

Photolysis of Dibenzyl Ketones Adsorbed on Zeolite Molecular Sieves. Correlation of Observed Cage Effects with Carbonyl ^{13}C Enrichment Efficiencies

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Abstract: The photolysis of 3-(4-methylphenyl)-1-phenyl-2-propanone (**1**) (4-MeDBK) and 1,3-diphenyl-2-propanone- $^{13}\text{C}_2$ (**2'**) (DBK- ^{13}C) has been carried out on several commonly available zeolites. Dramatic changes in product distributions for 4-MeDBK (**1**) photolysis were observed on the several zeolites. Percent cage effects were calculated and rationalized in terms of molecular mobility of photogenerated benzyl radicals in the void volumes of zeolites. Percent cage effects correlate well with ^{13}C -enrichment efficiencies for DBK- ^{13}C photolysis on these zeolites and, with the yield of a DBK isomer (PMAP), the para-coupling product of the primary geminate radical pair (Figure 3) in the photolysis of DBK- ^{13}C .

The past several years have witnessed an explosive increase in photochemical studies in ordered systems.¹⁻⁷ Although photochemical reactions have been performed in micelles, microemulsions, liquid crystals, in the solid state, and on silica gel,¹⁻⁷ only a small number of studies have dealt with photochemistry on zeolites, the majority of these being concerned primarily with the water-splitting process.⁸⁻¹² Recently, however, reports on the use of zeolites for organic photophysical and photochemical studies have appeared.¹³⁻¹⁵

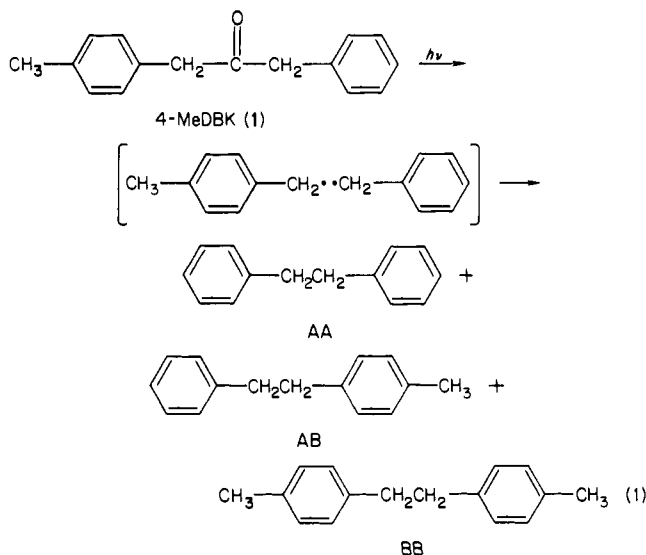
Zeolites are crystalline aluminosilicates of usually well-defined structure.¹⁶ Within the zeolite framework are a system of channels and/or supercages of varying dimensions (2-13 Å).¹⁶ The exact nature of these channels or supercages depends on the identity of the particular zeolite. Of importance to the organic chemist is that channel or pore diameters of ≥ 6 Å can allow the adsorption of benzene and other molecules of similar molecular size.¹⁶ Thus, the possibility that the internal spaces (or void volumes) of zeolites can exert topological control on organic photochemical reactions is an area that warrants investigation, since it is well-known that zeolites display shape-selective catalytic and absorptive properties in industrial chemical processes.^{17,18}

We report herein our study of the photochemical behavior of dibenzyl ketones adsorbed in a number of commonly available zeolites. The results indicate that significant changes in reaction product ratios can be effected by carrying out photochemical reactions in zeolites, thus opening the way for employing these substances as a medium for organic photochemical studies.

Results

Photolysis of 3-(4-Methylphenyl)-1-phenyl-2-propanone (1). The photolysis of 3-(4-methylphenyl)-1-phenylpropanone (**1**) (4-methyldibenzyl ketone; 4-MeDBK) and related compounds (eq 1) has been extensively employed as a probe of molecular mobility in micellar solution¹⁹ and on silica surfaces.²⁰ The photochemistry of 4-MeDBK (**1**) is characterized by a simple process:^{19,20} efficient decarbonylation to give a triplet radical pair, which can recombine in a number of ways to give the observed coupling products: AA, AB, and BB. To test whether the voids in zeolites can restrict the mobility of radical pairs produced by photolysis of 4-MeDBK (**1**), we have examined the product ratio of AA:AB:BB after photolysis of 4-MeDBK (**1**) on a number of readily obtainable zeolites.

The zeolites employed and their characteristic channel and/or cavity (supercage) diameters and other pertinent information are tabulated in Table I. These zeolites were obtained from Union Carbide and were activated at ~ 200 °C for 10 h prior to use. 4-MeDBK was deposited on these zeolites by mixing a solution of 4-MeDBK in CH_2Cl_2 with a preweighed amount of activated zeolite at room temperature. The CH_2Cl_2 was then removed under



vacuum, until a pressure of 10^{-4} mmHg was reached. The material was then transferred to a Pyrex vessel equipped with a high-

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Table I. Zeolites and Their Characteristic Parameters^a

zeolite ^b	channel/cavity (supercage) dimensions	nature of channel/cavity system	Si/Al ratio	kinetic diameter for adsorption, ^c Å
Na ⁺ -A (4A)	main cavity ~ 11 Å channel opening ~ 4 Å	3-Dimensional channel system with cavities (supercages)	0.7-1.2	4
Na ⁺ -X (13X)	main cavity ~ 13 Å channel opening ~ 8 Å	3-D channel system with cavities	1-1.5	8
Na ⁺ -Y (LZ-Y52)	main cavity ~ 13 Å channel opening ~ 8 Å	3-D channel system with cavities	1.5-3	8
Na ⁺ -Mordenite (LZ-M5) (large port)	main channels ~ 7 Å side channels ~ 3 × 6 Å	2-D channel system; pertinent unidimensional cavities	4.5-5	7
Silicalite (S-115)	main channels ~ 5.2 × 5.7 Å side channels ~ 5.4 Å	3-D channel system; no cavities	>99% Si	6

^a Tabulated information obtained from ref 16 and technical data sheets from Union Carbide Corp. ^b Designation in brackets are Union Carbide product codes. All zeolites are sodium exchanged forms, except for Silicalite, which has no ionic charges (>99% Si). For its synthesis and structural properties, see: Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Patton, J. P.; Kirchner, R. M.; Smith, J. V. *Nature (London)* **1978**, *271*, 512. ^c At room temperature. Indicates approximately the largest sized molecule that can be accommodated in the voids of the zeolite. Benzene has a kinetic diameter of 5.85 Å (see ref 16).

Table II. Yield of 1-(4'-Methylphenyl)acetophenone (PMAP) on Zeolites

zeolite	% PMAP ^a
Silicalite ^b	20 ± 5
Na ⁺ -X	2 ± 2
Na ⁺ -Mordenite	1 ± 0.5
Na ⁺ -Y	0 ± 0.3
Na ⁺ -A	0 ± 0.3

^a Absolute yields normalized to 100% conversion at 2% w/w loading of DBK-¹³C, assuming linear dependence of PMAP yield on conversion. ^b Maximum conversion is 25% on this zeolite. All others are >80%.

vacuum stopcock. After evacuation to 10⁻⁴-10⁻⁵ mmHg, the vessel was sealed and the sample photolyzed with a Hanovia 450-W Hg medium-pressure lamp for 15 min to ~2 h, depending on the zeolite. The photolysis vessel was tumbled continuously during the irradiation to ensure homogeneous photolysis of the sample.

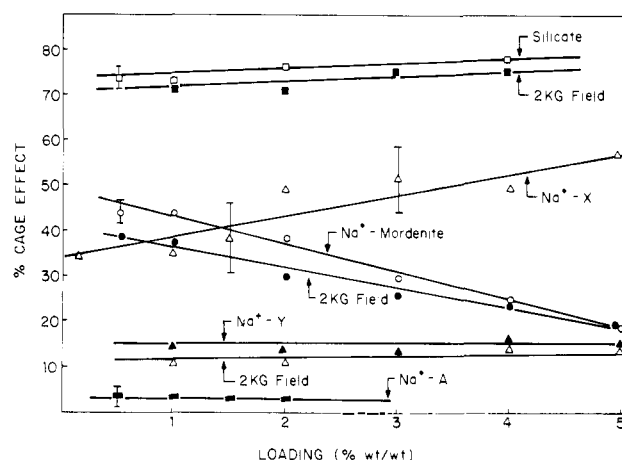
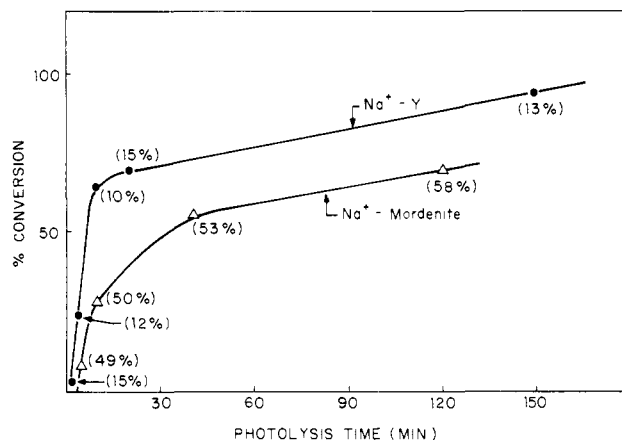
After photolysis, CH₂Cl₂ was added and the slurry sonicated prior to filtering. In this way, >80% of the organic material could be extracted out of the zeolite (with the exception of Silicalite, which gave up only ~20% of the organics). A continuous extraction process had to be employed for Silicalite, vide infra. Continuous extraction on a Soxhlet apparatus (CH₂Cl₂) resulted in >90% material balance in all the zeolites employed in this study. Control experiments demonstrated that thermal decomposition of 4-MeDBK on these zeolites was small (less than 5% give unidentified lower molecular weight products).

Since excellent mass balances are obtained by using the Soxhlet extraction, the molar ratio of products (AA, AB, and BB) may be employed to determine the % cage effect (% CE),¹⁹ i.e., the % of geminate recombinations of radical pairs produced by photolysis of 4-MeDBK via eq 2.

$$\% \text{ cage effect (\% CE)} = \frac{AB - (AA + BB)}{AA + AB + BB} \quad (2)$$

The % CE's for the photolysis of 4-MeDBK as a function of loading on these zeolites are summarized in Figure 1. The % CE's were calculated after >80% conversion for all the zeolites except Na⁺-Mordenite and Silicalite. However, additional experiments have shown (Figure 2) that % CE's are independent of conversion of 4-MeDBK photolysis on these zeolites. Additionally, it was found that % CE was not sensitive to the amount extracted from the zeolite during workup. Thus, a single CH₂Cl₂ extraction gave the same % CE as a continuous overnight Soxhlet CH₂Cl₂ extraction, even though the latter method gave better material balance.

Zeolites Na⁺-X, Na⁺-Y, and Na⁺-Mordenite are known to be capable of adsorbing organic molecules whose sizes are of the

**Figure 1.** % cage effect as a function of loading for zeolites.**Figure 2.** % cage effect as a function of conversion for Na⁺-Y and Na⁺-Mordenite. The values in parentheses are the cage effects measured at various photolysis times.

order of substituted benzenes.^{16,17} Therefore, it is reasonable to assume that DBK or substituted DBK's can be accommodated in the channels or cavities of these zeolites. Silicalite, however, is a relatively new zeolite (see footnote *b* in Table I) with a kinetic pore diameter of ~6 Å. Because of the possibility that DBK (or substituted DBK's) cannot be adsorbed into Silicalite, even though the benzene ring has a kinetic diameter of 5.85 Å,¹⁶ we have carried out adsorption isotherm studies with Silicalite and Na⁺-A. The experiments were carried out as follows. A preweighed amount of DBK dissolved in 2,2,4-trimethylpentane (kinetic diameter >6.2 Å^{14,16}) was added to the zeolite sample and stirred at room temperature (25 ± 3 °C) for 15 h. After filtering and washing the zeolite filtrate with 2,2,4-trimethylpentane, the filtrate was analyzed for unadsorbed DBK via GLC. In this way, the

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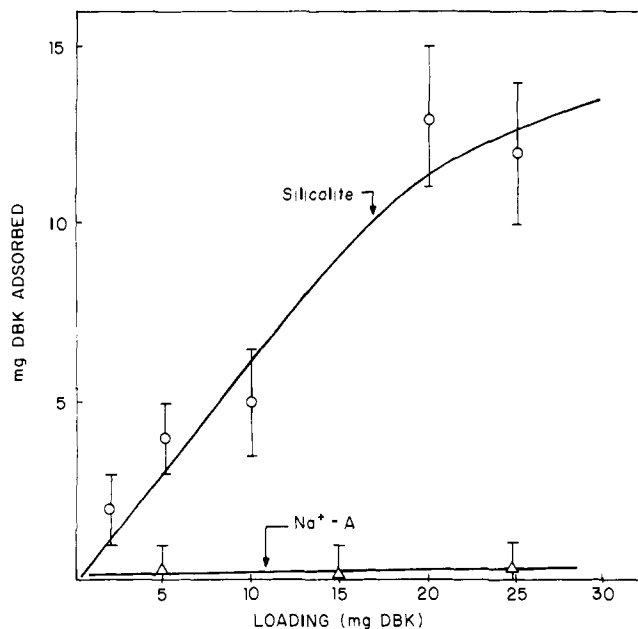
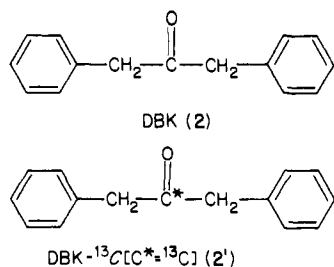


Figure 3. Adsorption isotherms for Silicalite and $\text{Na}^+\text{-A}$ at 25 ± 3 °C. The solvent was 2,2,4-trimethylpentane (kinetic diameter >6.2 Å). Amount of loading is weight of DBK dissolved in 2,2,4-trimethylpentane and exposed to zeolite for 15 h with rigorous stirring.

amount of DBK adsorbed from the solution was calculated. The results are shown in Figure 3 and clearly demonstrate that significant amounts (up to 14% w/w) of DBK can be accommodated in the Silicalite channel system. That these results can be rationalized in terms of an external surface adsorption phenomenon can be discarded, since the adsorption isotherm for $\text{Na}^+\text{-A}$ (whose 4-Å kinetic diameter precludes DBK absorption) shows essentially no adsorption of DBK under the same conditions. Any adsorption of DBK by this zeolite can only occur on the external surface. These results, of course, do not provide any information on how the DBK molecule is adsorbed on Silicalite. An interesting question one can pose is whether only one or both of the benzene rings is adsorbed into the channel system. These and related questions are topics for future study.

Photolysis of 4-MeDBK under a 2-kG magnetic field from a permanent magnet placed in the vicinity of the photolysis apparatus (2 kG is the effective field strength experienced by the sample) resulted in only a small decrease (3–5%) in observed % CE, except for $\text{Na}^+\text{-Mordenite}$, where a large 15% decrease in % CE is observed at 1% loading. Moreover, $\text{Na}^+\text{-Mordenite}$ was the only zeolite which displayed a decrease in % CE with loading in the 1–5% range studied in this work.

Photolysis of 1,3-Diphenyl-2-propanone (2). The photolysis of 1,3-diphenyl-2-propanone (2) (dibenzyl ketone; DBK) has been



extensively studied in our laboratories^{21–24} as a method for sep-

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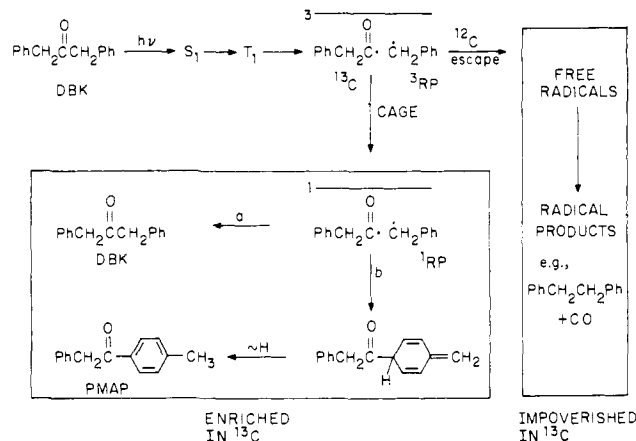


Figure 4. Working mechanism for the photolysis of $\text{DBK-}^{13}\text{C}$ and the ^{13}C -enrichment process. ^3RP = triplet radical pair; ^1RP = singlet radical pair; a = σ -bond formation to give back starting material; b = para coupling to give PMAP isomer.

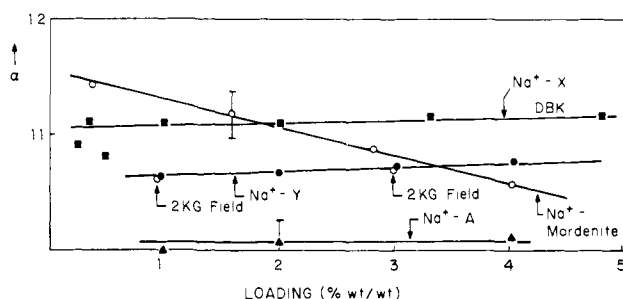
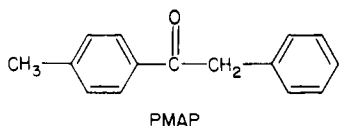


Figure 5. ^{13}C -Enrichment efficiencies, as measured by α , on zeolites as a function of loading.

arating ^{13}C from ^{12}C . The principle of the method^{21–24} involves taking advantage of the difference in hyperfine-induced (hfi) intersystem crossing rates from the triplet radical pair intermediate to a singlet radical pair between ^{13}C ($I = 1/2$; a magnetic nucleus) containing molecules and those molecules which contain only ^{12}C ($I = 0$; a nonmagnetic nucleus) (Figure 4). Those triplet radical pairs possessing a ^{13}C nucleus will have larger intersystem crossing rates (k_{isc}) and, hence, will produce the singlet radical pair more efficiently, which can then undergo σ -bond formation and a possible return to DBK starting material. Under high conversion of the photoreaction, the recovered DBK will be enriched in ^{13}C content, essentially only at the acyl carbon if this carbon is partially enriched in the starting material. Previous work from these laboratories^{21–24} has also shown that photolysis of ^{13}C -enriched DBK in homogeneous solution results only in very small enrichment efficiencies, while photolysis in micellar media results in greatly enhanced efficiencies. The conclusion from these studies was that a "supercage" media or environment was required to effect ^{13}C -enrichment, in which the photogenerated geminate triplet radical pair can have an "intimate" spatial relationship for a finite time interval, so that the mechanism of hfi intersystem crossing can operate to "separate" ^{13}C -containing from ^{12}C -containing molecules. Since photolysis of 4-MeDBK (1) on zeolites can give very high % CE's (e.g., as in Silicalite and $\text{Na}^+\text{-X}$), it seemed reasonable to assume that these zeolites should be suitable "supercage" environments for observation of ^{13}C -enrichment in DBK photolysis.

^{13}C -Enrichment studies were performed with $\text{DBK-}^{13}\text{C}$ (2') in which the molecule was enriched at the carbonyl (29.8% ^{13}C) carbon. Experimental conditions were identical with those employed for 4-MeDBK. Photolysis of $\text{DBK-}^{13}\text{C}$ on several zeolites resulted in a near-quantitative yield of diphenylethane (AA) and a smaller amount of the isomer of DBK, 1-(4-methylphenyl)acetophenone (PMAP).

The formation of PMAP arises via para coupling of the initially formed geminate radical pair (Figure 4).^{21,22} The highest yield of PMAP was observed in Silicalite (20%); no PMAP was ob-



served in $\text{Na}^+\text{-Y}$ and $\text{Na}^+\text{-A}$. Interestingly, the rank in amount of PMAP yield for these zeolites are in the same order as the % CE's for 4-MeDBK photolysis observed in Figure 1 (at 2% loading), although these relative yields may be related to features other than void characteristics, i.e., Lewis acid sites.

^{13}C -enrichment efficiencies, as measured by the parameter α , the single-stage isotope separation factor,²¹⁻²⁵ were found to be in the range 1.0-1.2. The rank in α -values (i.e., ^{13}C -enrichment efficiencies) appears to follow roughly the order of observed % CE's (Figure 1) at fixed loading. Experimental difficulties prevented the achievement of high conversions for the photolysis of DBK on Silicalite. As a result, the calculation of α (whose accuracy requires high conversion) on Silicalite were not considered reliable to compare with the other data. The accurate determination of α requires an accurate determination of the percent conversion of DBK in the photolysis. Because of difficulties in extraction of DBK from Silicalite, the scatter in computed α values was too large to allow meaningful comparison with the other data.

^{13}C -Enrichment experiments at 2-kG applied field were also carried out at selected % w/w loadings, but they failed to give noticeable differences in α -values (within ± 0.04 of the α -values at zero field). This is perhaps best explained by noting that α -values are generally much less sensitive than % CE's to external fields. Since the change in % CE with applied field is not exceptionally large, the change in α is probably much less, and in these experiments was undetectable.

Discussion

The results of this study have clearly shown that interesting effects can be obtained by carrying out photochemical reactions on zeolites. The rank in observed % CE's: Silicalite > $\text{Na}^+\text{-X}$ > $\text{Na}^+\text{-Mordenite}$ > $\text{Na}^+\text{-Y}$ > $\text{Na}^+\text{-A}$ (at 2% w/w) can be interpreted as reflecting the relative degree of molecular mobility of the photogenerated benzyl radicals on the zeolite. That is, benzyl radicals are *least able* to escape from the geminate radical pair on Silicalite, while on the other hand, on $\text{Na}^+\text{-A}$, they escape completely (vide infra) to give CE $\sim 0\%$, as observed in homogeneous solution.¹⁹ These results are completely in accord with the structure of these two zeolites. Silicalite is a hydrophobic and organophilic zeolite of kinetic channel (pore) diameter of $\sim 6 \text{ \AA}$. Thus, it is just sufficiently large to adsorb a benzene-type molecule.¹⁴ It is, therefore, reasonable to assume that benzene-type molecules undergo slower diffusional motion once adsorbed into Silicalite. Hence, one would expect more efficient geminate pair recombination of the photogenerated benzyl radicals on photolysis, to give a high % CE, since these radicals are more constrained from freely moving in the channel system. Casal and Scaiano¹⁴ have observed greatly enhanced phosphorescence lifetime of β -propiophenone when adsorbed into Silicalite. This was interpreted as being due to the inability of the β -phenyl ring to quench the benzoyl excited state as a result of constraints imposed by the Silicalite channel system on the molecule. For $\text{Na}^+\text{-A}$, however, benzene-type molecules cannot be adsorbed.¹⁶ So, at best, one would expect % CE to reflect those obtained in neat 4-MeDBK samples. Indeed, we find CE = $\sim 0\%$ for this zeolite, reflecting efficient escape of the benzyl radicals from the initial cage.

Zeolites $\text{Na}^+\text{-X}$ and $\text{Na}^+\text{-Y}$ gave very different % CE's even though these two zeolites are structurally quite similar (Table I). $\text{Na}^+\text{-X}$ gave the higher CE of $\sim 40\%$ compared to $\sim 15\%$ for $\text{Na}^+\text{-Y}$. Both of these two zeolites have kinetic pore diameters of 8 \AA and a supercage (cavity) diameter of 13 \AA . Since the Si/Al ratio for $\text{Na}^+\text{-X}$ is significantly lower than for $\text{Na}^+\text{-Y}$, $\text{Na}^+\text{-X}$ must necessarily possess a greater number of $\text{Na}^+\text{Al}(\text{OZ})_4^-$ species (where Z represents the zeolite framework) in the zeolite framework. The difference in electrostatic effects is probably at

least partially responsible for the observed difference in % CE's. Although the exact effect of increased electrostatic charges and/or more Lewis base sites ($\text{Al}(\text{OZ})_4^-$) on benzyl radical mobility is not understood, the mobility of these radicals by Lewis acid/base interactions or some other type of weak bonding. However, additional studies are warranted in order that these effects can be fully delineated.

The % CE decreases with increasing loading of 4-MeDBK on $\text{Na}^+\text{-Mordenite}$. This zeolite has essentially only one-dimensional channels capable of adsorption of 4-MeDBK, since the side channels within the framework are small ($3 \times 6 \text{ \AA}$). Because of this, the effective void volume is lower than for the rest of the zeolites,¹⁶ which have 3-dimensional frameworks for adsorption. The decrease in % CE with loading for this zeolite is, therefore, best explained by an "overloading effect". That is, as the % loading increases, a proportionately lesser amount of it is actually adsorbed into the void volume of the zeolite, thus resulting in a decrease of % CE. At the limit of infinite % loading, the behavior of $\text{Na}^+\text{-Mordenite}$ should duplicate that of $\text{Na}^+\text{-A}$.

The rank of ^{13}C -enrichment efficiencies is roughly in the order: $\text{Na}^+\text{-X} \sim \text{Na}^+\text{-Mordenite} > \text{Na}^+\text{-Y} > \text{Na}^+\text{-A}$ at 2% loading. This order of ranking is the same as that observed for % CE's and % PMAP yields on the same zeolites. Although measurement of % CE's is perhaps a more direct probe of molecular mobility within the zeolite framework, both the yield of PMAP and efficiency of ^{13}C -enrichment depend critically on the lifetime of the initially formed geminate radical pair (Figure 4). If a zeolite greatly restricts movement of benzyl radicals, it would follow that movement of the radicals away from the initially formed geminate radical pair (Figure 4) would be restricted as well. Since diffusion away from each other in the geminate radical pair is a contributing factor in decreasing the effective lifetime of the radical pair (in addition to decarbonylation of the phenylacetyl radical), prevention or slowing down of this will necessarily result in an increase in geminate radical lifetime. The opportunity for para coupling of these two radicals (to give PMAP) will thus be enhanced, as will be the opportunity of the hfi intersystem crossing mechanism to occur, which manifests itself in higher α -values.

In summary, we have shown that zeolites can be effectively used as a medium for photochemical reactions of large organic molecules. Several commonly available zeolites were found to give dramatic differences in observed product ratios for 4-MeDBK photolysis, and these results have been interpreted as due to differences in molecular mobility of photogenerated species in these zeolites. The effect of zeolite structure on structurally more complicated photoreactions are under investigation in this laboratory.

Experimental Section

Materials. Zeolites were Linde molecular sieves (powder form; $< 10 \mu$) and were provided by Union Carbide Corp. (Tarrytown, NY). All the zeolites (except for Silicalite) were sodium cation exchanged forms and were activated at $\sim 200 \text{ }^\circ\text{C}$ for 10 h prior to use.

4-MeDBK (**1**) was synthesized according to published procedures.⁹ $\text{DBK-}^{13}\text{C}$ (**2**) was synthesized as follows: Ten grams of phenylacetic acid ($^{13}\text{C}_2$ -90%) (KOR Isotopes) and 20 g of fresh calcium oxide were sonicated and stirred in 150 mL of distilled water. After drying at $\sim 140 \text{ }^\circ\text{C}$, the finely ground powder was pyrolyzed under a vacuum distillation (0.1 mmHg) set-up with a Bunsen burner, to yield $\sim 3 \text{ g}$ of an orange oil. Crystallization from ether (several times) at $-78 \text{ }^\circ\text{C}$ gave a white solid ($\sim 1.5 \text{ g}$), identified to be $\text{DBK-}^{13}\text{C}_2$. The material was diluted with natural abundance DBK, to give 29.8% $\text{DBK-}^{13}\text{C}$, the material employed for ^{13}C -enrichment studies.

Case Effects. The general procedures are similar to those described previously.⁹ A stock solution of 4-MeDBK was prepared in CH_2Cl_2 (Fisher ACS reagent) and a known volume added to a preweighed amount of activated zeolite. The CH_2Cl_2 was removed via three steps: (1) the majority of the solvent was evaporated under aspirator vacuum; (2) a rough pump was employed to remove residual solvent; (3) finally the material was transferred to a Pyrex photolysis vessel equipped with a vacuum stopcock and pumped down to 10^{-5} mmHg and sealed. Photolysis was carried out by using a Hanovia 450-W Hg lamp; the sample was tumbled continuously during the photolysis. Workup involved extracting (directly in the reaction tube) the zeolite with CH_2Cl_2 , either manually or via a Soxhlet apparatus (4-8 h). For all the zeolites except

Silicalite, either method gave the same % CE values. For Silicalite, a simple CH_2Cl_2 extraction failed to remove sufficient organic material for analysis. For this zeolite, we found that a simple MeOH extraction gave the same % CE values as from a Soxhlet extraction.

Analysis of AA, AB, and BB ratios were carried out by using a Varian Aerograph 3700 gas chromatograph. To check for possible interconversion of AA, AB, and BB on the zeolite, a known mixture of AA, AB, and BB (obtained via photolysis of 4-MeDBK in benzene) was deposited on the zeolites and reextracted via the above described procedures. Interconversion of AA, AB, and BB was not observed on any of the zeolites. A 5-10% loss of AA was observed on Silicalite, but % CE's are only affected by <4% due to this "preferential adsorption" of AA. Thus, no corrections were applied to the apparent % CE's observed for Silicalite.

^{13}C -Enrichment Studies. DBK- ^{13}C (2') was deposited on zeolites and photolyzed in the same manner as described above. ^{13}C -Content was determined by mass spectrometry using a Finnegan 3300 GC/MS system (SE-30 column; multiple ion detection mode). The details in calculating α are available elsewhere.²¹⁻²⁵ The identity of PMAP was confirmed by coinjection with an authentic sample of the compound. An additional isomer (as determined by its mass spectrum) (~1%) was observed on photolysis in $\text{Na}^+\text{-X}$, and is believed to be the ortho analogue of PMAP. However, due to the low yield observed, direct confirmation of its structure was not feasible. Conversions were >80% for all the zeolites except Silicalite, in which case <30% conversion was used. We found that it was not possible to take Silicalite to high conversion. The probable reason for this is that homogeneous tumbling of Silicalite samples proved to be problematic due to the extreme powdery form of the sample.

Adsorption Isotherms. For adsorption isotherm studies, 2,2,4-trimethylpentane (isooctane) was chosen as the solvent since it is known that the kinetic diameter is >6.2 Å based on the fact that for neopentane, the kinetic diameter is 6.2 Å.^{14,16} A preweighed amount of DBK dissolved in 30 mL of isooctane was added to 100 mg of zeolite and stirred rigorously with a magnetic stirring bar at room temperature ($25 \pm 3^\circ\text{C}$) for 15 h. The slurry was then filtered by using a microfiltration apparatus, and dodecane internal standard was added. After removal of most of the solvent, the mixture was analyzed for DBK content via GLC (capillary SE-30 column; Varian Aerograph Model 3700). The amount of DBK adsorbed was calculated by taking the difference of the amount of DBK exposed to the zeolite and the amount recovered in the solvent filtrate. Decomposition of DBK was not observed during the period of the experiment.

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Enantioselective Synthesis of 2,2',6-Trisubstituted Biphenyls

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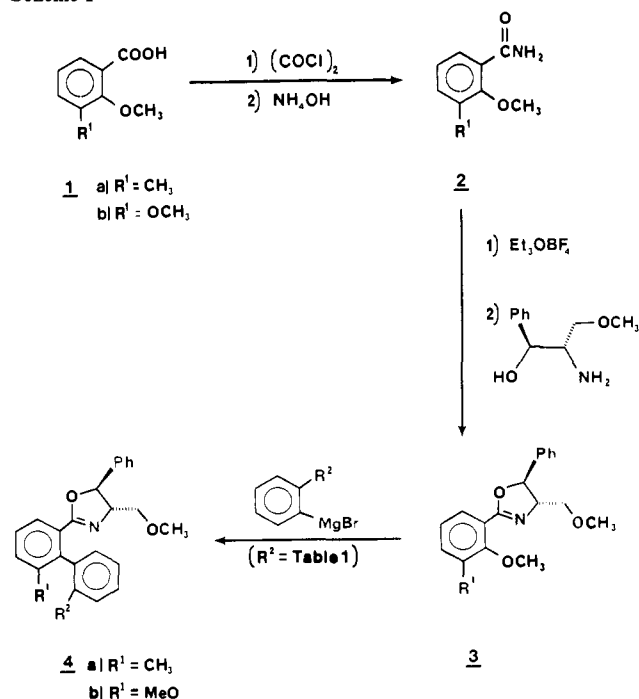
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Abstract: A general procedure is described for the synthesis of chiral biphenyls via nucleophilic aromatic substitution of an *o*-methoxy group by an aryl Grignard reagent with an oxazoline as a chiral auxiliary.

Substituted biphenyls have been synthesized by a variety of methods,¹ most notable of which are the Ullmann reaction,² the Kumada coupling³ of aryl Grignard reagents with aryl halides in the presence of a nickel phosphine catalyst, and the nucleophilic addition of an aryl Grignard reagent to *o*-methoxyaryloxazolines.⁴ As part of a program directed toward the synthesis of (-)-steganone, we were interested in developing a general enantioselective synthesis of substituted biphenyls which are chiral by virtue of hindered rotation about the central bond.

Based on work described by Adams and co-workers,⁵ we decided that a minimum of three ortho substituents would be required to impart a sufficient barrier to rotation to avoid racemization. Although 2,2'-disubstituted biphenyls have been resolved, they are generally not sufficiently stable toward racemization. Frejd⁶ has recently demonstrated that optically pure 2,2'-dilithio-6,6'-dimethylbiphenyl is stable toward racemization at -10°C and can be iodinated to provide optically pure 2,2'-diiodo-6,6'-dimethylbiphenyl. This approach can presumably be extended to provide a number of chiral biphenyls yet requires an optically pure biphenyl as the starting material. Indeed a number of optically active biphenyls have been prepared in the literature, but this is usually the result of a classical or kinetic resolution.⁷

Scheme I



Analogous to the recently reported preparation of optically active binaphthyls,⁸ we chose to prepare the chiral biphenyls 4

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