

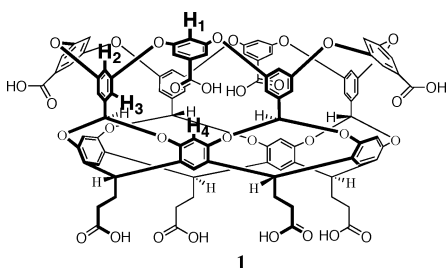
## Controlling Photochemistry with Distinct Hydrophobic Nanoenvironments

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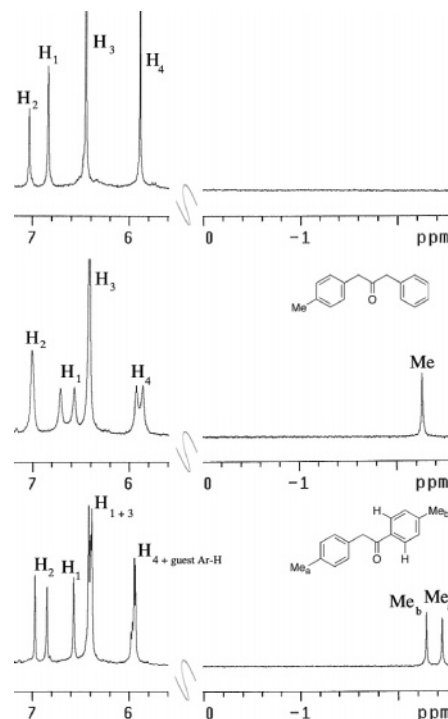
Mimicking the ability of enzymes to bring about highly selective reactions requires the formation of a suitably distinct "active site".<sup>1</sup> Thus, ordered media have been used to increase the selectivity of photochemical reactions,<sup>2,3</sup> while self-assembly via metal ion coordination<sup>4</sup> or hydrogen bonding<sup>5</sup> have been used to control a number of chemical processes. Recently, two of us reported on the self-assembly of cavitand **1**.<sup>6</sup> In aqueous solution and in the presence of a suitable guest molecule, this host dimerizes to form a capsular complex with a cavity 1 nm wide and 2 nm long.<sup>7</sup> In this communication, we examine the interior of this capsule using fluorescence spectrometry and present our first analysis of its ability to influence photoreactions of encapsulated guests. It transpires that through the assembly, the hydrophobic effect can engender transformations with specificities that rival those observed in the solid state.



The fluorescence spectrum of a turbid  $10^{-5}$  M solution of pyrene in aqueous borate buffer shows both monomer and ground-state dimer emissions.<sup>7</sup> The 1.70 ratio of the  $I_1/I_3$  peaks (a measure of micropolarity of the medium) is consistent with pyrene in aqueous solution. The addition of two equivalents of **1** gives a clear solution whose fluorescence spectrum shows only monomer emission and a  $I_1/I_3$  ratio of 1.01, similar to that observed for pyrene in benzene (1.05).<sup>8</sup> <sup>1</sup>H NMR confirms the formation of a 2:1 capsular complex that assembles and disassembles slowly on the NMR (500 MHz) time scale.<sup>7</sup> These analyses demonstrate that pyrene is encapsulated in an essentially hydrophobic environment inside the capsule dimer **1**.

1-Phenyl-3-*p*-tolyl-2-propanone **2a** (Scheme 1) also forms a strong capsular complex with host **1**.<sup>7</sup> The  $C_s$  symmetry of the guest and the pseudo- $D_{4h}$  symmetry of the capsule shell combine to form a  $C_s$  symmetric capsule in which each hemisphere is unique (Figure 1 and Figure S1 in Supporting Information).<sup>7</sup> The para  $CH_3$  group of the guest undergoes the most dramatic of environment changes upon binding. Its signal shifts upfield from 1.7 to  $-2.2$  ppm, indicating that it is located deep within one of the tapering ends of the cavity.<sup>9</sup>

Irradiation of **2a** (and analysis of photoproducts by GC and <sup>1</sup>H NMR) in aqueous borate buffer solution yields only decarbonylated



**Figure 1.** Selected regions of the <sup>1</sup>H NMR of: (top) host **1** (see structure for designations), (middle) the capsular complex **122a**, (bottom) the capsular complex **129a**. Host concentration = 1 mM; guest concentration = 0.5 mM. Further addition of guests results in <sup>1</sup>H NMR peaks corresponding to free guest.

**Table 1.** Product Distributions upon Irradiation of Guests Encapsulated in Host **12**<sup>a</sup>

guest	3	4	5	6–8(a–b)	9a/b	11
<b>2a</b>	–	–	41	15	44	–
<b>2b</b>	–	38	–	13	49	–
<b>2c</b>	96	–	–	2	–	2

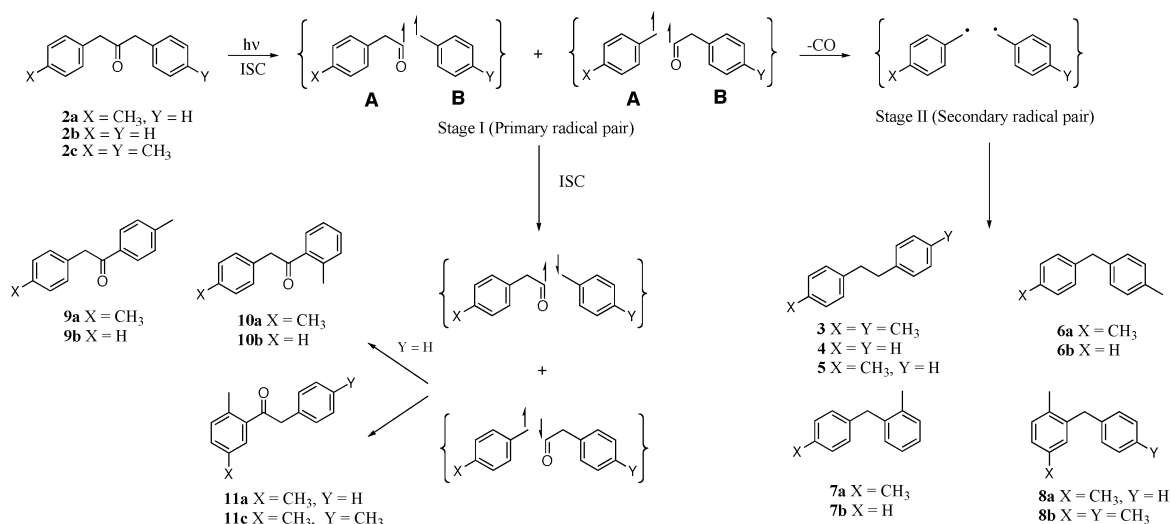
<sup>a</sup> Yields are an average of at least six runs and are estimated by GC using dodecane as the internal standard. Error limit  $\pm 3\%$ . For irradiation conditions, see Supporting Information.

products **3** (AA), **4** (BB), and **5** (AB) in the expected, statistical 1:1:2 ratio.<sup>10</sup> No rearrangement products **6–11** were formed. In contrast, encapsulated compound **2a** in the capsule **12** gave only AB-type products: the decarbonylated product **5**, the rearranged decarbonylated products, **6a**, **7a**, and **8a**, and the rearranged product, **9a** (Table 1). The observed 100% cage effect ( $5-3-4$ )/( $3+4+5$ ) is remarkable, and to our knowledge such high cage effects have only been reported in the solid state.<sup>11</sup> The more general observation that only AB-type products are formed from the secondary radical pair must arise from the differences in the rate of reaction and the rate of capsule disassembly. The rate of disassembly ( $<ca. 0.1-1 s^{-1}$ ) is much slower than the known decarbonylation rate of

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Scheme 1. Reaction Manifold of Guests 2a–c



phenyl acyl radical ( $\sim 6 \times 10^6 \text{ s}^{-1}$ )<sup>12</sup> and, by necessity, the rate of radical recombination. The capsule is leak proof on the time scale of the reaction.

The most striking observation from the photolysis of encapsulated **2a** is the high yield of para rearrangement product **9a** and absence of any ortho rearrangement product **10a** and **11a**. To investigate this further, the photolysis of 1,3-diphenylacetone **2b** inside capsule **1<sub>2</sub>** was also examined. Encapsulated **2b** gave a good yield of para rearrangement product **9b**, decarbonylated derivatives **4**, **6b**, and **7b**, but no ortho rearrangement product **10b** (Table 1). This is in contrast to its behavior in hexane where only 1,2-diphenyl-ethane **4** is obtained.<sup>10</sup> What is the origin of the high yields of **9a** or **9b**? To form these compounds the following criteria must be met:<sup>11,12</sup> (a) a longer than normal lifetime of the primary radical pair ( $>200$  ns), (b) intersystem crossing (ISC) from the triplet to the singlet radical pair—spin memory loss—faster than the rate of decarbonylation, (c) reorientation of the benzyl radical inside the cavity. The crucial factor is that the benzyl radical reorientation is controlled by the shape of the cavity. It is observed in cavitand-based hosts that guests with “knob-like” substituents adopt orientations in which the tapering end of the cavity is filled by the “knob”.<sup>6,9</sup> Upon generation of the radical pairs inside **1<sub>2</sub>** there must be a rapid reorientation of the benzyl radical to a thermodynamically lower state in which the benzyl/incipient-methyl group fills the tapering ends of the capsule. That the “new” methyl group of **9a** can occupy the base of the cavity was determined by <sup>1</sup>H NMR (Figure 1 bottom). Each guest methyl packs one of the “poles” of the capsule. On the other hand, **10a** and **10b** are not formed because they pack the cavity less efficiently. In stark contrast, encapsulation of guest **2c** “packs” each pole with a methyl group. Hence, irradiation forms two radicals that are already oriented optimally. Thus, the major product of photolysis is decarbonylated **3**. Only a trace of the ortho rearrangement product **11** is detected.

In summary, the nanoenvironment inside the capsule formed by cavitand **1** is essentially dry and leak-proof on the photolysis time scale. In addition to allowing photolysis reactions to be carried out in water, the capsule also controls (templates) the reaction outcome,

with selectivities comparable to those in the solid state. We are currently examining other reactions inside this capsule.

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**Supporting Information Available:** Experimental details, emission spectra, 1D and 2D <sup>1</sup>H-NMR spectra of the different host–guest complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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