Size, Shape, and Site Selectivities in the Photochemical Reactions of Molecules Adsorbed on Pentasil Zeolites. Effects of Coadsorbed Water

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Received October 10, 1986

Abstract: The photochemistry of methylbenzyl benzyl ketones (ACOB) in the presence of pentasil zeolites follows strikingly different pathways due to the location of the adsorbed ketone. The product distribution, in terms of the cage effect (efficiency of geminate radical combination), demonstrates the effects of sorption and diffusion on the radical species produced by photolysis. *p*-ACOB is readily adsorbed within the pentasil framework and produces *p*-AB as the primary product. In contrast, the photolysis product distributions of *o*-ACOB can be dramatically varied depending upon the extent of its adsorption into the framework. By addition of a nonreactive titrant, such as water, after the ketone adsorption, the photolysis product distributions can be systematically varied depending upon the aluminum content of the framework. The observed results are completely described by considerations of (a) the size and shape sorption of the pentasil zeolites, (b) the sorption of water by the hydrophilic sites of the pentasil zeolites (which depend upon the framework aluminum content), and (c) the hydrophobic characteristics of the pentasil channels which do not contain framework aluminum.

During the last two decades considerable attention has been given to investigations of the structure of the catalytic properties of highly siliceous synthetic zeolite molecular sieves and to the reaction mechanisms imposed by such structures.[1] In particular, the pentasil family of zeolites, of which ZSM-5 is an outstanding member, has exhibited very valuable catalytic properties including high chemical selectivity, low coking (aging) tendency, and high turnover activity for a variety of chemical reactions.[2] One reaction that has attracted considerable attention is the rather remarkable conversion of methanol into isoalkanes and aromatics that form gasoline[3a] as well as the selective alkylation of toluene with methanol to form *p*-xylene.[3b] The impressive catalytic selectivity and in-use stability of the pentasil family of zeolites are attributed to a unique combination of properties, such as size, shape, and site sorption selectivities, chemistry, and substrate diffusion on the internal surface.[4] An example of the size and shape sorption selectivities combined with substrate diffusion is the comparison of the diffusivities of xylene isomers in ZSM-5. The diffusivity of *p*-xylene is about 1000 to 10000 times faster than that of either *m*-xylene or of *o*-xylene, and this enormous difference is ascribed to the larger size and shape of the ortho and meta isomers relative to the size and shape of the ZSM-5 pore diameter of the framework channels.[5] Framework tetrahedral aluminum atoms and their associated cations occur in relatively dilute and isolated states in the pentasil structures and are believed to be the determining factor in the site specificity of catalysis by the ZSM family.[4a]

The dimensions of the pore diameters in zeolite molecular sieves depend on the number of Si or Al tetrahedra in the rings that make up the pore. X-ray diffraction analyses show that ZSM-5 possesses two types of pores, both of which are composed of 10 tetrahedral-membered rings:[6] one pore system is sinusoidal with a nearly circular cross section of about 5.5 Å, and the other pore system is straight and perpendicular to the sinusoidal system with elliptical pores of ca. 5.2 × 5.8 Å. A representation of the internal surface of the channels (void space) of the ZSM-5 internal framework and a simplified topological structure of this void space are shown schematically in Figure 1.

Of considerable practical importance and also of inherent interest to the fundamental theories of catalytic and interface science is the effect of coadsorbed additives on reaction mechanisms.[1c] In particular, the influence of water on the sorption and diffusional characteristics of substrates adsorbed on catalytic surfaces is of broad interest and significance. For example, in the methanol to gasoline reaction,[3] water accounts for a sizable fraction of the products, but the details of the possible modifying nature of water on the activity and specificity of the catalyst are not known. The adsorption of water in pentasils is intimately associated with the hydrophilic centers that exist in the internal surface, the most common of which are hydroxyl groups or cations associated with a tetrahedrally coordinated aluminum.[7] Evidence has been presented that several water molecules are associated, essentially stoichiometrically, to each framework aluminum atom for zeolites whose Si:Al ratio is of the order of 20 or greater.[7] Important issues to be considered in mechanistic studies are the extent of water uptake and its resulting impact on the sorption and diffusional characteristics of the substrate. Although it is to be expected that the adsorption of water will significantly modify the sorption and diffusional characteristics of substrates, it is not clear what microscopic mechanisms will operate as water is added and how these mechanisms will influence the catalytic properties of the zeolites. This report addresses these issues.

Photochemistry of Ketones Adsorbed on ZSM-5 Zeolites. Previously, we reported using the photolysis of dibenzyl ketone, DBK, as a probe of surface and pore geometry of various solids.[8,9]

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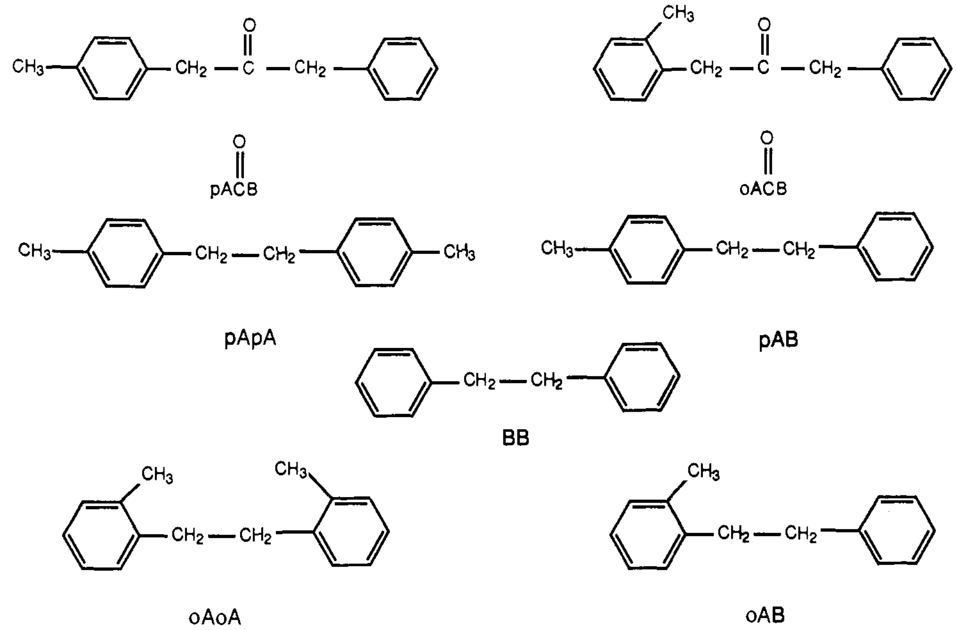
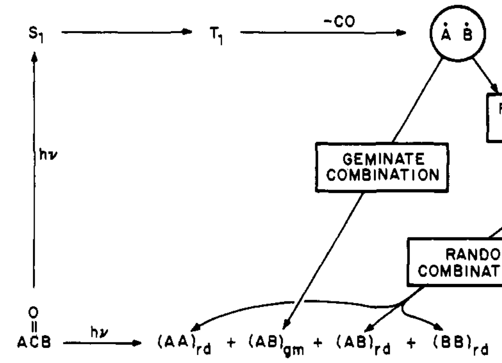
Chart I



We have shown[8,9] that the cage effect (vide infra) increased for DBK sorbed on the internal surfaces of silicas and zeolites with decreasing substrate pore dimension; for pores ~6 Å, the cage effect is ~100%, and we showed that the photolyses of substituted DBK derivatives would result in different product distributions due to the sorption and molecular diffusional characteristics of radicals on the zeolite surfaces.[8] We also demonstrated that selective adsorption of radicals could produce high negative cage effects (vide infra). For all of those experiments, simple arguments based on *size and shape* selective sorption coupled with diffusion phenomena are sufficient to completely explain the experimental results. We now report an investigation of the photochemistry of ketones adsorbed on pentasils of varying Si/Al ratio and a study of the influence of coadsorbed water on the products of photolysis. We also introduce the concept of site selective chemistry, because we find that the water that is coadsorbed with ketones is able to dramatically modify the location of the sorbed ketones, to modify diffusional characteristics of radical intermediates, and to alter, in a systematic and predictable manner, the product distributions of the photolyses.

Substrates, Mechanistic and Experimental Strategies. The probe molecules (Chart I) selected were 1-(4-methylphenyl)-3-phenylpropan-2-one (*p*-methylbenzyl benzyl ketone, *p*-ACOB) and 1-(2-methylphenyl)-3-phenylpropan-2-one (*o*-methylbenzyl benzyl ketone, *o*-ACOB). The photochemistry of these dibenzyl ketone derivatives is expected to mimic that of the parent of this mechanistically well-understood family of ketones.[10] The relevant steps in the photochemistry of an asymmetric DBK are shown in Scheme I.

Scheme I



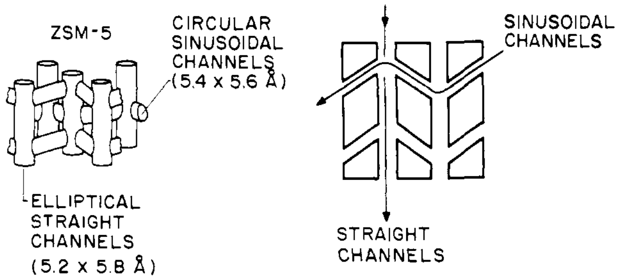


Figure 1. Simplified representations of the ZSM-5 channel system: left, three-dimensional representation of the internal void system; right, topological representation of the internal void system.

Absorption of light cleaves the ketone into two radical fragments (termed a primary geminate radical pair) with high efficiency.[11] The primary radical pair then has two major options of consequence: (1) diffusional separation and (2) decarbonylation to produce a pair of benzyl radicals. The rate of decarbonylation at room temperature has been measured[12] to be ca. 10^7 s^{-1}. If diffusional separation occurs and the radical pair is separated for longer than 10^{-7} s, decarbonylation will therefore be efficient. For the present study, we assume that decarbonylation occurs rapidly relative to other processes that remove ketone from the system, because the only photoproducts of significance are the benzyl–benzyl radical coupling products (diphenylethanes). Thus, to interpret microscopic behavior of the radicals in terms of product distributions, we need only be concerned with the competition between diffusion separation of the benzyl radicals from geminate pairs and the combination of benzyl radicals in geminate pairs to produce diphenylethanes. Radicals that escape geminate combination become "free" radicals that eventually reencounter

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and combine in a random fashion to also produce diphenylethanes but in a different mix than that produced from geminate pair combination. In the systems reported here decarbonylation products account for >90% of the products observed by quantitative vapor phase chromatographic analysis.

In order to distinguish the extent of geminate radical combination from the extent of random radical combinations, it is convenient to label one of the benzene rings of the DBK in order to produce an asymmetric ketone which will produce products that will allow direct evaluation of the fraction of geminate pairs that recombine. The other reason is the structural similarity of the *o*-A and the *p*-A moieties to *o*-xylene and *p*-xylene, respectively. As mentioned above, the use of pentasils to separate *o*-xylene from *p*-xylene is the result of sorption selectivity of the pentasil internal surface topology.[5] The *o*-xylene shape cannot fit readily or diffuse within the framework of ZSM-5 as suggested by the sorption data presented in our previous paper.[8] The *p*-xylene shape, on the other hand, can orient itself (i.e., with the long axis of the molecule coinciding with the long axis of the straight framework channel) so that pore penetration and diffusion within the internal voids can readily occur.

Therefore, we reasoned that *o*-ACOB, to the extent that it resembles *o*-xylene, would be obliged to reside for a much longer time on the external surface (or at best would be able to have only the smaller B moiety penetrate into the framework at the external/internal interface of the zeolite particle). Furthermore, *p*-ACOB, to the extent that it resembles *p*-xylene, should be able to diffuse into and to be adsorbed within the zeolite framework. If these premises are correct, then some very intriguing effects of sorption selectivity of the pentasil structure will be manifest in the product distributions and the cage effects resulting from photolyses of *p*-ACOB and *o*-ACOB.

Use of the Cage Effect as a Probe of Size/Shape and Internal/External Surface Characteristics of Pentasil Zeolites. The above considerations led us to the strategy of employing the cage effect as a probe of internal/external surface diffusional characteristics and of size/shape selectivity of organic radicals adsorbed on zeolites. The cage effect is usually defined as the percent of geminate pair combination that occurs when a pair of radicals is produced by homolytic cleavage of a radical pair precursor.[13] In the case of an asymmetric ketone, ACOB, the cage effect can be evaluated by simply measuring the ratio of the three possible products resulting from decarbonylation, i.e., AA, AB, and BB, and by applying eq 1. For example, if the asymmetric molecule

$$\%\ \text{cage effect} = \frac{(\mathrm{AB}) - (\mathrm{AA} + \mathrm{BB})}{\mathrm{AA} + \mathrm{AB} + \mathrm{BB}} \times 100 \qquad (1)$$

AB is the only product, then the cage effect is *positive* and equal to 100%. On the other hand, if the symmetrical molecules AA and BB are the only products, then the cage effect is *negative* and equal to −100%. Finally, if the ratio AA:AB:BB is 1:2:1, then the cage effect is 0% (i.e., typical of random coupling). As long as AA, AB, and BB are the major products of photolysis of ACOB, the cage effect can be calculated from eq 1 and may achieve any value ranging from 100% to −100%. Mechanistically, the percent cage is a probe of the diffusional and *size/shape* sorptive characteristics of the radicals formed by photolysis and is also a probe for the *location* of the ketone immediately before it is photolyzed.

Given the above considerations we can now establish the expectations for the cage effect resulting from photolyses of ketones adsorbed on pentasils. For the limiting cases of adsorption solely on the external surface or of adsorption solely on the internal surface as the location of photochemical reaction, there are four expected cases as shown in Table I. For case 3a, a high positive cage effect (ca. 100%) is expected for radicals that are generated within the internal framework and which experience restriction of diffusional separation. Furthermore, both the starting ketone and the product will be difficult to extract with a solvent that does not penetrate the internal surface. For case 3b, a high negative cage effect is expected for radicals that are generated on the external surface and that experience efficient *sieving* of the smaller radical moiety into the internal framework. In addition, it is expected that the ketone and the coupling products containing the larger moiety will be readily extracted by a solvent that does not penetrate the internal surface, and the coupling product containing only the smaller moiety will be difficult to extract. For case 3c, a (formal) zero cage effect is expected for radicals produced and remaining exclusively on the external surface when diffusional separation is rapid relative to combination processes.[9] In this case, the ketone will be readily extracted but the products which can be sorbed to the internal surface will be extracted only with difficulty. A high positive cage is expected, as shown in case 3d, when the recombination rate is rapid relative to the diffusion process, irrespective of whether the geminate pair is generated on the internal or on the external surface.

Table I. Photochemistry of ACOB: Location and Product Extraction Dependence

case	location	ACOB products$_{\text{location}}$	cage effect	ketone recovery[a]
3a	interior	$(\mathrm{AB})_{\text{internal}}$	+	difficult
3b	exterior	$(\mathrm{AA})_{\text{external}} + (\mathrm{BB})_{\text{internal}}$	−	AA easy BB difficult
3c	exterior	$(\mathrm{AA} + \mathrm{BB} + 2\mathrm{AB})_{\text{external}}$	0	easy
3d	exterior	$(\mathrm{AB})_{\text{external}}$	+	easy

[a] Refers to the ease or difficulty of extraction of adsorbed ketone by isooctane. See text for discussion.

Table II. Effects of Coadsorbed Water on the Cage Effects in the Photolysis of *p*-ACOB and *o*-ACOB on ZSM-5 Zeolites

S:Al	ketone	H_2O adsorbed,[a] % w/w	cage effect, %[b]
20	*p*-ACOB	0	94
20	*p*-ACOB	10	5
20	*o*-ACOB	10	5
80	*p*-ACOB	0	73
80	*p*-ACOB	8	84
80	*o*-ACOB	0	−28
80	*o*-ACOB	8	−2

[a] Estimated error limits 1%. [b] Estimated error limits 3%.

Isooctane's size and shape characteristics prevent it from being sorbed into the pentasil internal framework, so that it is a selective solvent for extraction of species weakly adsorbed on the external pentasil surface.[14] For case 3a, solvent extraction of the adsorbed ketone and the photolysis product with isooctane is expected, therefore, to be difficult, whereas for cases 3b, 3c, and 3d solvent extraction of the adsorbed ketone with isooctane is expected to be easy. However, in the case of 3b, the product resulting from coupling of the smaller radical moiety is expected to be difficult, because the latter is adsorbed on the internal framework. Thus, cases 3a and 3d, both of which imply a high positive cage effect, can be differentiated by solvent extraction tests. Notice that cases 3b, 3c, and 3d correspond to limiting cases of −100%, 0%, and 100% cage effects, respectively.

Results

From the above considerations, measurements of the cage effect and the ease of extraction of ketone and products as a function of adsorbed water should provide information concerning the location and the diffusional dynamics of *p*-ACOB and *o*-ACOB adsorbed on pentasil zeolites. Table II summarizes the measurement of cage effects for ZSM-5 samples of varying Al composition for samples containing no added water ("dry" pentasils) and for samples saturated with water ("wet" pentasils). Table III summarizes the measurement of ease of extraction of adsorbed ketones and products with isooctane solvent. The method of sample preparation and product analysis is important in interpreting the results. The samples were prepared by deposition of

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Table III. Effects of Coadsorbed Water on the Recovered Yield of *p*-ACOB and *o*-ACOB from ZSM-5 Zeolites by Isooctane Extraction[a]

Si/Al	ketone	H_2O adsorbed, % w/w	recovered yielded, %[b]
20	*p*-ACOB	0	0
20	*p*-ACOB	10	75
20	*o*-ACOB	0	0
20	*o*-ACOB	10	>95
40	*p*-ACOB	0	0
40	*p*-ACOB	10	25
40	*o*-ACOB	0	55
40	*o*-ACOB	10	>95

[a] Percent of ketone that is extractable by isooctane. Estimate of weight and yield errors is 1%. Analyses were made by quantitative vapor chromatography. [b] For the dry samples the *p*-A–*p*-A, *p*-AB, and BB products were not extractable by isooctane, but for the wet samples with Si/Al = 20 these products were extractable. In contrast, the products were only extracted with difficulty for wet samples with Si/Al = 40 or greater. For the dry or wet samples *o*-A–*o*-A and *o*-AB products were easily extractable by isooctane, independent of the Si/Al ratio.

the ketone from pentane solvent followed by evaporation of the solvent and addition of controlled amounts of water vapor. Thus, the water was added "all at once", and then the samples were photolyzed in a time period of the order of minutes and worked up immediately. It is to be emphasized that the measurements were made under *kinetic* conditions. This feature is clear in the photolysis of *o*-ACOB for which the kinetic separation of the radicals produced by photolysis is dramatic (vide infra). The error of the measurements for a given sample was low (generally ±10% or less). Other important points to note are that the "coverage" of the zeolite internal surface was low in all cases, usually about 1 mg of ketone/100 mg of zeolite, the mass balances were high (>80%) in all cases reported, the product ratios were independent of conversion over the ranges investigated, and controls were run which demonstrated that the product ratios found by extraction of the photolysates were reflective of those actually produced and were not biased by the extraction procedure.

The photolyses of *p*-methylbenzyl benzyl ketone (*p*-ACOB) adsorbed on dry pentasils[8] of varying Al composition yield *p*-AB as the major product; i.e., high positive cage effects are observed, indicating the system follows the mechanism of case 3a or of case 3d. Extraction and radical scavenger experiments[8] indicate that case 3a is operating; that is, the *p*-ACOB is located within the framework prior to photolysis. In contrast, the photolyses of *o*-methylbenzyl benzyl ketone (*o*-ACOB) adsorbed on dry pentasil zeolites follow strikingly different pathways, more in accord with case 3b; i.e., negative cage effects are observed. Depending on the amount of sorption into the framework, photolysis product distributions of *o*-ACOB can be dramatically varied.[8] These contrasting results derive from the size and shape sorption selectivity of the pentasils toward *o*-xylene (*o*-X) and *p*-xylene (*p*-X) type structures.[5] The *p*-X structures can readily diffuse into the internal framework of the pentasils resulting in photolysis according to case 3a. The adsorption of *o*-X type structures varies somewhat depending upon the specific sample of ZSM-5 zeolite[8] with the consequence that the products may be derived from a combination of the various cases 3a–d.

The photolysis experiments described above were repeated after samples were allowed to adsorb controlled amounts of water from the vapor phase. Again the method of preparing the samples is important. A controlled amount of water vapor was added to a dry sample containing adsorbed ketone, and the latter was photolyzed. The experiment was then repeated by adding a different amount of water vapor until the saturation point of water adsorption was reached. The resulting product distributions for dry and wet (saturated) samples are listed in Table II for ZSM-5 zeolites of Si:Al ratios varying from 20 to 80. Typical data for varying loadings of water are shown in Figure 2 (Si:Al = 20) and Figure 3 (Si:Al = 80). The latter two zeolites will serve as representative samples with a "high" Al content (Si:Al = 20 corresponds to ca. 4% Al) or a "low" Al content (Si:Al = 80 corresponds to ca. 1% Al). Results analogous to those found for Si:Al = 80 were found for a sample with Si:Al = 40.

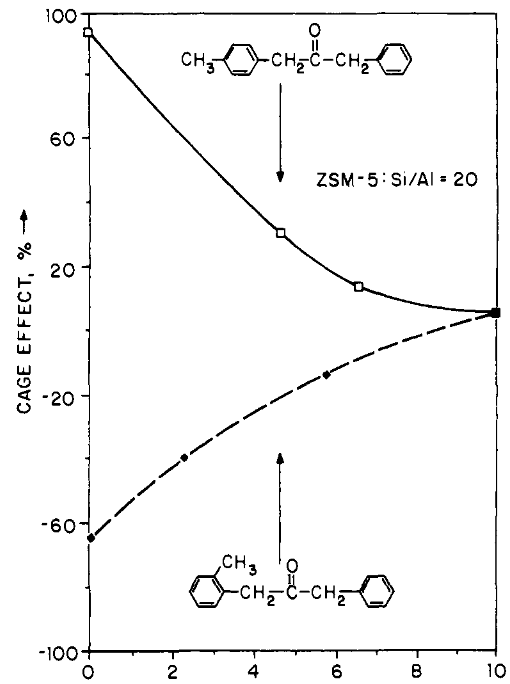


Figure 2. Variation of cage effect with added water for a high Al content ZSM-5 zeolite. The error limits for the cage effects are estimated to be no more than ±3% and for the water added no more than ±1%.

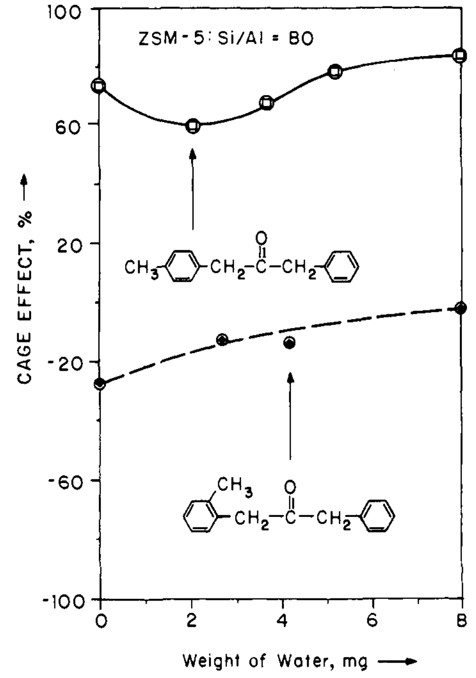


Figure 3. Variation of cage effect with added water for a low Al content ZSM-5 zeolite. The error limits for the cage effects are estimated to be no more than ±3% and for the water added no more than ±1%.

The following qualitative trends are apparent from Table II and the figures. (1) For all dry samples independent of the Si:Al ratio, the photolysis of *p*-ACOB shows a very high positive cage effect and the ketone is extracted only with difficulty. (2) For the dry samples independent of the Si:Al ratio, the photolysis of *o*-ACOB shows a high negative cage effect and the ketone is readily extractable. (3) For wet pentasils of high Al content (low Si:Al ratio), the addition of water causes the cage effect for both *o*-ACOB and *p*-ACOB to approach a limiting value near zero.

(4) For wet zeolites of relatively low Al content (high Si:Al ratio), the addition of water causes the cage effect to approach zero for *o*-ACOB, while for *p*-ACOB, addition of water causes an initial decrease in the cage effect, followed by an increase, i.e., a minimum occurs in the cage effect vs. water content profile.

Table III summarizes the qualitative results of the isooctane extraction test for ketone and product locations for pentasils of different Al content. The salient results are as follows: (1) For dry samples *p*-ACOB is not extracted. (2) For wet samples *p*-ACOB is extractable and is more readily extracted for pentasils of higher Al content. (3) For dry samples or wet samples *o*-ACOB is readily extracted, irrespective of the Al content.

Discussion

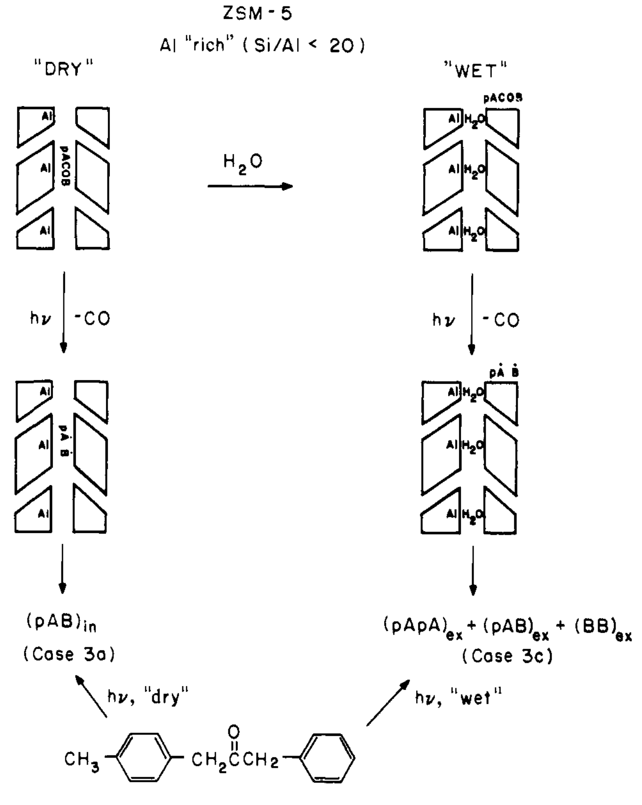
For dry samples, the product distributions for *p*-ACOB (mainly *p*-AB, high positive cage) are explained[8] by the assumption that photolysis of the ketone occurs exclusively within the framework. Decarbonylation of the resulting geminate radical and subsequent combination to form *p*-AB all occur in competition with diffusion and randomization of the *p*-A and B radicals throughout the pentasil internal surface. Thus, photolysis of *p*-ACOB adsorbed on dry pentasils results in a high positive cage effect which indicates that recombination is faster than diffusion within the framework. Although the results of the dry samples are readily understood from considerations of size and shape selective sorption of the substrates by the pentasil pore system,[8] the influence of added water requires consideration of the chemical composition, of the *sites* available for adsorption of water on the pentasil framework, and of the "hydrophobic" nature of the remaining pentasil framework.[7] Recent investigations of the adsorption of water on pentasil materials have shown that the extent of water uptake is directly attributable to the aluminum sites in the channels or on the external surface.[4a,7] It is generally agreed that the charge-balancing cations associated with each aluminum atom can coordinate a "cluster" of water molecules. For example, a slow diffusional rate of water in pentasil zeolites has been suggested as resulting from a two-step mechanism of diffusion: (1) a fast uptake of water on the zeolite external surface by adsorption to surface hydroxyl and the concomitant formation of water clusters which are too large to pass through the pores and to enter the internal framework and (2) the breakup of the water clusters by aluminum sites at the pore mouths, thereby allowing individual water molecules to enter the internal framework. By extension of this thinking, water molecules bound within the framework near the Al sites are also expected to form clusters (whose size will be constrained by the size and shape requirements and hydrophobic nature of the internal void space). The portion of the pentasil internal framework that is not near the water clusters is expected to be hydrophobic, 50% (maximum) of the volume of water is needed to completely fill their internal void space. This demonstrates that a considerable portion of the internal framework is classificable as hydrophobic. However, nearly 100% of the void space of the pentasils is filled by hydrocarbons such as pentane, hexane, and *p*-xylene.

For the purposes of the discussion of the photolysis of *o*-ACOB, we shall consider molecules which are partially adsorbed on the external and on the internal surface (i.e., with the *o*-methylbenzene group external and the benzyl protruding into a hole at the external/internal surface interface). Photolysis of this ketone thus occurs essentially entirely on the external surface. This corresponds to case 3b in Table I. We assume that separation and decarbonylation of the primary geminate radical pair occurs with resultant production of radicals on the external surface and that sieving of the smaller B radicals occurs in competition with recombination of *o*-A and B radicals. As a result, in the absence of adsorption into the framework, photolysis of *o*-ACOB adsorbed on the external surface of dry pentasils results in a high negative cage effect via case 3b (*o*-A–*o*-A and BB as the major products).[4] Some of the dry pentasils investigated display near zero cage effects which become more positive with added water. This phenomenon suggests that external surface recombination may increase upon addition of water according to case 3d (radical diffusion is hampered by coadsorbed water). However, only 50% of the *o*-ACOB is extractable, which indicates that at least some of the ketone is adsorbed and photolyzed within the framework; case 3a would then provide the observed positive cage effect. Previous results[9b] on the photolysis of *p*-DBK adsorbed on silica showed that significant positive cage effects occur and that the extent of the cage effect is a function of the pore diameter of the silica and the level of coverage by the adsorbed ketone. We must therefore consider the possibility that some fraction of the positive cage effects is due to the occurrence of case 3d. In particular, it has been suggested in the literature[7] that added water may slow down diffusion of molecules adsorbed on low Al content zeolites.

Mechanistic Interpretation of the Effect of Added Water on the Cage Effect. We now seek a mechanistic basis to explain the influence of added water on the cage effect (product yields). The results for the photolysis of *o*-ACOB are qualitatively the same, independent of the Al content of the pentasil zeolite. The product distributions shift, as more water is adsorbed, from one typical of efficient sieving of the B radical into the framework, i.e., internal surface (case 3b: *o*-A-*o*-A + BB as major products), to one typical of random coupling on the external surface (case 3c: *o*-A–*o*-A + *o*-AB + BB in the ratio 1:2:1). The slight positive cage observed for some samples indicates that some *o*-ACOB is photolyzed within the framework (case 3a: *o*-AB the only product).

As noted previously, water molecules are probably adsorbed in clusters at or near the hydrophilic aluminum sites in the zeolite framework. At the higher concentration of Al employed in this study, there is a high probability that there will be at least one Al atom per channel (based on 0.19 cm^3/g of void space and 1.04 $\times 10^{20}$ unit cells/g).[6] Because the channel lengths are of the order of roughly 60–80 Å, at the loadings employed, the ketone molecules, because of their relatively large size ($\sim$15 Å), are probably adsorbed in the internal framework near an Al atom before the water is added. As water is added, the hydrophobic ketone molecules are displaced or repelled by the more strongly bound water molecules. Furthermore, the clustering water molecules will tend to block the diffusion of molecules in the internal framework surface. Thus, in the case of *p*-ACOB, water has the effect of displacing ketone molecules from the internal surface to the external surface or to the hydrophobic regions within the internal framework, and in the case of *o*-ACOB, water has the effect of blocking the entrance of photochemically produced B radicals into the internal surface (switching from case 3b to case 3c, in the extreme situation).

The influence of added water is readily understood qualitatively for the case of Al-rich pentasils. Consider the limiting model for which *p*-ACOB produces a positive cage effect of 100% (dry) and 0% (wet) and for which *o*-ACOB produces a negative cage effect of −100% (dry) and 0% (wet). The positive cage effect in the case of *p*-ACOB is due to the generation of *p*-A and B on the internal surface and efficient geminate combination. This result requires only that the rate of geminate combination of radical pairs is much faster than the separation and diffusion of the radical pair into random radicals. Addition of water immediately displaces the ketone to the external surface and, following photolysis, blocks the sieving of radicals into the internal surface. The more water adsorbed, the more ketone displaced to the external surface; there are sufficient framework adsorption sites for water to permit complete displacement of the sorbed ketones from the internal framework. On the external surface, radical coupling is random and the cage effect tends to zero. Thus, in going from the dry to the wet situation, the systems go from case 3a (*p*-AB) to case 3c (*p*-A–*p*-A + *p*-AB + BB). The negative cage effect in the case of *o*-ACOB on dry pentasils is due to the generation of *o*-A and B radicals on the external surface and efficient sieving of the B radicals into the internal surface. Addition of water blocks the sieving of radicals into the internal surface and causes the radical combinations to occur entirely on the external surface, where only random couplings occur and the cage effect again tends to zero. Thus, in going from the dry to the wet situation, the systems go from case 3b (*o*-A–*o*-A + BB) to case 3c (*o*-A–*o*-A + *o*-AB + BB). Figures 4 and 5 show, in a schematic way, the mechanistic



pACOB

Figure 4. Schematic interpretation of the influence of water on the photolysis of *p*-ACOB adsorbed on ZSM-5 samples of high Al content (i.e., Si:Al < 20).

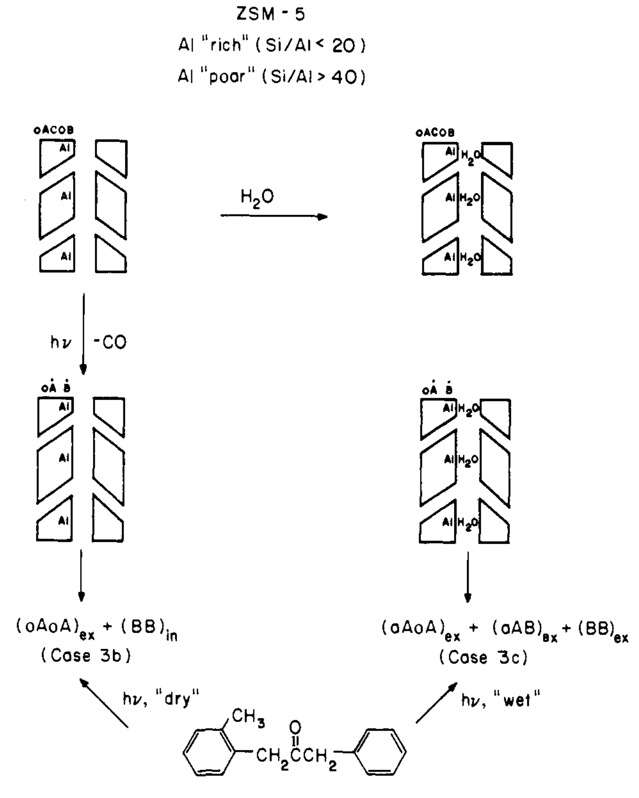
Table IV. Calculated Amounts of Water Sorbed into Pentasils as Function of Their Aluminum Contents
Unit-Cell Formula: $Na_x(Si_{96-x}Al_x)O_{192}$

x	Si/Al ratio	wt % of Al_2O_3	wt % of adsorbed H_2O for coordination of H_2O:Na	
			1:1	6:1[a]
1	96	0.88	0.31	1.86
2	47	1.76	0.62	3.72
3	31	2.63	0.93	5.58
4	23	3.49	1.23	7.38
6	15	5.19	1.83	11.0

[a] The calculated amounts of adsorbed water (assuming a coordination of 6:1) agree quite well with the amounts measured by Hill and Seddon.[7] The designation of the cation as sodium is for illustrate purposes only. The important point is that the amount of sorbed water is directly related to the aluminum content and that framework chemistry (i.e., sites) is important.

switch overs. For low Al pentasils (Si:Al > 40), the explanation for the effect of added water on the cage effects for *o*-ACOB is the same as that given for the Al-rich pentasils, i.e., addition of water blocks the sieving of radicals into the internal surface, and random coupling of radicals occurs on the external surface (Figure 5).

The minimum in the profile of the cage effect vs. water for *p*-ACOB requires a new consideration. We can explain the minimum by noting that *there are fewer sites available for water adsorption in the case of Al-poor pentasils than there are for Al-rich pentasils.* The amount of water required for site saturation may be estimated by assuming a coordination to the cations compensating for the amount of Al in the framework as shown in Table IV. Therefore, a pentasil sample with high Al content (Al rich) can adsorb more strongly bound water than samples possessing a low Al content. For Al-rich samples (Si:Al < 20), there is a high probability that strong adsorption sites for water



oACOB

Figure 5. Schematic representation of the influence of water on the photolysis of *o*-ACOB adsorbed on ZSM-5 samples of low or of high Al content.

exist throughout the channel system. Therefore water adsorption, at all loadings, can displace ketones to the surface by a combination of site adsorption and displacement of the organic ketone to the surface where it can be photolyzed according to case 3c. In the case of low Al content pentasils, the ketone is sorbed near Al sites or is located near the weaker binding hydrophobic regions within the framework. Low loadings of water saturate the strong binding sites; this accounts for the decrease of the (positive) cage effect with addition of small amounts of water; i.e., some ketone is displaced to the surface (case 3c). Increasing the amount of sorbed water cannot displace all of the ketone from the internal framework because some of the displaced ketone is now contained in hydrophobic pockets which do not contain Al atoms. In these cases, water is able to displace the ketone toward the hydrophobic portions of the framework as well as toward the surface and to block the exit of ketones from the hydrophobic regions. As a result, when all exits from the hydrophobic regions of the framework are blocked by adsorbed water, some ketone molecules are entombed in the hydrophobic portions of the framework (on the time scale of our experiments). Photolysis of such ketones results in high positive cage effects because the radical pairs thereby produced cannot escape from the cage and eventually undergo geminate combination.

The dependency of water adsorption on the aluminum content is shown schematically in the upper graph of Figure 6. The lower graph shows how the conflicting effects of ketone displacement and ketone entrapment produce the minima observed in the cage effect vs. water sorption profiles. The tie line indicates that as water is coadsorbed on the zeolite and into the framework a corresponding amount of ketone is displaced from the internal surface to the external surface where it is photolyzed according to case 3b and leads to a zero cage effect. The linear displacement of ketones is followed until the amount of titrant added corresponds to the amount required to saturate the available water (or titrant) adsorption sites. After the sites are saturated, excess water impedes the migration of the displaced ketone to the external surface. The greater the amount of the excess water dosed onto the sample,

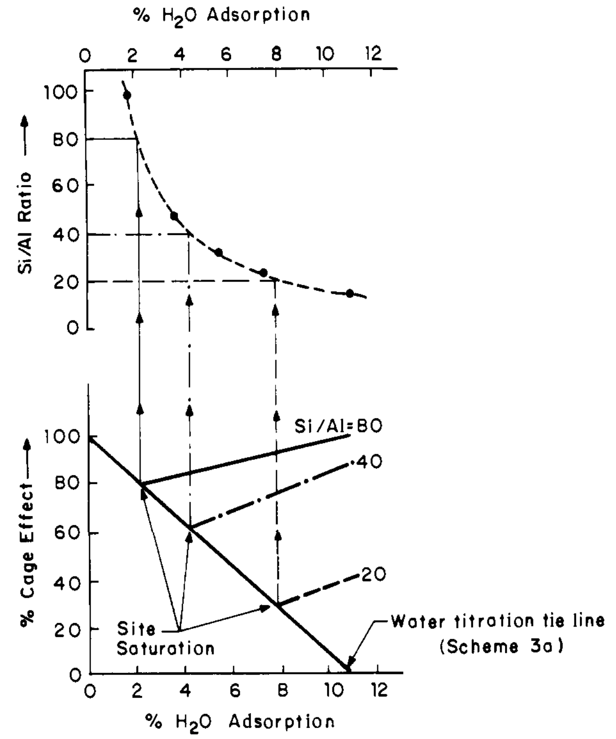


Figure 6. Schematic representation of the relationship of water adsorption to aluminum content of ZSM-5 (top) and the relationship of the percent cage effect of the photolysis of *p*-ACOB to the extent of water adsorption (bottom).

the more pronounced the effect. The greater the extent that the ketone becomes entrapped within the internal framework and the greater the extent of photolysis via case 3a, which leads to a strong positive cage effect (i.e., if a ketone is blocked in a channel), then it is both protected from displacement (at least kinetically on the time scale of our experiments) and is obligated to undergo efficient geminate combination, because escape to form random radicals is not an option during the geminate pair lifetime. This interpretation of the results is shown schematically in Figure 7 for the extreme situation of dry and wet samples of low Al content.

Thus, the minimum in the cage effect/water profile is directly related to the site chemistry of the sample and provides dramatic evidence for the modification of product distributions by a nonreactive coadsorbant. The quantitative aspects of this competition between displacement of the ketone and blocking of the channels have not been established by our experiments. We speculate, however, that the greater importance of blocking relative to displacement as the pentasil becomes more Al poor may reflect the tendency of some pentasil preparations to be more Al rich near the external surface than the interior surface of a pentasil particle. This feature will tend to enhance water binding near the external surface relative to the internal surface and thereby lead to a more rapid blocking of the escape routes of internally bound ketones. Recent evidence in the literature is consistent with a nonuniform distribution of Al in some samples of pentasil zeolites,[15] but in other cases close to homogeneous distributions have been found.[16] The variety of results emphasize that ZSM-5 should not be considered to be a unique material (i.e., its properties vary quantitatively from sample to sample) and that the Al distribution will depend to some extent on the method of preparation.

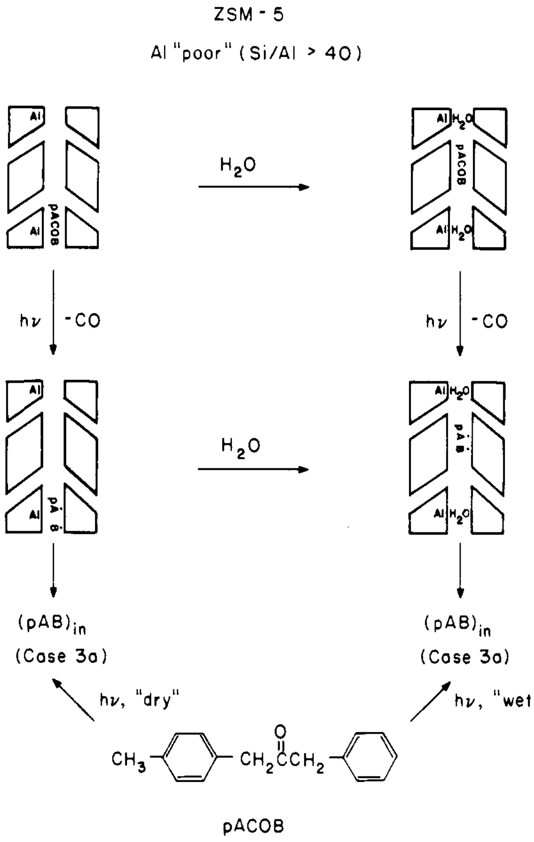


Figure 7. Schematic representation of the influence of water on the photolysis of *p*-ACOB adsorbed on ZSM-5 samples of low Al content.

The site effects of the photolyses of ketones adsorbed on pentasils can also be considered in terms of the number of Al atoms per unit cell, the size of the unit cell (ca. 14 × 20 × 20 Å), and the size of the ketone (ca. 15 Å). At high Al content the relatively large size of the ketone implies that nearly every ketone will be near an Al atom. The information in Table IV shows that for a given unit cell content of Al, there are sufficient sites for water adsorption to produce a significant displacement of ketone to the external surface or to hydrophobic regions. Thus, we conclude that the number of Al sites determines the amount of water sorbed and the location of the minimum of the cage effect vs. water profile as shown in Figure 3. Indeed, for several samples of Si:Al ratios of 20, 40, and 80, the minimum was found to occur in the order and location predicted by Figure 6.

In the methanol to gasoline reaction, water is a product and is formed within the pentasil framework. Our results and those of others[17] suggest that coadsorbed water might perturb or displace organic reactants or products to the hydrophobic regions of the framework or the external surface and consequently alter the product distributions. The role of Al in the framework would therefore be bifunctional: to provide the active catalytic site as well as an adsorption site.

Conclusions

The photolyses of *o*-ACOB and *p*-ACOB on pentasil zeolites show a strong sensitivity to size and shape sorption selectivity. Thus, for dry pentasils the major products of *o*-ACOB are *o*-AA and BB, while the major product of *p*-ACOB is *p*-AB, corresponding to a high negative cage effect and a high positive cage effect, respectively. By addition of a nonreactive titrant, such as water, the product distributions can be varied dramatically. Coadsorption of water significantly modifies the pattern of product formation in a manner which depends on the Al content of the pentasil: for high Al content (Si:Al $\leq$ 20) coadsorption of water causes the cage effect to tend toward zero for both *o*-ACOB and for *p*-ACOB, whereas for low Al content (Si:Al $\geq$ 20) the cage effect tends toward zero for *o*-ACOB but shows a minimum for *p*-ACOB as water is coadsorbed.

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These results are completely described by considerations of (a) the size and shape sorption selectivity of the pentasil zeolites, (b) the sorption of water by the hydrophilic sites of the pentasil zeolites (due to the presence of Al atoms and their associated cations), and (c) the hydrophobic characteristics of the pentasil channels which do not contain an Al atom. The above ideas are summarized in Figures 4, 5, 6, and 7.

Experimental Section

Photolysis Experiments. The zeolite samples were activated at 550 °C for at least 1 h prior to use. For a typical photolysis experiment, an activated sample was charged with a minimum amount of dry *n*-pentane (with care taken to minimize the time in which the sample was exposed to the atmosphere), and then 1.0 mg of ketone in 0.5 mL of *n*-pentane was added to the sample. The bulk of the solvent was removed by placing the sample in a stream of warm (50 °C), dry air. The solid was subsequently placed into a quartz photolysis cell, equipped with a side arm which allowed for vacuum degassing. The dry samples were degassed to a pressure of 2×10^{-4} torr. For the photolysis experiments involving dry samples, the latter was maintained under vacuum and tumbled during photolysis at ambient temperature. A 400-W medium-pressure Hanovia Hg lamp was employed as the light source with an aqueous K_2CrO_4 (10-mm) filter employed to isolate the 313-nm line. For the preparation of the wet samples, the sample cell was connected to a vacuum line on which a reservoir of water served as the source of water vapor. The whole line was throughly degassed via the freeze–thaw method before the water vapor was admitted to the sample. The amount of water adsorbed by the zeolite sample was controlled by the time of exposure and was determined by weighing of the sample. The resulting sample was tumbled during photolysis as described above. After irradiation, the sample was soaked in 6 mL of benzene overnight. Analysis of the filtered sample was performed by vapor phase chromatographic analysis on a Varian 3700 gas chromatograph equipped with a 50-m SE-30 capillary column at 180 °C. The areas of the peaks in the GC traces were integrated on a Hewlett-Packard 3390 integrator. The cage effect was found to be independent of ketone coverage up to at least 20% by weight; however, in the experiments reported, the coverage was maintained at ca. 1% (1 mg of ketone/100 mg of zeolite).

For the isooctane washing experiments the samples were prepared in a manner described above. The sample was soaked in isooctane (6 mL) for 1 min and then filtered, and the filtrate was subjected to vapor phase chromatographic analysis as described above.

Benzene (Fischer spectroanalyzed), *n*-pentane (EM, Omnisolv), and isooctane (MCB, Omnisolv) were used without further purification. 1-(4-Methylphenyl)-3-phenylpropan-2-one (*p*-MeDBK, *p*-ACOB) was prepared by a literature procedure.[18] 1-(2-Methylphenyl)-3-phenylpropan-2-one (*o*-MeDBK, *o*-ACOB) was prepared by a modification of the same procedure.

Samples of Na, TPA–ZSM-5 with Si:Al = 20, 40, and 80, were prepared by the methods of Rollman and Volyocsik,[19] calcined in flowing air at 60 °C/h to 550 °C, and then held at 550 °C for 10 h. The samples were then exchanged 3 times with a 10% NH_4NO_3 solution at 90 °C for 1 h and calcined as described above to give the acid form. The materials were then exchanged 3 times with a 10% $NaNO_3$ solution at 90 °C for 1 h, dried, and recalcined as above. A sample of ZSM-5 (Si:Al = 70) was a gift of the Mobil Corp.

Acknowledgment. The authors at Columbia thank the AFOSR and the NSF for the generous support of this research. Dr. Edith Flanigen of the Union Carbide Corp. is thanked for numerous helpful discussions. Dr. Paul Weisz, of the Mobil Corp. and the University of Pennsylvania, is thanked for his perceptive and stimulating discussions on the size and shape selectivities of ZSM-5 materials and for the generous gift of several samples of varying Al content.

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1,2,4,6-Cycloheptatetraene: The Key Intermediate in Arylcarbene Interconversions and Related C_7H_6 Rearrangements

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Abstract: Thermolysis or photolysis of phenyldiazomethane (**2**) produces phenylmethylene (**3**), which ring-expands to give 1,2,4,6-cycloheptatetraene (**6**). Spectroscopic and chemical evidence rule out bicyclo[4.1.0]hepta-2,4,6-triene (**4**), cycloheptatrienylidene (**5**), and bicyclo[3.2.0]hepta-1,3,6-triene (**11**) intermediates. The strained allene in cycloheptatetraene (**6**) exhibits infrared absorptions at 1824 and 1816 cm^{-1}. Deuterium substitution produces the expected 10-cm^{-1} shift in the allene absorption. Fluorine or chlorine substitution substantially enhances the allene absorption intensity. Deuterium labeling studies reveal that the intramolecular chemistry of cycloheptatetraene (**6**) involves reversible thermal or photochemical equilibration with phenylmethylene (**3**). The intermolecular chemistry of **6** involves dimerization. At temperatures as low as 10 K, **6** forms a labile [2 + 2] dimer, **7**, which undergoes thermally allowed, electrocyclic ring opening to give heptafulvalene (**8**) upon warming to room temperature. The rearrangements of 7-acetoxynorbornadiene (**9**), 2-diazobicyclo[3.2.0]hepta-3,6-diene (**31**), and 8-diazobicyclo[2.2.2]octa-2,5-dien-7-one (**33**) all involve cycloheptatetraene (**6**) intermediates.

The opposing tendencies of arylcarbenes and nitrenes to preserve their aromaticity and to seek restoration of tetravalency result in a singularly fascinating series of multiple rearrangements.[2] A detailed understanding of the mechanisms involved is of importance from the point of view of both basic science and industrial

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