investigated here, the $X_{Nu}$ values were consistently greater than for all the dioxiranes, i.e., $X_{Nu} = 0.80-0.96$ vs. $X_{Nu} = 0.57-0.67$, respectively.

Consequently, thianthrene 5-oxide should serve as diagnostic test for carbonyl oxide vs. dioxirane intermediates in unknown oxygen-transfer reactions by determining the degree of nucleophilic attack ($X_{Nu}$). For example, oxygen transfer by 2,5-diphenylfuran endoperoxide (Table I, entry 8) appears to involve a carbonyl oxide as intermediate.[7] Similarly, oxygen transfer by the oxidant produced in the singlet oxygenation of alkyl sulfides (Table I, entry 5) is best reconciled in terms of persulfoxide intermediate.[8]

In summary, the present results with thianthrene 5-oxide demonstrate that this probe serves as a useful chemical monitor for differentiating the nucleophilic character of oxygen-transfer agents. In the particular case of carbonyl oxides and dioxiranes, on the basis of the differing degree of nucleophilic attack on SSO, distinct chemical entities are proposed for these oxidants. Although theoretical work[9] designates the dioxirane as the more stable entity by quite a margin ($\Delta E \sim 34$ kcal/mol), the activation barrier for interconversion between these two species is sufficiently high to distinguish them on chemical grounds.

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**Registry No.** SSO, 2362-50-7; SOSO, 951-02-0; $SSO_2$, 2362-53-0; $SOSO_2$, 2362-54-1; MCPBA, 937-14-4; $t\text{-BuC}(=N_2)CH_3$, 65496-01-7; $Na(HO_2)$, 25277-93-4; $t$-BuOOK, 14970-33-3; $KO_2$, 12030-88-5; $^1O_2$, 7782-44-7; $Et_2S$, 352-93-2; $t\text{-BuCH}=N_2$, 762-64-1; $Ph_2C=N_2$, 883-40-9; $PC(O)C(=N_2)Ph$, 3469-17-8; $Me_2C=O$, 67-64-1; $t$-BuC(O)Me, 75-97-8; $c\text{-}C_6H_{10}(=O)$, 108-94-1; $t$-BuCHO, 630-19-3; $KSO_5H$, 10058-23-8; $O_3$, 10028-15-6; $H_2O_2$, 7722-84-1; 18-crown-6, 17455-13-9; 2,5-diphenylfuran, 955-83-9.

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## Photochemistry on Porous Silica. Correlation of Cage Effects and Magnetic Field Effects with Pore Size

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deMayo and co-workers[1] have published an impressive series of papers dealing with the photochemistry of organic compounds adsorbed on porous silica gel. These authors have convincingly demonstrated that adsorption on silica gel can significantly restrict the translational movement of radical pairs produced by photolysis of adsorbed carbonyl compounds. Results from our laboratory[2] have demonstrated that environments which restrict the translational movement of radical pairs and which encourage recombination of radical pairs are reaction spaces that are suited excellently for the observation of magnetic field and magnetic isotope effects on the chemistry of the radical pairs. Current theory[3] of magnetic field and magnetic isotope effects on the chemistry of radical pairs suggests that both the microviscosity and the size of the reaction space are critical parameters in determining the efficiency of these magnetic effects. We report here a systematic investigation of the influence of pore size, substitute coverage, and applied magnetic field on the photochemistry of ketons adsorbed on porous silica.

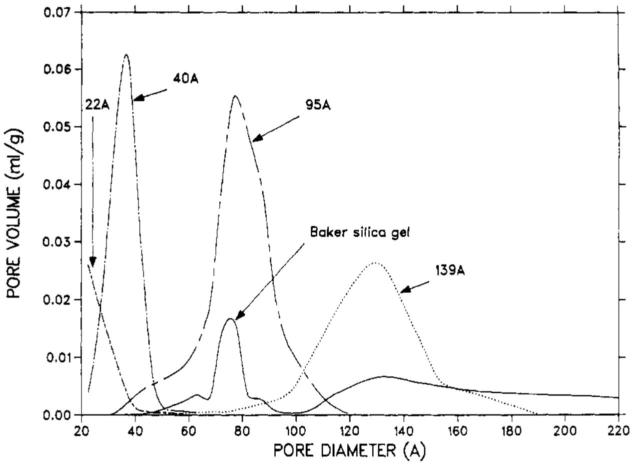
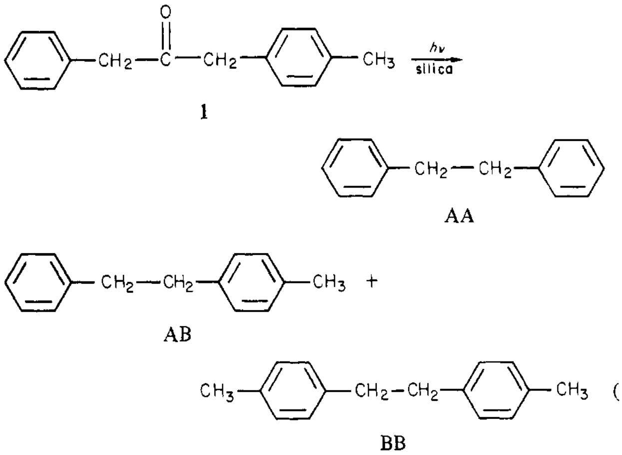


**Figure 1.** Pore diameter distributions of freeze-formed silicas and Baker silica gel measured by BET. The freeze-formed silicas are designed by their average pore diameters.

3-(4-methylphenyl)-1-phenylacetone (**1**) was deposited on porous silica by adding a calibrated amount of **1** in *n*-pentane to a sample of porus silica soaking in *n*-pentane. The *n*-pentane was evaporated slowly and the resulting sample was placed in a quartz cell equipped with an arm which allowed vacuum degassing (ca. $2 \times 10^{-4}$ torr). After irradiation of the sample (which was tumbled in order to increase efficiency and reproducibility), $CH_2Cl_2$ was added to the photolysate which was subjected to GC analysis. In the cases reported, conversions were close to 100%, the cage effects were independent of conversion, the precision was ±5%, mass balances were excellent (>90%), and (unless specified) the only detectable products[4] were those shown in eq 1.



(1)

Since excellent mass balances are obtained, the molar ratio of products (AA, AB, and BB) may be employed to determine via eq 2 the cage effect,[5] i.e., the percent of geminate recombinations

$$\%\ \text{cage} = \frac{\text{AB} - (\text{AA} + \text{BB})}{\text{AA} + \text{AB} + \text{BB}} 100\% \tag{2}$$

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[1] deMayo, P.; Nakamura, A.; Tsang, P. W. K.; Wong, S. K. *J. Am. Chem. Soc.* **1982**, *104*, 6824 and references therein. For a review, see: deMayo, P. *Pure Appl. Chem.* **1982**, *54*, 1623.

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[4] In the absence of evidence to the contrary, it will be assumed that the conventional mechanism of photolysis of dibenzyl ketone and its derivatives (vide supra, ref 2a) in homogeneous solution and in micellar super cages applies to photolysis of **1** on porous silica.

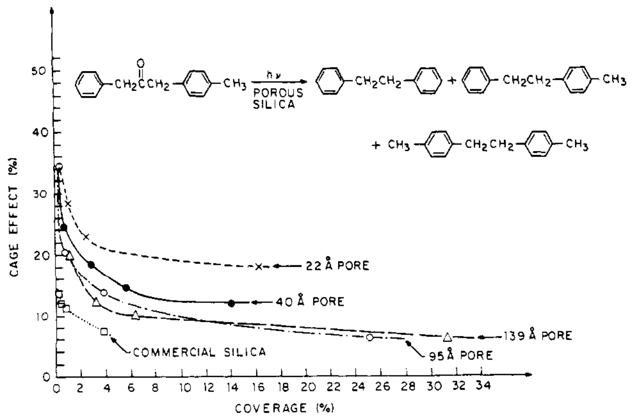

**Figure 2.** Cage effect as a function of coverage for the photolysis of **1** on porous silica of various pore sizes.

of radical pairs produced by photolysis of **1**.

High-purity silica of known median pore size and fairly narrow pore size distribution[6] (Figure 1) was employed for the photolysis. The % cage was determined for the photolysis of **1** as a function of coveage on porous silica of various pore sizes.[7] For comparison, a sample was photolyzed on commerical silica gel. The results are summarized in Figure 2.

For each of the silicas investigated, the profile of % cage as a function of coverage is qualitatively similar and consists of two distinct regions: (I) for "low" coverage (<5%) the % cage is substantial and decreases slowly with increasing coverage, and (II) for "high" coverage (>5%) the % cage reaches a limiting value, which is maintained to higher coverages. Significantly, the family of curves produced by a plot of % cage vs. coverage is correlated with pore size. The smaller the median pore size, the higher the limiting % cage at high coverage. For comparison, Baker silica is found to behave more similar to the largest pore silicas investigated.

An interpretation of the results in Figure 2 is possible by assuming there is an analogy between the properties of the reaction space provided by silica pores and the restricted reaction space provided by micelles.[3c,8] This analogy suggests that the larger the pore size, the lower the efficiency of return of geminate pairs to a common space which is needed for cage recombination and the more efficient escape of radicals from an initial pore. Once geminate radical pairs escape the pore in which they were generated, they are equivalent to "free radicals" and combine in a random fashin corresponding to 0% cage.

One of the consequences of the analogy between micelles and silica pores is the expectation that the % cage will be magnetic field dependent.[5] The expectation is realized experimentally. Significantly, a large magnetic field effect was found only in region I (low coverage). For 22- and 95-Å pores, the magnetic field effect becomes less significant for coverage about ca. 5%. There is only an insignificant effect in region II. There is no significant effect at any coverage for commerical silica. Our results may be most simply interpreted in terms of a two-site model for adsorption of **1** on silica which results in behavior characteristic of regions I and II, respectively. Such phenomenological behavior is well-known in the chromatographic literature,[7] but the interpretation of the molecular basis for the difference in sites has been the subject of controversy. For example, the difference has been ascribed to (a) differences in hydrogen bonding in the two sites, (b) differences in pore size distribution, and (c) differences in surface "viscosity". Although our results do not allow a distinction between these alternatives and other possibilities (e.g., pore shape) to be made at this moment, we believe that use of cage effects and magnetic effects can be developed into a powerful and normal tool to examine the behavior of radicals on silica and other porous surfaces, such as zeolites, and vice versa to study the properties of porous surfaces.

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**Registry No. 1**, 35730-02-0; silica, 7631-86-9.

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(6) The silica (surface area ca. 900 $m^2/g$ and average pore diameter 20 Å) employed in this study was prepared by freezing poly(silic acid) (Mahler, W.; Bechtold, M. *Nature* (*London*) **1980**, *285*, 27). Silica with larger pores was obtained by soaking this material in 0.05 N $NH_4OH$ for various periods of time, followed by washing with water and drying at 150 °C for 3 h. Surface areas and average pore diameter distributions were obtained by the conventional BET($N_2$) method: Brunauer, S.; Emmett, P.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309. The BET($N_2$) method does not reveal information concerning pore sizes smaller than 20 Å.

(7) For example, see: Snyder, L. R. *Sep. Sci.* **1966**, *1*, 191. Snyder, L. R.; Ward, J. W. *J. Phys. Chem.* **1966**, *70*, 3941.

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## Photoinduced Electron-Transfer Reactions. Radical Cations of Methylenebicyclo[2.2.0]hexene Derivatives

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Nuclear spin polarization effects observed during the reactions of photoexcited electron acceptors (chloranil) with two derivatives of 5-methylene-1,2,3,4,6-pentamethylbicyclo[2.2.0]hex-2-ene (**1**) allow the conclusion that radical cations of two principally different structure types are involved. In the case of the chloro derivative, **1a**, the available evidence supports a radical cation with a methylenecyclohexadiene skeleton (**2a**) whereas the effects observed for the methoxy derivative, **1b**, suggest that the interesting doubly allylic radical cation **3b** is an intermediate.

As part of a research program to elucidate the structures of radical cations derived from strained-ring hydrocarbons,[1-6] we have investigated the photoreactions of strong electron acceptors with two derivatives (**1a,b**) of methylenebicyclo[2.2.0]hex-2-ene.[7] This ring system has two different doubly allylic carbon-carbon bonds which may be involved in delocalizing spin and charge of the resulting radical cations. The transannular bond (|||||) appears to be essentially orthogonal to both $\pi$ bonds whereas the doubly allylic bond (△△△) of the methylenecyclobutane fragment may interact readily with the $\pi$ bond of the cyclobutene fragment. Selective participation of one or the other of these bonds would generate radical cations with substantially different structures,

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(7) Derivative **1a** is synthesized from hexamethyl(Dewar benzene)[8] by chlorination with *tert*-butyl hypochlorite. Derivative **1b** is one of two products obtained from **1a** by nucleophilic substitution with sodium methoxide in methanol. Both **1a** and **1b** have been demonstrated to have *exo* stereochemistry.[9]

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