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Role of Free Space and Conformational Control on Photoproduct Selectivity of Optically Pure α-Alkyldeoxybenzoins within a Water-Soluble Organic Capsule†

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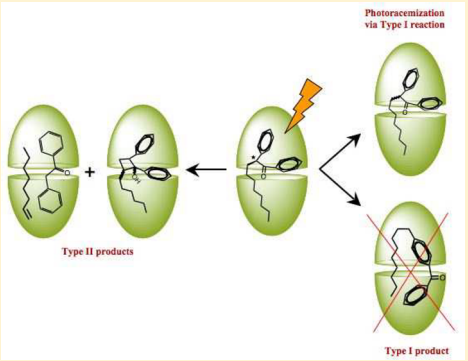
Supporting Information

ABSTRACT: Optically pure α-alkyl deoxybenzoins resulting in products of Norrish Type I and Type II reactions upon excitation has been investigated within the octa acid (OA) capsule in water. The product distribution was different from that in an organic solvent and was also dependent on the length of the α-alkyl chain. Most importantly, a rearrangement product not formed in an organic solvent arising from the triplet radical pair generated by Norrish Type I reaction was formed, and its yield was dependent on the alkyl chain length. In an organic solvent, since the cage lifetime is shorter than the time required for intersystem crossing (ISC) of the triplet radical pair to the singlet radical pair the recombination with or without rearrangement of the primary radical pair (phenylacetyl and benzyl) does not occur. Recombination without rearrangement within the capsule as inferred from monitoring the racemization of the optically pure α-alkyl deoxybenzoins suggesting the capsule's stability for at least 10^{-8} s (the time required for ISC) is consistent with our previous photophysical studies that showed partial opening and closing of the capsule in the time range of microseconds.



INTRODUCTION

Excited-state process manipulation through supramolecular effects has drawn considerable attention during the last three decades.[1−3] The controlling factors of the product distribution have been understood in terms of cage, conformational, preorientational, and local-concentration factors[4] with the effects attributed to weak intermolecular forces and confinement provided by the supramolecular assemblies. While early investigations of supramolecular photochemistry were confined to crystals,[5] with time the emphasis shifted to aqueous medium.[6,7] In this context, water-soluble hosts such as micelles, cyclodextrins, cucurbiturils, calixarenes, and Pd-nanocage and various organic cavitands have played a significant role as reaction containers.[3,8−15] Efficient exploitation of the hosts as reaction containers requires an understanding of the translational and rotational mobility of molecules within these confined spaces. In this paper, we explore one such motion by examining the excited- state behavior of optically pure α-alkyl deoxybenzoins included within a water-soluble organic capsule.

From our investigations on the utility of a synthetic water-soluble deep cavity cavitand octa acid (Scheme 1; OA)[16] as a host for manipulating the excited state processes of organic guest molecules,[17,18] we have demonstrated that the photochemistry of α-alkyl dibenzyl ketones could be controlled within this host.[19] In organic media, these ketones undergo conformation dependent Norrish Type I and Type II reactions. The reaction of immediate concern to the question addressed here is Norrish Type I reaction. In general, α-cleavage reaction due to Norrish Type I reaction of carbonyl compounds yields a radical pair. The short 0.1 ns cage lifetime in solution prohibits the intersystem crossing (ISC) of the triplet radical pair within a solvent cage.[20] It normally does not recombine with or without rearrangement within the solvent cage. Interestingly, irradiation of dibenzyl ketone,[21] short-chain α-alkyl dibenzyl ketones, and *p*-alkyl dibenzylketones[22] included within OA although underwent Norrish Type I reaction they yielded significant amount of a rearrangement product of the Type I primary radical pair (phenylacetyl and α-alkyl benzyl pair) in competition with decarbonylation of phenylacetyl radical (three examples chosen from our previous studies are highlighted in Scheme 1). This is consistent with the notion that unlike in organic solvents, the cage lifetime within a capsule was longer (>5 μs)[23] and the singlet radical pair was generated via ISC of the initially formed triplet radical pair before it could escape to the aqueous solution. This permitted the singlet radical pair to give recombination products (with rearrangement) that are not obtained in organic solvents. Although formation of rearranged product suggested that the primary radical pair following Norrish Type I recombined following tumbling of the α-alkyl benzyl radical it was not clear whether the phenylacetyl and benzyl radical pair recombined without rearrangement to generate the reactant ketone. We felt it is important to learn whether the recombination process was possible without rearrangement within the OA capsule.

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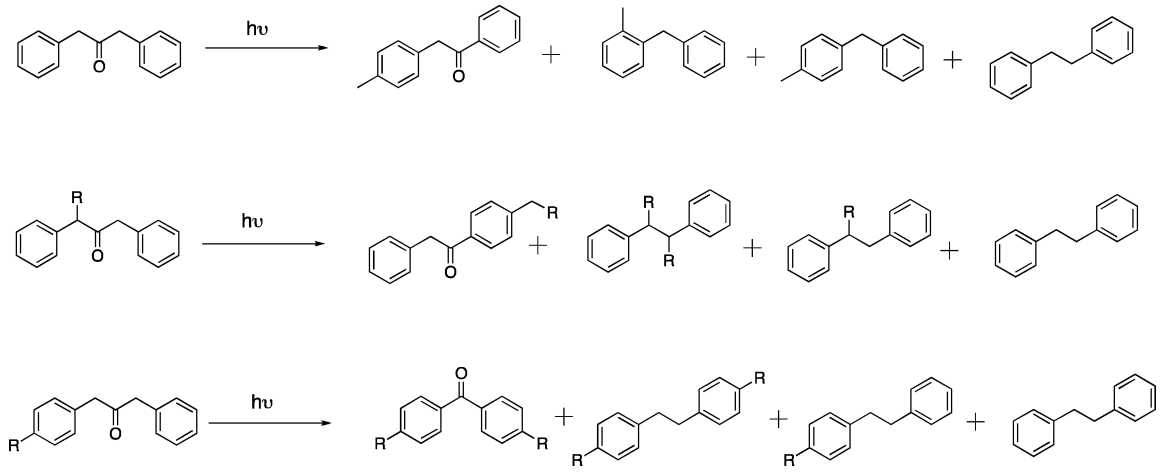
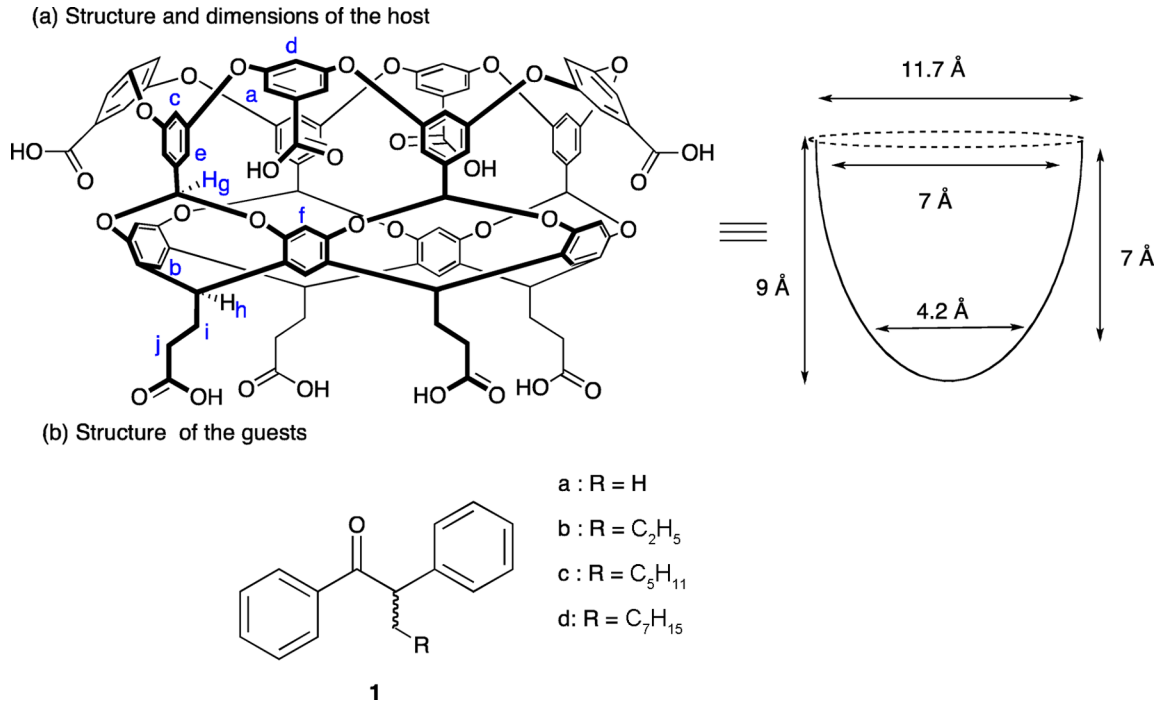
Scheme 1. Examples Illustrating the Difference in Product Distribution between Solution and OA Photochemistry



Scheme 2. Chemical Structure of OA and α-Alkyldeoxybenzoins



To address the above question we have examined the photochemistry of optically pure α-alkyl deoxybenzoins **1a–d** (Scheme 2; ADB) that could be readily synthesized following a recently reported procedure.[24,25] Similar to α-alkyl dibenzyl ketones, these deoxybenzoins are established to undergo both Type I and Type II reactions (Scheme 3) from excited triplet state.[26,27] By HPLC monitoring of the racemization of photoexcited optically pure **1a–d** we have established the cage recombination of the primary radical pair to yield the starting ketone within the OA capsule regardless of the alkyl chain. The results suggest the lifetime of the capsule confined triplet radical pair to be long enough to intersystem cross to the singlet radical pair and recombine to the racemic reactant. As anticipated, product distributions monitored by GC and HPLC revealed that the excited state behavior of the ADBs and their corresponding radical intermediates were distinctly different within OA capsule solubilized in aqueous solution from that in benzene solution and are discussed below.

To appreciate the results presented here it is important to be aware of the following characteristics of the supramolecular assemblies of OA and guests: (a) OA forms 1:1 cavitandplex with guest molecules that contain polar head groups such as ammonium or carboxylic acid. With hydrophobic guest molecules, depending on the size it forms either a 1:2 or 2:2 (guest to host) complex that is termed "capsule".[28] (b) Within the capsule the guest molecule depending on its size and shape have some mobility; in other words, they are not stationary.[29] (c) The capsule itself partially opens and closes in the time scale of 0.5 μs[23] and fully opens in ~2.7s.[30] Therefore, in the excited time scale of the carbonyl compounds investigated here the capsule is expected to be stable. (d) Using photophysical probes and EPR techniques the internal polarity of the capsule is determined to be close to that of benzene.[31,32] This is not surprising as the internal cavity of OA is laced with substituted benzenes. Determined polarity suggests that there are no water

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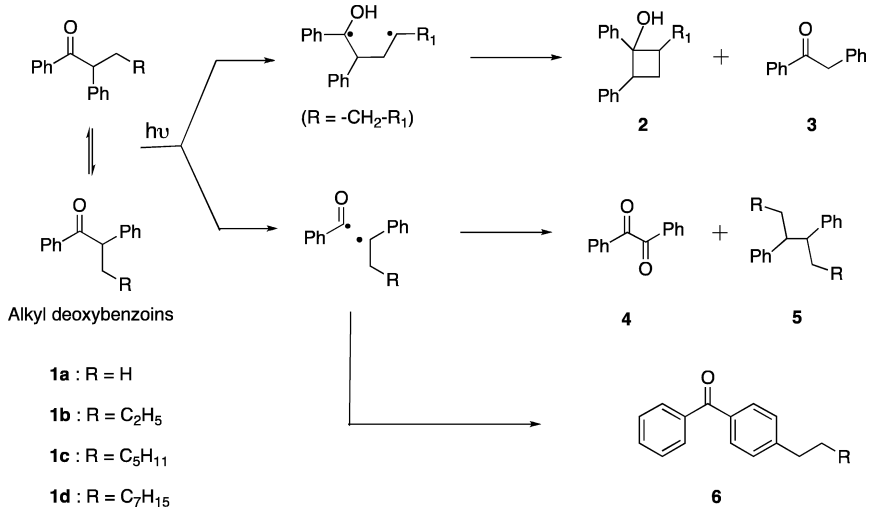
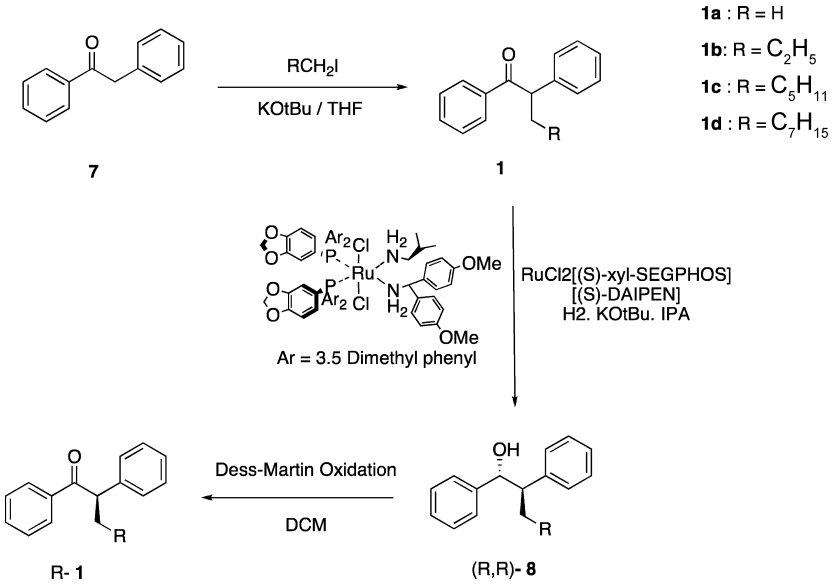
Scheme 3. Product Distribution upon Irradiation of α-Alkyldeoxybenzoins



Scheme 4. Synthetic Scheme for the Preparation of Racemic and Optically Pure α-Alkyl Deoxybenzoins



molecules within the capsule and the capsule is stable in the excited-state time scale.

RESULTS AND DISCUSSION

Optically pure ADBs were synthesized by following the recently reported procedure for propyl deoxybenzoin (**1b**) (Scheme 4).[25] As expected, the synthesized ADBs ((*R*)-**1**) gave a single peak upon analysis by HPLC (Chiralpak ADH, hexane/2-propanol 98:2, 0.35 mL/min, T = 25 °C, λ = 254 nm) as opposed to the racemic ADBs (**1**) with two peaks (Figure S1, Supporting Information). As shown in Scheme 4, optically pure (*R*,*R*)-diastereomer (**8**) was prepared by asymmetric hydrogenation reaction via dynamic kinetic resolution with excellent enantio- and diastereoselectivities by using the chiral catalyst ($RuCl_2$[(*S*)-(DM-SEGPHOS)][(*S*)-DAIPEN]). The absolute stereochemical integrity of the α-carbon center was also maintained when **8** (99% ee) was subjected to Dess–Martin oxidation reaction.[33] Product (*R*)-**1** thus obtained was optically pure.

Capsular host–guest assemblies (2:1) of OA and **1a–d** were formed upon stirring an aliquot of DMSO stock solution of water-insoluble **1a–d** with OA in the ratio of 1:2 in borate buffer solution (pH ∼9). In Figure 1 ^{1}H NMR spectra of the alkyl part of ADB@OA_2 are provided. Evidently, all alkyl proton signals were upfield shifted with respect to that in $CDCl_3$, most dramatically in propyl-, hexyl-, and octyl-substituted ones. This is an indication of inclusion of guests within the OA host.[28] ^{1}H NMR titration experimental data (Figures S2–S5, Supporting Information) as well as the measured diffusion constants by DOSY (diffusion ordered spectroscopy) experiments (Table S1, Supporting Information) suggested the **1a–d** location within the capsule formed by two molecules of OA. During the titration experiments as followed by ^{1}H NMR there was only one set of upfield-shifted signal for the guest molecules, suggesting that there are no free molecules in solution. Furthermore, the chemical shift for the guest molecules was constant independent of the ratio of OA to the guest, suggesting that there is no exchange between free and complexed guest molecules in the NMR time scale.

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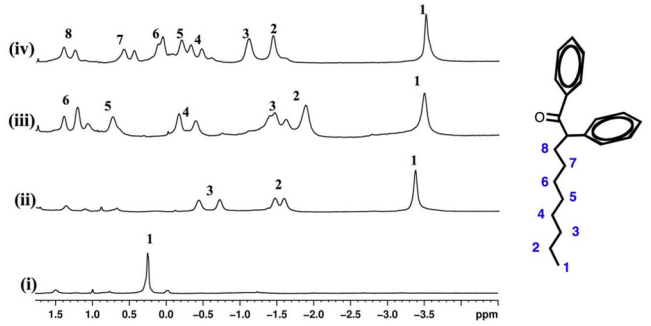

Figure 1. Partial ^{1}H NMR (500 MHz) spectra of various complexes of doexybenzoins with OA: (i) **1a**@OA_2, (ii) **1b**@OA_2, (iii) **1c**@OA_2, and (iv)**1d**@OA_2. The protons of the aliphatic chain of guests are numbered with methyl as 1.

Consistent with the observed chemical shifts of the methyl groups in methyl deoxybenzoin and octyldeoxybenzoin (δ ~0.2 and −3.6 ppm, respectively), the NOESY correlations shown in Figure 2 suggested that the methyl group in the former was closer to the middle region while being buried at the narrower part of the capsule in the latter. Based on the chemical shifts of the methyl and methylene signals and their NOESY correlations with the host OA protons, we believe that the alkyl chains in **1b**, **1c**, and **1d** were linearly placed along the long axis of the capsule (Figures S6−S11, Supporting Information). Based on the above data, we visualized that increasing chain length (methyl, propyl, hexyl and octyl) would decrease the free volume of the capsular assembly and consequently limit the freedom of the guest molecules therein (i.e., methyl deoxybenzoin would be more mobile than octyl deoxybenzoin) and be reflected in the product distribution upon excitation of the ADBs@OA_2

In Table 1, results of photolysis of (*R*)-ADBs in benzene and (*R*)-ADBs@OA_2 in borate buffer solution are presented. Consistent with literature reports all four ADBs gave products of Type I reaction in benzene (Scheme 3).[20,24,26,27,34] As expected, while methyl deoxybenzoin (**1a**) did not give Type II products, ADBs **1b**−**d** gave products of both Type I and Type II reactions. The alkyl chain-length dependent photochemistry of ADBs@OA_2 was significantly different from that in benzene. Notably unlike in solution, methyl and propyl deoxybenzoins (**1a** and **1b**) within OA underwent Type I reaction yielding rearrangement product **6** (Scheme 3). On the other hand, capsule included **1c** and **1d** upon excitation preferentially yielded Type II products (**2** and **3**, Table 1). No rearrangement products of the starting ketone were detected by GC analysis. We believe these observations result from the influence of the OA capsule on the conformation of ADBs' alkyl chain in a manner similar to that of the α-alkyl dibenzyl ketones.[19]

To fully understand the influence of OA on the products distribution in the above systems, we irradiated optically pure **1a**−**d** included within OA capsule for 10 min (conversion was less than 20%) under identical conditions and analyzed the

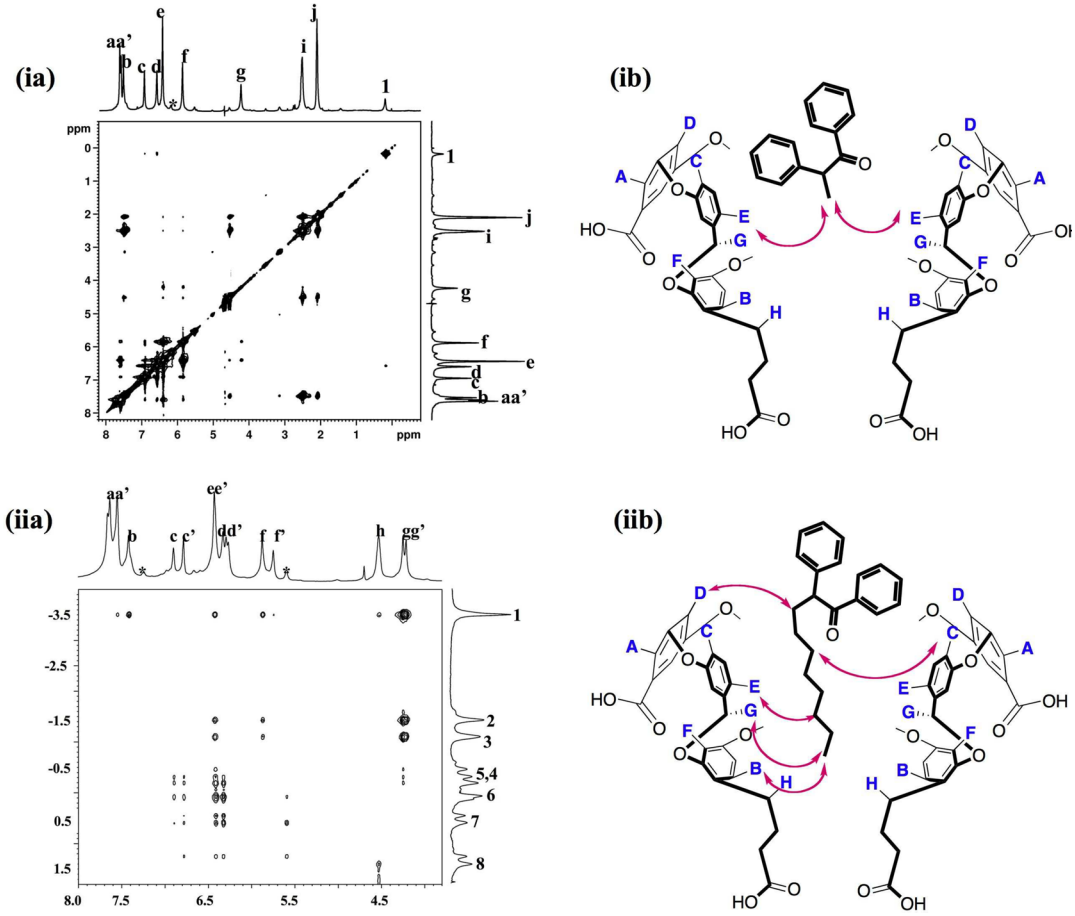

Figure 2. (Left) Comparison of NOESY correlations of (ia) **1a**@OA_2 and (iia) **1d**@OA_2. (Right) Pictorial representation of the NOESY interactions in the above systems is shown in (ib) and (iib).

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Table 1. Product Distribution upon Photolysis of α-ADBs in Benzene and as Complexes within the Capsule in Borate Buffer

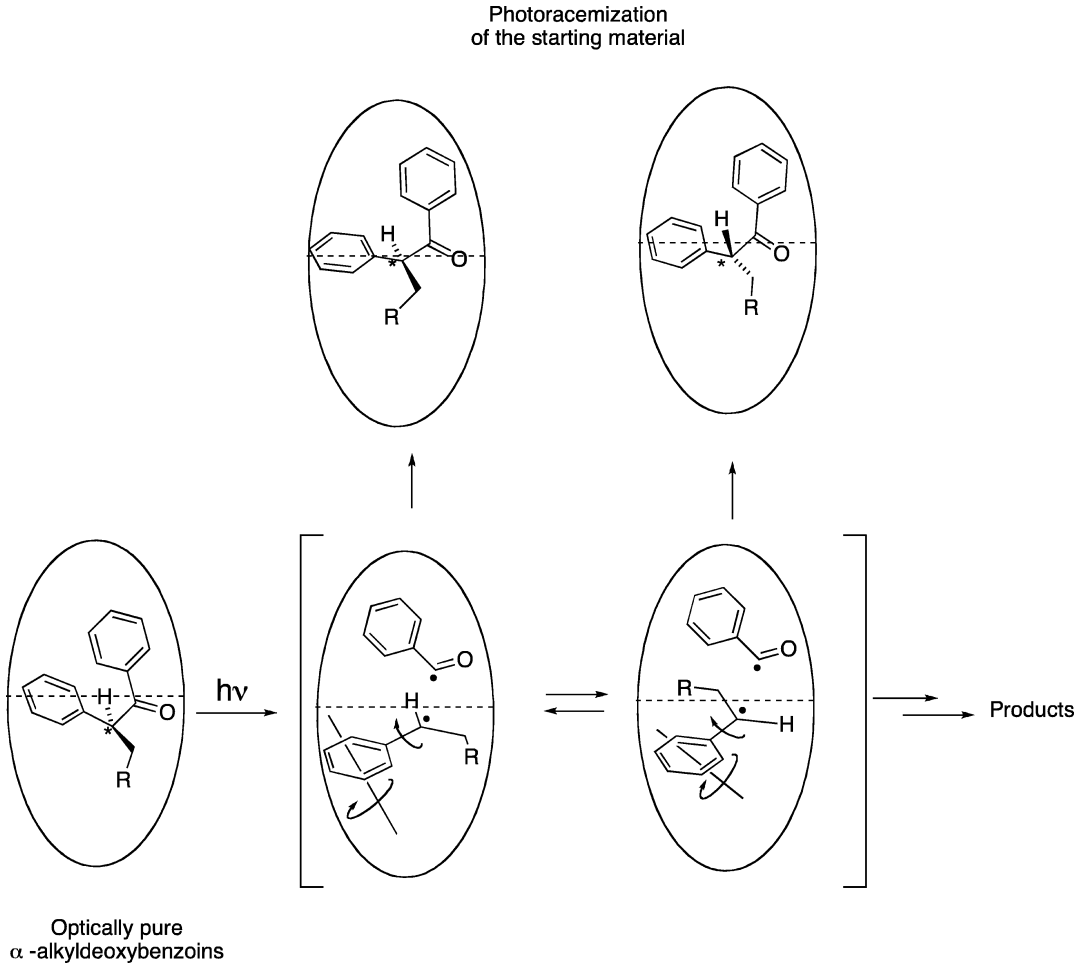
alkyldeoxybenzoin/medium[a]	type I products			type II products		composition of optical isomers[b,c]	
	4	**5**	**6**	**2**	**3**	*R* isomer	*S* isomer
1a/benzene	26	74				95	5
1a@OA_2/buffer			100			75	25
1b/benzene	12	17		54	17	96	4
1b@OA_2/buffer			60	34	6	80	20
1c/benzene	12	24		36	32	96	4
1c@OA_2/buffer				83	17	84	16
1d/benzene	6	49		24	21	96	4
1d@OA_2/buffer				46	54	88	12

[a]The samples were irradiated in Pyrex tubes (>280 nm) using a medium-pressure Hg lamp for 10−30 min (to ensure at least 20−25% conversion); all products were analyzed by GC using an HP-5 column. [b]To begin, all chiral alkyl deoxybenzoins were of 99% optical purity. [c]Analyzed by HPLC (Chiralpak ADH, hexane/2-propanol 98:2, 0.35 mL/min, T = 25 °C, λ = 254 nm).

optical purity of the isolated reactant ketones by HPLC (Chiralpak ADH column). We hypothesized Type I cleavage as illustrated in Scheme 5 would lead to racemization of the optically pure ketone provided the OA capsule did not prohibit the rotational motion of the radical pair resulting via the Type I process and keeps them within the capsule.

Upon examination of the results obtained upon photolysis of optically pure ADBs presented in Table 1, one should note three important observations: (a) Consistent with literature reports there was very little racemization when the ketones were irradiated in benzene.[20] (b) When the ADBs included in OA capsule were irradiated the optical purity of the ketone was lost in all cases. (c) The extent of loss of optical purity was dependent on the alkyl chain length. For example, under identical conditions and irradiation timing α-methyldeoxybenzoin racemized more readily (24% *S*-isomer) than α-octyldeoxybenzoin (12% *S*-isomer). The racemization of **1c** and **1d** despite not giving any rearrangement product **6** via recombination of the primary radical pair (benzoyl−alkyl benzyl radical pair) clearly suggested that enhancement of the Type II products within OA was not entirely due to suppression of the Type I reaction. These results imply that the influence of OA capsule on product distribution occurs by controlling the conformation of the reactant ketone and not by prohibiting the Type I process. The 100% rearranged product yield from α-methyl deoxybenzoin and none from α-octyl deoxybenzoin is suggestive of the importance of the free space within the cavity in controlling the behavior of the radical pair. The definition of free space within a reaction cavity formed by an organized assembly is illustrated in a cartoon fashion in Figure 3.[35] The long α-octyl benzyl radical nearly filling the

Scheme 5. Photoracemization of α-Alkyldeoxybenzoins Occurring within the Capsular Assembly of OA



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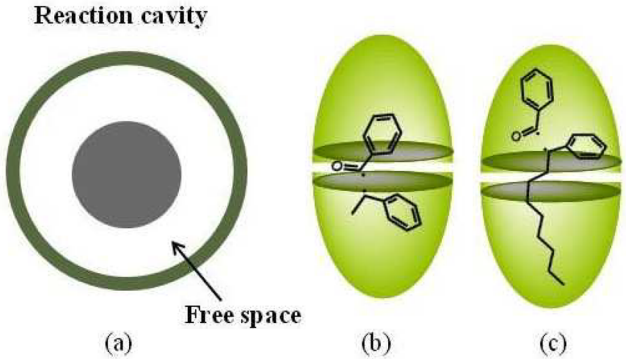

Figure 3. Cartoon representation of the reaction cavity in an organized assembly. (a) General representation showing the reaction cavity and the guest inside. Available free space following the occupation of the guest is projected with a white space indicated by an arrow. (b) Capsule has more free space when α-methyl deoxybenzoin is the guest. (c) Capsule has less free space when α-octyl deoxybenzoin is the guest.

entire cavity very likely could not tumble within the capsule as freely as the small α-methyl benzyl radical and proceeded through a Type I reaction to yield the starting ketone. For easy visualization, the variation of free space with alkyl chain length is illustrated in Figure 3.

The rearrangement of the primary Norrish Type I radical pair could occur by tumbling of the α-alkyl benzyl radical or sliding of the benzoyl radical within the capsule. Both motions require free space within the capsule. The availability of the free space within the capsule is dependent on the length of the alkyl chain. Once the capsule is filled by the alkyl chain of the guest as in the case of α-octyl deoxybenzoin neither of these motions are likely. The absence of rearranged product **6** in the case α-octyl deoxybenzoin is supportive of this model. Epimerization of optically pure α-octyl deoxybenzoin in spite of the absence of rearrangement product suggests that rotational motion of the radical pair along the long axis of the capsule is not prohibited although tumbling and sliding of the radical pair seem to be curtailed. To gain better insight into the role of the length of the alkyl chain on the racemization process quantum yield data would be needed that we do not have at this stage.

SUMMARY

The above photochemical studies have established that the OA capsule holds the primary radical pair generated by the Type I process for longer than 10^{-8} s, a period long enough for the triplet radical pair to undergo intersystem crossing. In this time period the α-alkyl benzyl radical tumbles and rotates to yield the racemic reactant and rearranged product. The extent of product formation via Type I and Type II reactions within the capsule is dictated by the length of the α-alkyl chain that determines the available free space within the capsule and also the conformation of the reactant ketone. All molecules independent of the chain length underwent racemization suggesting that the radical pair generated by the Norrish Type I reaction has enough free space to tumble and rotate within the confined space. Dependence of racemization on the alkyl chain length highlights the role of the available free space on rotational mobility with the reaction cavity. The current study has unequivocally established the value of confining molecules within a molecular container to achieve selectivity in photoreactions. This study also brings out the value of classical photochemical investigations with optically pure organic molecules in understanding the molecular motions in confined spaces. This approach along with NMR and molecular modeling could be of great value in understanding time-dependent host–guest structures.

EXPERIMENTAL SECTION

Materials and Methods. Octa acid was synthesized according to the reported procedure.[16] Racemic as well as chiral guest molecules (**1a–d**) were prepared by adopting the procedure detailed below.[25]

General Synthetic Protocol for Chiral α-Alkyl Deoxybenzoin. *Synthesis of* ***1****.* To a suspension of potassium *tert*-butoxide (1.85 g, 16.5 mmol) in tetrahydrofuran (THF) was added a solution of deoxybenzoin (**2**) (2.5 g, 12.7 mmol, 1 equiv) in THF dropwise over a period of 45 min at 0 °C. Iodoalkane (1.1 equiv) solution in THF was added gradually to keep the internal temperature <3 °C. The reaction was then allowed to warm to room temperature. After 2 h of stirring at room temperature, the reaction mixture was slowly quenched with 2 N HCl and diluted with ethyl acetate. The aqueous layer was removed and the organic layer washed with water and brine and purified by flash chromatography (ethyl acetate/hexane).

Synthesis of ***8****.*[25] In a glovebox, chiral catalyst ($RuCl_2$[(*S*)-(DM-SEGPHOS)][(*S*)-DAIPEN]) (0.015 g, 0.012 mmol, 0.001 equiv), potassium *tert*- butoxide (0.22 g, 0.2 mmol), and 2-propanol (3 mL) were mixed together in a flask and stirred at room temperature for 2 h. The resulting activated yellow catalyst solution was charged into a hydrogenation glass reactor vessel, and a solution of α-alkyl deoxybenzoin (1 equiv) in 2-propanol (13 mL) was added to it. The vessel was capped and hydrogenated at 100 psi hydrogen for 40 h at 25 °C. The reaction mixture was treated with 0.5 g of Norit-A decolorizing carbon and stirred at room temperature for 40 min. The mixture was filtered over a Celite pad and washed with 10 mL of 2-propanol. The volume of 2-propanol was adjusted to about 40 mL. To this 80 mL of H_2O was added slowly over 45 min to crystallize the product. The resultant slurry was filtered by gravity filtration (without applying vacuum) and washed with 1:2 2-propanol/H_2O (40 mL), and the wet cake was air-dried and further dried in high vacuum to afford *anti*-**8** (*R,R* diastereomer).

*Synthesis of (R)-(−)-****1****.*[33] (1*R*,2*R*)-1,2-Diphenylalkan-1-ol (1 equiv) was dissolved in dichloromethane, Dess–Martin periodinane (1.4 equiv) was added, and the mixture stirred for 45 min at room temperature. The reaction mixture was filtered over a Celite pad, and the filtrate was washed with sodium bicarbonate solution. The resultant organic layer was distilled to yield an off-white crystalline solid.

HPLC Analysis. Chiralpak AD-H, hexane/ethanol 98/2, 0.35 mL/min, T = 25 °C, λ = 254 nm. Retention times of racemic mixture (**1a**): 23.4 and 26.9 min, chiral (**1a**): 26.9 min. Retention times of racemic mixture (**1b**): 19.8 and 22.5 min, chiral (**1b**): 22.5 min. Retention times of racemic mixture (**1c**): 19.7 and 21.6 min, chiral (**1c**): 21.7 min. Retention times of racemic mixture (**1d**): 18.9 and 20.9 min, chiral (**1d**): 21.0 min (Figure S1, Supporting Information).

^{1}H NMR and MS Data of the Guests. All ^{1}H NMR spectra were recorded on a 500 MHz NMR spectrometer. ESI-MS spectra were obtained using mass spectrometers equipped with time-of-flight (TOF) and ion trap analyzers.

1a: (300 MHz, $CDCl_3$) δ 8.04 (d, 2H), 7.22–7.50 (m, 8H), 4.57 (t, 1H), 1.69 (d, 3H); HRMS (ESI-LC-MS) solution of **1a** in hexane/acetone/acetonitrile (25:25:50) + 0.1% formic acid) calcd $C_{15}H_{14}O$ $[M + Na]^+$ 233.0942, found 233.0917.

1b: (300 MHz, $CDCl_3$) δ 7.95 (d, 2H), 7.15–7.46 (m, 8H), 4.53 (t, 1H), 2.15 (m, 1H), 1.80 (m, 1H), 1.28 (m, 2H), 0.90 (t, 3H); HRMS (ESI-LC-MS) solution of **1b** in hexane/acetone/acetonitrile (25:25:50) + 0.1% formic acid) calcd $C_{17}H_{18}O$ $[M + Na]^+$ 261.1255, found 261.1239.

1c: (300 MHz, $CDCl_3$) δ 8.04 (d, 2H), 7.26–7.62 (m, 8H), 4.65 (t, 1H), 2.24 (m, 1H), 1.90 (m, 1H), 1.35 (m, 8H), 0.89 (t, 3H); HRMS (ESI-LC-MS) solution of **1c** in hexane/acetone/acetonitrile (25:25:50) + 0.1% formic acid), calcd $C_{20}H_{24}O$ $[M + Na]^+$ 303.1725, found 303.1714.

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1d: (300 MHz, $CDCl_3$) δ 8.02 (d, 2H), 7.22−7.59 (m, 8H), 4.62 (t, 1H), 2.26 (m, 1H), 1.87 (m, 1H), 1.35 (m, 12H), 0.88 (t, 3H); HRMS (ESI-LC-MS) solution of **1d** in hexane/acetone/acetonitrile (25:25:50) + 0.1% formic acid) calcd $C_{22}H_{28}O$ $[M + Na]^+$ 331.2030, found 331.2021.

Procedure for Preparation of Octa Acid−guest Complex, Photolysis and Analysis of Photoproducts. Stock solution of the guest (**1a−d**) was prepared in DMSO-d_6. Octa acid solution (5 mM) was prepared in sodium tetraborate buffered D_2O. Aliquots of the guest solution were added to octa acid solution maintaining a host−guest ratio of 2:1, and the solution was sonicated for 30 min. NMR analysis of the solution showed formation of a complex. The solution was then bubbled with nitrogen for 30 min and irradiated using a medium-pressure Hg lamp for 10−30 min (to ensure at least 20−25% conversion). The photoproducts were extracted from the aqueous solution with chloroform and the organic layer was analyzed by GC. Retention times of each guest and its products are as given below.

Substrate ***1a***. Column: HP-1, temperature program: initial temp, 70 °C; initial time, 1 min; rate, ramp 10 °C/min; ramp ends, 220 °C; ramp time, 1 min; rate, 3 °C/min final temp, 270 °C; final time, 10 min. Retention times: **1a**, 14.00 min; **4**, 14.93 min; **5a**, 12.56, 12.913 min; **6a**, 15.52 min. Irradiation time: 15 min.

Substrate ***1b***. Column: HP-1, temperature program: initial temp, 70 °C; initial time, 1 min; rate, ramp 10 °C/min; ramp ends, 220 °C; ramp time, 1 min; rate, 3 °C/min final temp, 270 °C; final time, 10 min. Retention times: **1b**, 17.99 min; **2b**, 15.78 min; **3**, 14.13 min; **4**, 14.93 min; **5b**, 16.19, 16.39 min; **6b**, 18.01 min. Irradiation time: 15 min.

Substrate ***1c***. Column: HP-1, temperature program: initial temp, 70 °C; initial time, 1 min; rate, ramp 10 °C/min; ramp ends, 220 °C; ramp time, 1 min; rate, 3 °C/min final temp, 270 °C; final time, 10 min. Retention times: **1c**, 19.42 min; **2c**, 19.49, 19.69 min; **3**, 14.13 min; **4**, 14.93 min; **5c**, 22.27, 23.14 min. Irradiation time: 15 min.

Substrate ***1d***. Column: HP-1, temperature program: initial temp, 70 °C; initial time, 1 min; rate, ramp 10 °C/min; ramp ends, 220 °C; ramp time, 1 min; rate, 3 °C/min final temp, 270 °C; final time, 10 min. Retention times: **1d**, 22.23 min; **2d**, 22.29, 22.52 min; **3**, 14.13 min; **4**, 14.93 min; **5d**, 26.14, 26.45 min. Irradiation time: 15 min.

GC−MS (EI) (*m*/*z*, relative intensities) of photoproducts: GC−MS analysis. GC−MS analyses were performed on a GC instrument fitted with a HP-5 column and EI detector. **1a**: 210 (M^+, 6), 196 (11), 105 (100), 91 (15). **1b**: 238 (M^+, 2), 196 (10), 165 (2), 105 (100), 91 (32). **1c**: 280 (M^+, 1), 196 (55), 176 (45), 134 (100), 120 (30), 105 (16), 91 (14). **1d**: 308 (M^+, 1), 196 (8), 134 (16), 105 (100), 91 (39). **3**: 196 (M^+, 3), 105 (100), 91 (8). **2b**: 238 (M^+, 0), 221 (8), 196 (67), 148 (100), 133 (45), 105 (85), 91 (28). **2c**: 280 (M^+, 1), 262 (3), 196 (61), 148 (100), 133 (45), 105 (71), 91 (31). **2d**: 308 (M^+, 0), 291 (11), 205 (4), 196 (51), 148 (100), 133 (49), 105 (63), 91 (41). **6a**: 210 (M+, 10), 181 (100), 105 (45). **6b**: 238 (M+, 14), 196 (20), 181 (100), 105 (35).

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR titration spectra, 2-D COSY and NOESY spectra of host−guest complexes. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

†This paper is dedicated to the memory of Professor N. J. Turro, an outstanding teacher and selfless mentor.

■ REFERENCES

(1) Whitten, D. G.; Russell, J. C.; Schmehl, R. H. *Tetrahedron* **1982**, *38*, 2455.
(2) Ramamurthy, V. *Photochemistry in Organized & Constrained Media*; VCH: New York, 1991.
(3) *Supramolecular Photochemistry*; Ramamurthy, V.; Inoue, Y., Eds.; John Wiley: Hoboken, 2011.
(4) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530.
(5) Schmidt, G. M. J.et al. *Solid State Photochemistry*; Ginsberg, D., Ed.; Verlag Chemie: New York, 1976.
(6) Breslow, R. *Science* **1982**, *218*, 532.
(7) *Artificial Enzymes*; Breslow, R., Ed.; Wiley-VCH: Weinheim, 2005.
(8) *Molecular Encapsulation*; Brinker, U. H., Mieusset, J.-L., Eds.; John Wiley & Sons: Chichester, 2010.
(9) Masson, E.; Ling, X.; Joseph, R.; Mensah, L.-K.; Lu, X. *RSC Adv.* **2012**, *2*, 1213.
(10) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844.
(11) Inokuma, Y.; Kawano, M.; Fujita, M. *Nature Chem.* **2011**, *3*, 349.
(12) Murase, T.; Fujita, M. *Chem. Rec.* **2010**, *10*, 342.
(13) Arumugam, S.; Kaanumalle, L. S.; Ramamurthy, V. *J. Photochem. Photobiol.* **2007**, *185*, 364.
(14) Kaliappan, R.; Kaanumalle, L. S.; Natarajan, A.; Ramamurthy, V. *Photochem. Photobiol. Sci.* **2006**, *5*, 925.
(15) Pemberton, B. C.; Raghunathan, R.; Volla, S.; Sivaguru, J. *Chem.—Eur. J.* **2012**, *18*, 12178.
(16) Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2004**, *126*, 11408.
(17) Choudhury, R.; Gupta, S.; Da Silva, J. P.; Ramamurthy, V. *J. Org. Chem.* **2012**, DOI: 10.1021/jo301499t.
(18) Porel, M.; Chuang, C.-H.; Burda, C.; Ramamurthy, V. *J. Am. Chem. Soc.* **2012**, *134*, 14718.
(19) Gibb, C. L. D.; Sundaresan, A. K.; Ramamurthy, V.; Gibb, B. C. *J. Am. Chem. Soc.* **2008**, *130*, 4069.
(20) Step, E. N.; Buchachenko, A. L.; Turro, N. J. *J. Org. Chem.* **1992**, *57*, 7018.
(21) Kaanumalle, L. S.; Gibb, C. L. D.; Gibb, B. C.; Ramamurthy, V. *J. Am. Chem. Soc.* **2004**, *126*, 14366.
(22) Sundaresan, A. K.; Ramamurthy, V. *Photochem. Photobiol. Sci.* **2008**, *7*, 1555.
(23) Jayaraj, N.; Jockusch, S.; Kaanumalle, L. S.; Turro, N. J.; Ramamurthy, V. *Can. J. Chem.* **2011**, *89*, 203.
(24) Reddy, G. D.; Ramamurthy, V. *J. Org. Chem.* **1987**, *52*, 5521.
(25) Chung, J. Y. L.; Mancheno, D.; Dormer, P. G.; Variankaval, N.; Ball, R. G.; Tsou, N. N. *Org. Lett.* **2008**, *10*, 3037.
(26) Lewis, D. F.; Magyar, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 5973.
(27) Lewis, F. D.; Lauterbach, R. T.; Heine, H. G.; Hartmann, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519.
(28) Jayaraj, N.; Zhao, Y.; Parthasarathy, A.; Porel, M.; Liu, R. S. H.; Ramamurthy, V. *Langmuir* **2009**, *25*, 10575.
(29) Kulasekharan, R.; Jayaraj, N.; Porel, M.; Choudhury, R.; Sundaresan, A. K.; Parthasarathy, A.; Ottaviani, M. F.; Jockusch, S.; Turro, N. J.; Ramamurthy, V. *Langmuir* **2010**, *26*, 6943.
(30) Tang, H.; de Oliveira, C. S.; Sonntag, G.; Gibb, C. L. D.; Gibb, B. C.; Bohne, C. *J. Am. Chem. Soc.* **2012**, *134*, 5544.
(31) Porel, M.; Jayaraj, N.; Kaanumalle, L. S.; Maddipatla, M. V. S. N.; Parthasarathy, A.; Ramamurthy, V. *Langmuir* **2009**, *25*, 3473.
(32) Chen, J. Y. C.; Jayaraj, N.; Jockusch, S.; Ottaviani, M. F.; Ramamurthy, V.; Turro, N. J. *J. Am. Chem. Soc.* **2008**, *130*, 7206.
(33) Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7549.

(34) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Org. Chem.* **1990**, *55*, 5269.
(35) Parthasarathy, A.; Ramamurthy, V. *Photochem. Photobiol. Sci.* **2011**, *10*, 1455.