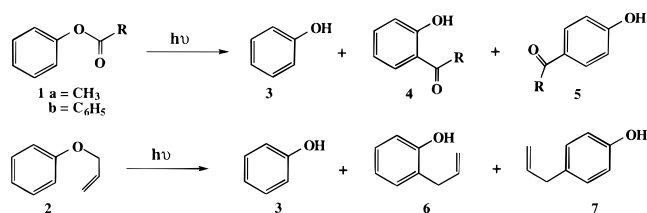
In order to obtain a high product selectivity, one should utilize a reaction cavity that is large enough to respond to the shape changes that occur along the reaction coordinate but at the same time hard and small enough to provide relatively different extents of restriction on various reaction pathways available to the reactive intermediates.[9]

The experimental procedure consisted of stirring known amounts of **1** or **2** and activated zeolite (X or Y) in hexane, followed by filtering, washing with excess hexane, and drying under reduced pressure (10^{-4} Torr). These dried samples were irradiated (∼2 h) in hexane as a slurry. For inclusion within ZSM-5 and ZSM-11, 2,2,4-trimethylpentane was used as the solvent and the irradiations were conducted as a slurry in either hexane, 2,2,4-trimethylpentane, or water. Following irradiation, the products were extracted with ether and analyzed by GC. Mass balances were excellent (>90%). Spectral data for the products matched well with the reported data,[10] and results are presented in Table 1.[11]

One of the most remarkable observations is that in all three cases the product distribution is altered within zeolites from that in isotropic solvents. Furthermore, while in solution, nearly a 1:1 mixture of ortho and para isomers (Scheme 1) is the norm. Within zeolites, one is able to direct the photoreaction selectively toward either the ortho or the para products by conducting the reaction either within faujasites or pentasils, respectively (Table 1). Both photo-Fries and photo-Claisen rearrangements proceed via a similar mechanism (Scheme 2).[4,5] Excitation to the excited singlet state results in fragmentation of the phenyl esters and allyl phenyl ether. Cage escape, recombination, and hydrogen migration results in both ortho and para products. While in solution, the ratio of the ortho and the para products is determined by the electron densities at the ortho and para positions in the phenoxy radical; clearly, this is not the controlling factor within zeolites. Phenol could form either by an in-cage or out-of-cage process. We are unable to obtain any evidence in favor of ketene, which would be an expected product during the incage process.

Photo-Fries reaction of phenyl acetate and phenyl benzoate is highly selective within X and Y zeolites. While in Li- and NaX and -Y zeolites a small percentage (<10%) of the para isomer is formed, within KX and KY zeolites the ortho isomer is the exclusive product. Phenol yield reported in the table is a sum of thermal (dark) and photochemical reactions. Only for phenyl acetate, the thermal reaction contributed significantly.[12] The ortho selectivity is truly remarkable. The above selectivity is not the result of shape exclusion since both the

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(10) Products of photo-Fries reaction are all commercially available. Spectral data of photoproducts were compared with the authentic commercial samples. Products **6** and **7** are not commercially available but are known in the literature. Spectral data were compared with literature reports.[5]

(11) In addition to hexane slurry, solid zeolites were also photolyzed. Conversion obtained by the latter technique was significantly low. Reflection as well as nonuniformity of absorption by solid samples contributed to the low conversion.

(12) Contribution due to thermal reaction was monitored by analyzing an identical sample kept in the dark for the same duration as the photolyzed sample. The dark reaction was significant only for phenyl acetate and the percentage contribution increased with the cation size (Cs$^+$ > Rb$^+$ > K$^+$).

Communications to the Editor

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Table 1. Product Distribution upon Photolysis of Phenyl Esters and Allyl Phenyl Ether

	phenyl acetate (**1a**)[a,b]			allyl phenyl ether (**2**)[a,b]			phenyl benzoate (**1b**)[a−c]		
	3	**4a**	**5a**	**3**	**6**	**7**	**3**	**4b**	**5b**
hexane	20	53	27	48	21	31	12	49	37
methanol	17	44	39	16	42	42	6	49	43
benzene	15	54	31				6	53	38
LiY−hexane[d]	7[e]	87	6	6	76	18	1	92	7
NaY−hexane	5	91	4	3	79	18	1	93	6
KY−hexane	17	83		4	78	18	2	98	
LiX−hexane[d]	15[e]	77	8	4	81	15	1	96	3
NaX−hexane	21	79		6	78	14	5	93	2
KX−hexane	27	73		3	83	14	7	93	
Na ZSM-5−hexane[f]	27	35	38	40	31	29	10	34	27
Na ZSM-5−TMP[g,h]	32	5	63	5	5	90	17	38	24
Na ZSM-5−water	32	6	62	2	7	91	40	18	28
Na ZSM-11−TMP[g,h]	18	8	74	7	20	73	8	48	29
Na ZSM-11−water	18	12	7[j]		27	73			

[a] Irradiations were conducted to about 30% conversion. This amount of conversion was reached in 1 h for phenyl benzoate, 2 h for phenyl acetate, and 4 h for allyl phenyl ether. Ratios of products were independent of the conversion in the range of 15 to 90%. All yields presented in the table are an average of at least five independent runs with an error limit on yields of ±2%. [b] Occupancy level was kept at ~1 molecule per supercage for X and Y zeolites. Loading level for ZSM-5 was 5 mg of substrate to 300 mg of ZSM. [c] Difference between the reported yield and the total theoretical yield (100%) is due to formation of benzoic acid and benzaldehyde. [d] Ortho selectivity was also observed when Mg-, Ca-, Sr-, and BaX or -Y zeolites were used. Results were similar to the ones presented for alkaline metal cation exchanged X and Y zeolites. [e] Phenol yield presented here is a sum of blank thermal reaction and photochemical reaction. Control experiments showed that blank reaction was higher in **1a** than in **1b**. See ref 13 for details. [f] In hexane, the molecules remained either on the external surface or in the solution. Product distribution obtained is close to that in hexane in the absence of zeolite. Under such conditions, contribution due to thermal reaction is very small (<5%). When the reaction is conducted with TMP as the solvent, phenyl acetate remained within the zeolite. Under such conditions thermal reaction was significant (~26%). [g] Selectivity did not depend on the Si/Al ratio (24: 400) of ZSM-5 and ZSM-11 used. [h] TMP refers to 2,2,4-trimethylpentane.

Scheme 2
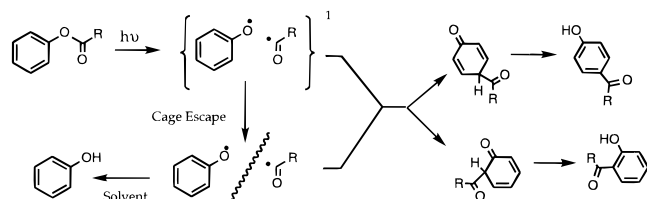
ortho and the para isomers (**4** and **5**) fit well within the supercage. This is indicated by the fact that when these isomers were included independently, they were readily incorporated within X and Y zeolites. Also, they can be easily extracted from the zeolite. Selectivity, we believe, results from the restriction imposed on the mobility of the phenoxy and the acyl (benzoyl) fragments by the supercage framework and cations. Several features contribute to the restriction. The cage free volume plays an important role, as evident from the increased selectivity with the increase in size of the cation.[13] It is important to note that when cations larger than K$^+$ were used, the reaction was extremely slow. This complication resulted from the heavy cation induced intersystem crossing from the reactive excited singlet to the unreactive triplet.[14,15]

In addition to the cage free volume, an interaction between the cation and the two reactive fragments must be contributing to the selectivity.[16] This becomes clear when one compares the results of phenyl acetate and allyl phenyl ether. In the latter compound, a small percentage of the para isomer (~15%) always accompanied the major ortho isomer. While the size and shape of acyl and allyl radicals are expected to be similar, the strength of interaction between the cations and these two fragments is expected to differ; the former is expected to bind more strongly than the latter.[17] Such a difference, we believe, is translated into an increased yield of the para isomer for phenyl allyl ether.

The shape and size of pentasils are such that only the para isomers (**5** and **7**, Scheme 1) fit within the channels of these zeolites. Indeed, under conditions in which the para isomers **5** and **7** were readily incorporated within ZSM-5 and ZSM-11, the ortho isomers **4** and **6** remained in the solvent (2,2,4-trimethylpentane) portion. On the basis of the above shape selectivity, one would have predicted selective formation of the para isomers within ZSM zeolites. However, no selectivity was achieved when the photolysis of **1a** and **2** included within ZSM-5 and ZSM-11 was conducted as a hexane slurry. What was surprising was the fact that the unexpected ortho isomer was obtained in significant yield. An insight into the lack of selectivity was gained when the GC analysis of the hexane layer prior to the photolysis was performed. This analysis revealed that hexane displaced the reactants **1a** and **2**, from the interior of ZSM. Under these conditions, most of the reactants were present in the hexane solvent and not inside the zeolite. Absence of selectivity is the result of reaction occurring in the isotropic hexane medium. We reasoned that selectivity should be possible if we can keep the reactants within the channels of ZSM zeolites. This was achieved by using solvents which will not displace the included **1a** and **2** from the interior of ZSM. Since the internal structure of ZSM is highly hydrophobic, water is not expected to fill the channels of ZSM. Similarly, 2,2,4-trimethylpentane solvent molecules, being too large, are not expected to enter the channels of ZSM. We visualized that these solvent molecules would serve as lids on the channels and keep both the reactants and the reactive fragments within the channels of ZSM. Thus, the fragments would be forced to recombine in such a way that the product that fits within the narrow channels of ZSM would predominate. Indeed, when photolysis was conducted in these solvents a clear preference for the para isomer resulted (Table 1). A small amount of the ortho isomer that is formed, we believe, comes from reactions that occur in the solvent portion. This is supported by the results obtained with **1b**. This molecule, being too large to enter into the internal structure of ZSM, is expected to remain on the external surface. Under such conditions, no selectivity is expected and indeed we did not obtain any.

We have shown that with the proper choice of medium one can achieve very high selectivity on photochemical reactions. Detailed mechanistic studies of the above rearrangements within zeolites are underway.

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