Pulse Radiolysis. The pulse radiolysis apparatus, which makes use of 5-ns electron pulses from Notre Dame ARCO linear accelerator (8 MeV, $\sim 10^{17}$ eV/g per pulse) and allows spectrophotometric observation of transients on microsecond-to-second time scales, is described elsewhere.[27,28]

Registry No. **1a**, 110971-39-6; **1b**, 96555-76-9; **1c**, 110971-40-9; **1d**, 110971-41-0; **1e**, 110971-42-1; **1f**, 111004-89-8; **7**, 110971-45-4; **8a**, 110971-44-3; **8b**, 96555-83-8; **8d**, 110971-48-7; **9**, 111004-90-1; **10**, 96555-79-2; **13d**, 110971-47-6; **13e**, 110971-49-8; **13f**, 110971-50-1; **15b**, 110971-46-5; DTBN, 2406-25-9; DBA, 1087-09-8; O_2, 7782-44-7; ferrocene, 102-54-5; 9-(hydroxymethyl)anthracene, 1468-95-7; 9-(phenylmethyl)anthracene, 1498-71-1; 9-cyclopentylanthracene, 110971-43-2; 9-isopropylanthracene, 1498-80-2; 9-cyclohexylanthracene, 4368-48-3.

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Modification of Photochemical Reactivity by Cyclodextrin Complexation: A Remarkable Effect on the Photobehavior of α-Alkyldibenzyl Ketones

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The Norrish type I and type II reactions of cyclodextrin-included α-alkyldibenzyl ketones have been investigated in the aqueous solution and in the solid state. The photolysis of solid cyclodextrin complexes led to a single product, diphenylethane (AB), and that of complexes in the aqueous solution resulted in a product arising from the rearrangement of α-alkyldibenzyl ketones. Conformational and super-cage effects are proposed to be responsible for the dramatic alteration observed in the above photobehavior. The difference in the product distribution between solid and solution complexes is attributed to the differences in the restriction imposed by the host on the translational motions of the geminate radical pairs.

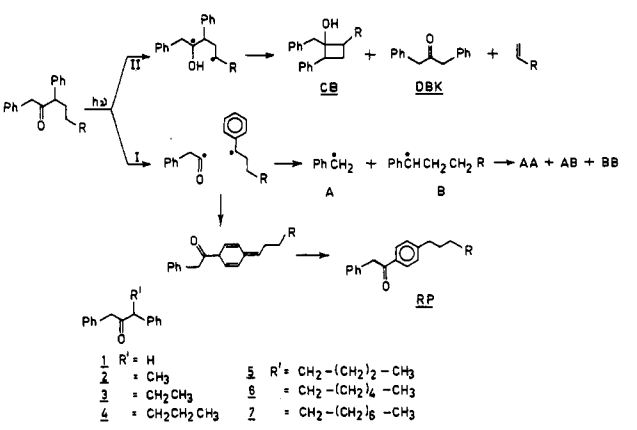
During the last few years, our group has been investigating the influence of cyclodextrin cavity on the photochemical reactions in host–guest complexes.[1,2] The goal is to achieve selectivity in photochemical reactions using this unusual environment and to understand the features controlling such selectivity. During one such study a remarkable effect was observed on the photoreactivity of benzoin alkyl ethers and alkllkyldeoxybenzoins upon cyclodextrin complexation.[3] This was attributed to a combination of the "cage effect" and "conformational control" afforded by the cyclodextrin.

In order to explore the general utility of the "conformational control" and the "cage effect" offered by cyclodextrin in modifying photoreactions, we have investigated the photobehavior of dibenzyl ketones **1–7** (Scheme I). The photolysis of dibenzyl ketones has been explored extensively in several anisotropic environments.[4] We envisioned that cyclodextrin encapsulation of **3–7** can impose a conformational control on these substrates and thus alter the type I and the type II product distributions with respect to an isotropic medium. Further, we noted that the cavity might have an impact on the diffusional separartion of the radical pairs resulting from the type I process and also on the choice of reactions that these radical pairs might undergo. The results of such a study are presented below.

Results

Photolysis of dibenzyl ketones **3–7** in nitrogen-saturated benzene and methanol gave products resulting from the Norrish type I and the type II reactions. A statistical

Scheme I



mixture of the coupling products AA, AB, and BB (1:2:1) resulting from the photodecarbonylation were major and those from the γ-hydrogen abstraction minor (~15%). Expectedly, from **3–7**, the products resulting from the

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Table I. Product Distribution upon Irradiation of α-Alkyldibenzyl Ketones under Various Conditions

medium	% of type I products[a] AA	AB	BB	RP	% of type II products[b] DBK	CB
α-Ethyldibenzyl ketone (3)						
benzene	21	44	20		13	
methanol	22	43	21		13	
β-cyclodextrin (aq) 1:10, N_2	1	46	1	49		
β-cyclodextrin (solid) H:G = 1:1		100				
α-Propyldibenzyl ketone (4)						
benzene	22	45	21		4	7
methanol	21	39	19		4	8
β-cyclodextrin (aq) 1:10	1	39	1	59		
β-cyclodextrin (solid) H:G = 1:1		100				
α-Butyldibenzyl ketone (5)						
benzene	16	38	17		4	8
methanol	17	35	17		6	7
β-cyclodextrin (aq) 1:10	1	35	1	63		
β-cyclodextrin (solid) H:G = 1:1		100				
α-Hexyldibenzyl Ketone 6[b]						
benzene	24	52	24		5	7
β-cyclodextrin (aq) 1:10		23		77		
β-cyclodextrin (solid)		100				
α-Octyldibenzyl Ketone 7[b,c]						
benzene	25	53	21		6	6
β-cyclodextrin (solid)		100				

[a] For details of structures, see Scheme I; product yield based on GC analysis; error limit ±5%. [b] Type II products were not characterized [c] β-Cyclodextrin complex of α-octyldibenzyl ketone and other higher homologues were not soluble in water. Therefore, aqueous solution irradiation could not be conducted.

γ-hydrogen abstraction were also obtained. Both cyclization and elimination products of the type II 1,4-diradical were isolated from **4–7**, whereas **3** gave only the elimination product—dibenzyl ketone. The cyclobutanols were characterized on the basis of their spectral properties. No products resulting from rearrangement of the type I primary radical pair were isolated. The photobehavior of **1** and **2** have already been reported[5] and the same were observed in this study too. Based on the established behavior of **1** and **2**, we assume that **3–7** also react from their lowest $n\pi^*$ triplet state.[6]

The photolysis of solid cyclodextrin complexes of **1–7** gave exclusively the diphenylethane (AB) in quantitative yield. The presence of oxygen did not influence the reaction. More remarkably, the cyclodextrin complexes of **1–7** behaved differently in aqueous solution from that in the solid state. The products under this condition, although resulted from the same primary process—the Norrish type I as in the solid state—the rearranged product was the major component in the product mixture.[7,8] The results of irradiations of **1–7** in various media are summarized in Tables I and II.

The formation of the coupling product AB in aqueous cyclodextrin solution was most suprising. Initially, we

Table II. Product Distribution upon Irradiation of Dibenzyl Ketone and α-Methyldibenzyl Ketone under Various Conditions

medium	% of type I products[a] AA	AB	BB	RP
Dibenzyl Ketone (1)				
benzene	100			
methanol	100			
β-cyclodextrin (aq) 1:10; N_2	19			81
β-cyclodextrin (aq) 1:10; O_2	21			78
β-cyclodextrin (aq) 1:10; $CuCl_2$ (1:100)[b]	25			75
β-cyclodextrin (solid)	100			
α-Methyldibenzyl Ketone				
benzene	24	51	25	
methanol	25	52	23	
β-cyclodextrin (aq) 1:10; N_2	2	35	2	61
β-cyclodextrin (aq) 1:10; O_2	2	37	2	60
β-cyclodextrin (solid)	1	96	1	2

[a] For structures of products, see Scheme I; product yield based on GC analysis; error limit ±5%. [b] $CuCl_2$ was used in excess, mole ratio was 1:100, even at lower mole ratio no variation in product distribution was observed.

Table III. Product Distribution upon Irradiation of β-Cyclodextrin Complex of α-Hexyldibenzyl Ketone in Aqueous Solution[a]

condition	AA	AB	BB	RP
Variation of H:G Ratio[b]				
H:G 1:1		45		55
2:1		38		82
4:1		29		71
10:1		23		77
Dilution Experiments[c]				
amount of water				
200 mL		95		5
450 mL		76		24
550 mL		56		44
650 mL		38		62

[a] For structures of products, see Scheme I; product yield based on GC analysis; error limit ±5%. [b] Amount of cyclodextrin was increased by maintaining the amount of the guest and water constant. [c] Amount of water was increased by keeping the host/guest ratio constant (1:5); α-hexyldibenzyl ketone, 20 mg; β-cyclodextrin, 300 mg.

suspected that AB resulted from the undissolved suspended solid complexes in aqueous solution. To verify this, dilution experiments were carried out. As seen in Table III, the amount of water used for the reaction had an important influence on the product distribution. The ratio of AB to RP remained unaltered after a particular volume of water, indicating that above a certain volume AB originates only from the dissolved complexes, although with smaller volumes of water solid-suspended complexes contribute significantly toward the high yield of AB. Both cupric chloride and oxygen, established quenchers of radicals, did not have any effect on the product distribution (Table II).

It was also noted that the ratio of AB to RP in aqueous media was slightly dependent on the amount of excess cyclodextrin used (Table III) and on the percent conversion (duration of photolysis). The latter was identified to be due to the disappearance of RP through secondary photoreactions while the former have its origin on the formation of multiple complexes.

The complexes of β-cyclodextrin with dibenzyl ketone and α-ethyldibenzyl ketone (**3**) were chosen as model systems for the structural analyses in aqueous solution. The 270-MHz ^1H NMR spectra of aqueous solutions of β-cyclodextrin and solutions containing various ratios of the host to the guest were recorded. The chemical shifts

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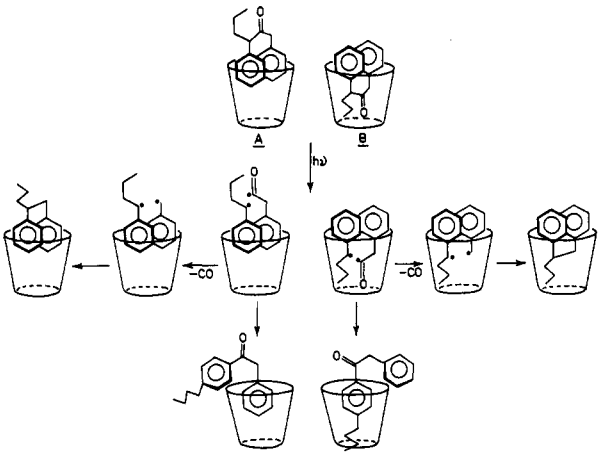
Table IV. 270-MHz ^{1}H NMR Chemical Shifts of β-Cyclodextrin Protons in Complexes[a]

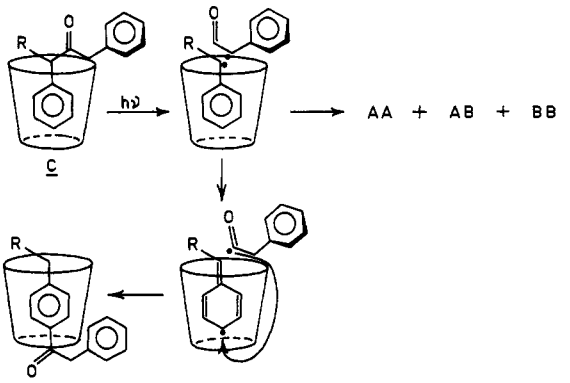
compound	H-1	H-2	H-3	H-4	H-5	H-6
β-cyclodextrin	1359.6	975.7	1059.6	958.4	1030.0	1039.1
β-cyclodextrin complex with dibenzyl ketone	1356.2	976.4	1049.9	960.3	993.3	1029.3
β-cyclodextrin complex with α-ethyldibenzyl ketone	1357.5	976.0	1049.8	960.2	1006.3	1031.2

[a] Chemical shifts are expressed in hertz with reference to Me_4Si; solvent, D_2O.

Scheme II



Scheme III



of β-cyclodextrin protons in the uncomplexed and in the complexed forms were utilized for analysis and are tabulated in Table IV. From Table IV it is evident that the cyclodextrin protons H-1, H-2, and H-4 are virtually unaffected while the inner protons H-3, H-5, and H-6 are shifted upfield to various extents. These upfield shift of protons provide evidence for the inclusion of the guest molecule into the hydrophobic cavity of β-cyclodextrin in aqueous solution. Further support for the inclusion phenomena in the aqueous solution was obtained through the fluorescence emission studies of dibenzyl ketone and α-butyldibenzyl ketone (**5**). Addition of β-cyclodextrin to aqueous solutions of **1** and **5** brought a shift on the fluorescence maxima to shorter wavelength to the extent of 15–25 nm with enhancement of fluorescence intensity. The dissociation constants (K_d) for the complexes of **1** and **5** with β-cyclodextrin in aqueous solution were estimated by making use of the difference in emission intensities in the presence and absence of β-cyclodextrin. The K_d values were quite low (**1**, 8×10^{-4} M^{-1} L, and **5**; 1.4×10^{-5} M^{-1} L), suggesting that β-cyclodextrin forms strong complexes with **1–7**. Evidence for the formation of complexes in the solid state came from the X-ray powder photographs and measurement of host–guest ratios.

Discussion

Although the photobehavior of dibenzyl ketones has attracted a great deal of attention over the last decade,[6,7] no dibenzyl ketones with an α-alkyl chain capable of undergoing both the Norrish type I and type II reactions have been investigated. Following the studies on 1,2-diaryl systems[3] (benzoin ethers and deoxybenzoins), our interest turned to exploring the possible conformational control exerted by cyclodextrin on 1,3-diaryl systems. In this context, α-alkyl dibenzyl ketones **3–7** appeared as suitable substrates.

One could visualize several structures for the cyclodextrin complexes of **1–7** (Schemes II and III). Of these, one class involves inclusion of only one phenyl ring into the cavity, similar to C, and the other similar to A involves inclusion of both the phenyl rings. In addition, inclusion could occur either from the narrower or broader opening of the cavity. Although the results of ^{1}H NMR studies in aqueous solution could be utilized to support either of these classes of structures, we only point out that the ^{1}H NMR results are not inconsistent with the structure B.[3,9] Additional support for structure B comes from the luminescence studies on closely related systems.[10,11] 1-Phenyl-3-naphthylpropan-2-one upon complexation to β- and γ-cyclodextrins was found to yield enhanced excimer emission and the emission was not quenchable by oxygen.[10] This observation and others on related systems[11] suggest that the equilibrium concentration of the eclipsed conformations of 1,3-bichromophoric propanes can be greatly enhanced by inclusion in a cyclodextrin cavity.

Photolysis of Cyclodextrin Complexes in the Solid State. Examination of Tables I and II reveals that the distribution of products of photolysis of cyclodextrin complexes of **1–7** in the solid state is unique and different from that of these complexes in an aqueous solution and from **1–7** in organic solvents. This is remarkable since the photolysis of **3–7** in organic solvents yields products resulting from both the Norrish type I and the type II reactions. In an aqueous cyclodextrin solution, while selectivity is achieved, the major product is different from that in the solid state. The importance of the present observation becomes evident when the results are analyzed in light of the photobehavior of the β-cyclodextrin complexes of benzoin alkyl ethers and alkyldeoxybenzoins. In these two series, the photolysis of cyclodextrin complexes selectively gave products resulting from the Norrish type II hydrogen abstraction,[3] although the Norrish type I products are obtained as major products in organic solvents.

Generally, intramolecular hydrogen abstraction by a carbonyl chromophore is governed by conformational factors, which limit the accessibility of abstractable hy-

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drogens in a given molecule.[3,12] It has been established that the extent of the type II reaction depends upon the probability that the excited triplet can reach a conformation which brings the hydrogen within the bonding distance to the carbonyl oxygen. We propose that cyclodextrin imposes a conformation on α-alkyldibenzyl ketones upon inclusion that is not suitable for γ-hydrogen abstraction. The formation of the coupling product AB in quantitative yield in the solid state is not totally unexpected. The unit cage effect can be the result of either the cavity or the intermolecular packing in the solid state. The translational motion of the benzyl radical pairs (after decarbonylation) would be restricted in the solid state, thus favoring the geminate recombination. Since the formation of RP is facilitated in the aqueous solution (see below) and is not favored in the solid state, we believe that absence of RP in the solid complexes is due to restriction of the rotational motion of the geminate radical pair.

Photolysis of Cyclodextrin Complexes in Aqueous Solution. The most remarkable alteration in the photobehavior of 1–7 was observed upon photolysis of cyclodextrin complexes of 1–7 in the aqueous solution. Among the type I and the type II processes that occur in isotropic solvents, products derived exclusively from the type I α-cleavage were obtained in aqueous cyclodextrin solutions. Most unexpectedly, the rearranged product (RP, Scheme I) constituted a major portion of the product mixture.

On the basis of the experiments outlined in the Results section, the products RP and AB (Scheme I) obtained upon photolysis of 1–7 in aqueous solution containing an excess of cyclodextrin are thought to derive from those inclusion complexes dissolved in water. The absence of the type II products in aqueous solution is believed to be due to the inclusion of 3–7 in a conformation that is unsuitable for the γ-hydrogen abstraction into the hydrophobic cavity of the cyclodextrin. The preference for the formation of products resulting from the "cage effect" (AB and RP, Scheme I) is found to be general in this series. We believe that the selective formation of AB provides an important clue to the nature of modification imposed by cyclodextrin on the photobehavior of 1–7.

Had the structure of the inclusion complex been C (Scheme III) with only one phenyl ring included in the cavity of the cyclodextrin, the photolysis would result in diffusion of one fragment of the molecule into the aqueous phase following α-cleavage leading to a statistical distribution of the radical coupling products AA, AB, and BB. Moreover, complex C would not be expected to yield RP, as the formation of such a product requires a "super-cage effect" which cannot be provided by C. The absence of quenching by O_2 and cupric chloride further rule out the structure C for the inclusion complex of β-cyclodextrin with 1–7.

However, the selective formation of AB and RP can be understood on the basis of structure A and/or B (Scheme II). The proposed mechanism for formation of the isomeric 1–7 (RP) is illustrated in Scheme II. The primary geminate triplet radical pair (before decarbonylation) is compelled to undergo self-reaction rather than diffusion and decarbonylation. Radical coupling may occur to regenerate α-alkyldibenzyl ketones themselves. Since this would regenerate the starting material, it would not be observed in normal product analysis. Coupling of the acyl radical to the benzene ring of the benzyl radical would lead to an isomeric 1–7. Further, decarbonylation results in the benzyl radical fragments A^0 and B^0 trapped in the cavity of cyclodextrin. Combination of these, before diffusion, results selectively in AB. The absence of any cupric chloride trapped products (even at very high concentrations of cupric chloride) suggests that both the primary and secondary radical pairs do not escape into the aqueous phase and that they spend their entire lifetime within the hydrophobic cavity of the cyclodextrin.

The results on dibenzyl ketones presented here clearly establish that the cyclodextrin cavity can impose unique restrictions and bring about remarkable alterations on the photobehavior of the molecules included. It is important to note that the photobehavior of dibenzyl ketones have been extensively studied in various ordered and/or constrained media. Such a dramatic alteration especially in the primary step has hitherto not been reported in any media. This clearly calls for further extensive study on the utilization of cyclodextrin as a reaction medium.

Experimental Section

β-cyclodextrin obtained from Aldrich was used as received. Dibenzyl ketone (Aldrich) was twice distilled prior to use. The α-alkyldibenzyl ketones 2–7 were prepared by following the literature procedures[13] and purified by column and thin layer chromatography (silica gel, hexane/chloroform) prior to use. Doubly distilled water and distilled solvents were used.

^{1}H NMR spectra were recorded on a Bruker WH 270-MHz NMR spectrometer. Powder diffractograms were recorded on a Phillips X-ray powder diffractometer equipped with Cu Kα radiation. Vapor chromatographic analyses were carried out on a Chemito gas chromatograph (Model 3800) using a 5% SE-30 column (8 ft × $^1/_8$ in.). Absorption and emission spectra were recorded on a Shimadzu UV-180 spectrometer and Shimadzu spectrofluorometer (Model RF 540), respectively.

Preparation and Characterization of β-Cyclodextrin Complexes. To an aqueous solution of β-cyclodextrin (0.05 M, 10 mL) were added equimolar amounts of the guest ketones 1–7, and the solutions were magnetically stirred for 24 h at room temperature. The white precipitate thus obtained was filtered, washed with cold water several times, and dried at 50 °C for 4–5 h. Aqueous solutions of β-cyclodextrin complexes were prepared by dissolving the above microcrystalline complexes in sufficient amount of water (200 mL). Generally, these complexes were less soluble in water compared to the cyclodextrin complexes of benzoin ethers, phenyl esters, and aryl alkyl ketones. Vigorous stirring and slight warming were required to obtain transparent solutions suitable for photolysis. For solid irradiations the microcrystalline materials were used as such.

The X-ray powder diffractograms of β-cyclodextrin and complexes of β-cyclodextrin and ketones 1–7 were recorded. The guest ketones were liquids. The powder photographs of the complexes were different from that of β-cyclodextrin. On this basis it was concluded that inclusion complexes between cyclodextrin and the guest ketones 1–7 have been formed.

^{1}H NMR spectra of D_2O solutions containing 10 equiv of ketone (1.1×10^{-2} M of 1 and 3) and 1 equiv of β-cyclodextrin (1.0×10^{-3} M) were recorded on a Bruker WH 270-MHz FT NMR spectrometer. The guest-induced shift in the cyclodextrin protons were computed by comparing the above spectra with that of pure cyclodextrin. Spectra were also recorded for solutions containing varying ratios of the guest and the host.

The host/guest ratios of solid inclusion complexes were determined by gravimetry and by GC analysis. The amount of guest ketones 1–7 present in a known amount of the complex were determined by GC integration of the guest peak with respect to the added internal standard (diphenylethane) and by weighing the extracted ketone. The measured host/guest ratios are presented in Tables I and II.

The stability constants for the complexes of 1 and 5 were determined by spectrofluorometry. Since there was no observable change in the absorption spectra of the guest molecules after

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inclusion, the variation in the fluorescence intensity was monitored. Stock solutions of 1.1×10^{-2} M of 1 and 5 were prepared in methanol. Small portions (30 μL) of the stock solution were added to 10-mL standard flasks containing varying amounts of β-cyclodextrin solution (4–8 mL of 10^{-3} M stock solution). These solutions were made up to 10 mL and magnetically stirred well for 24 h. Fluorescence emission spectra ($\lambda_{excitation}$ = 310 nm) were recorded and emission intensity at 390 nm was used for the stability constant calculations. A plot of [guest]/ΔI vs. 1/[host] was linear with the slope and intercept being equal to $1/K_d\Delta I$ and $1/\Delta I$, respectively (ΔI = increment of the fluorescence intensity of guest molecule on addition of cyclodextrin). The value of K_d was obtained from these linear plots. K_d values for dibenzyl ketone and α-ethyldibenzyl ketones were 8.6×10^{-4} and 1.4×10^{-4}, respectively.

Photolysis. (a) Homogeneous Solution. Preparative-scale irradiations of 1–7 in benzene and methanol were carried out in Pyrex vessels at room temperature by using a 450-W medium pressure mercury arc lamp. The samples were deaerated before irradiation by passing dry nitrogen gas for 30 min. After about 40% conversion (12 h), the solvent was evaporated and the products were separated by repetitive column and preparative thin layer chromatography (silica gel, hexane/chloroform). The products were identified on the basis of their spectral properties. The products formed from 3–7 were the diphenylalkanes AA, AB, and BB, cyclobutanols, and dibenzyl ketone and from 1 and 2 decarbonylated coupling products were the only products. Since the spectral data for products derived from 1–7 were closely similar, the spectral data of products from α-propyldibenzyl ketone alone are presented below as an example.

1,2-Diphenylpentane: IR (neat) cm^{-1} 2980, 2920, 1600, 1490, 1450, 1260; ^1H NMR ($CDCl_3$) 0.78 (t, 3 H), 0.85–1.33 (m, 6 H), 2.75–2.86 (m, 3 H), 7.0–7.38 (m, 10 H).

1-Phenyl-4′-butylacetophenone: IR (neat) cm^{-1} 3020, 2940, 1680, 1600, 1220; ^1H NMR ($CDCl_3$) 0.93 (t, 3 H), 1.25–1.42 (m, 4 H), 2.65 (t, 2 H), 4.26 (s, 2 H), 7.0–7.36 (m, 7 H), 7.94 (d, 2 H).

1-Benzyl-2-phenyl-4-methylcyclobutanol (two isomers): IR (neat) cm^{-1} 3520–3200 (b), 2940, 1600, 1500, 1460, 1060; ^1H NMR ($CDCl_3$) (i) 0.84 (d, 3 H), 1.25–1.44 (m, 3 H), 2.92 (s, 2 H), 3.41 (dd, 1 H), 7.14–7.44 (m, 10 H); (ii) 1.21 (d, 3 H), 1.98–2.4 (m, 3 H), 2.58 (s, 2 H), 3.6 (dd, 1 H), 7.14–7.44 (m, 10 H).

The small-scale analytical irradiations were carried out either in NMR tubes or in small Pyrex test tubes. Conversions were kept below ~15% and the products were analyzed by GC. The product distribution was calculated on the basis of the area of the peak corresponding to each product on the GC trace. No correction for detector response was made.

(b) Solid Cyclodextrin Complexes. Photolysis of microcrystalline complexes was carried out by using a Hanovia 450-W medium pressure mercury arc lamp. Samples were degassed, sealed, and irradiated for 24 h. In order to obtain a uniform exposure, the sample tubes were rotated periodically. The irradiated cyclodextrin complexes were dissolved in warm water and extracted with chloroform. The products were analysed by GC and ^1H NMR.

(c) Cyclodextrin Complexes in Aqueous Solution. Aqueous solutions of the complexes prepared by dissolving the microcrystalline complex (50 mg) and an excess of β-cyclodextrin in 250 mL of water were irradiated in Pyrex tubes, using a 450-W medium pressure mercury arc lamp after purging with dry nitrogen for about 45 min. After irradiation (3 h) the products were extracted by using warm chloroform and analyzed by GC.

Experiments with varying ratios of host/guest were also carried out as above. Irradiations under an oxygen atmosphere were carried out by photolyzing as described above while oxygen was continuously bubbled through the solution. Photolysis of dibenzyl ketone complex in the presence of excess cupric chloride (3 M) was conducted in Pyrex vessels using a 450-W medium pressure mercury lamp with a potassium chromate solution filter.

Registry No. 1, 102-04-5; 1·β-cyclodextrin complex, 99765-87-4; 2, 13363-25-2; 3, 6363-21-9; 3·β-cyclodextrin complex, 110826-48-7; 4, 110826-44-3; 5, 110826-45-4; 6, 110826-46-5; 7, 110826-47-6; β-cyclodextrin, 7585-39-9; 1,2-diphenylpentane, 110826-49-8; 1-phenyl-4′-butylacetophenone, 69383-34-2; 1-benzyl-2-phenyl-4-methylcyclobutanol, 110826-50-1.

Modification of Photochemical Reactivity by Cyclodextrin Complexation: Alteration of Photochemical Behavior via Restriction of Translational and Rotational Motions. Alkyldeoxybenzoins

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The photochemical behavior of alkyldeoxybenzoins has been investigated in isotropic organic solvents, in aqueous cyclodextrin solutions, and when they are bound to cyclodextrin in the solid state. Norrish type I and type II reactions occur in these media and the product distributions resulting from these primary processes are dependent on the medium. While in organic solvents the type I and the type II products are obtained in equal amounts, in the aqueous cyclodextrin solution the type II products are formed in large excess. In the solid state the type II products constitute more than 90% of the product distribution. Ratios of products resulting via elimination and cyclization from the type II 1,4-diradical are also altered by the host cyclodextrin. Conformational and super-cage effects have been invoked to rationalize the dramatic alteration of the photobehavior of alkyldeoxybenzoins by the cyclodextrin.

The continuing strive of chemists for selectivity in chemical reactions has led to the alteration of chemical properties through host–guest complexation.[1] The chemistry of cyclodextrins has occupied a central interest in host–guest phenomenon for the last 2 decades.[2] The facility with which cyclodextrins form inclusion compounds

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