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Modification of chemical reactivity by cyclodextrins. Observation of moderate effects on Norrish type I and type II photobehavior

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epoxides are not useful in this reaction because decomposition of the vinyl lithium species via elimination is faster than the desired nucleophilic substitution. Reaction of the acyclic dimethylketene dithioacetal analogous to **2** under the same conditions gave <10% elimination but suffered from lower yields in both the bromination and alkylation steps.

This convenient two-step procedure thus complements existing methods of ketene dithioacetal formation, and while it is limited to relatively reactive electrophiles, it nonetheless provides a convenient method of preparing and/or elaborating a wide variety of these synthetically useful derivatives.

Experimental Section

Preparation of 2. *N*-Bromosuccinimide (3.30 g, 18.5 mmol) was added in small portions to a solution of **1** (*R* = *n*-pentyl, 2.49 g, 12.3 mmol), triethylamine (3.40 mL, 24.4 mmol), and methylene chloride (15 mL). The resulting solution was stirred for 5 min and then poured into a mixture of ether and saturated aqueous NaHCO₃. The aqueous phase was extracted with ether, and the combined organic extracts were dried (MgSO₄) and concentrated in vacuo. Flash chromatography of the crude mixture (silica gel, petroleum ether/ether, 95:5) gave 3.00 g (86%) of **2** as an oil which is stable at -20 °C in the dark: IR (neat) 2920, 2860, 1560, 1420, 1250 cm⁻¹; ¹H NMR (CDCl₃) δ 2.90 (m, 4 H), 2.70 (t, *J* = 7.3 Hz, 2 H), 2.06 (m, 2 H), 1.50 (m, 2 H), 1.28 (m, 4 H), 0.86 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (CDCl₃) δ 126.8, 122.2, 38.5, 30.7, 29.8, 29.4, 28.0, 23.7, 22.5, 14.0; MS (EI, 70 eV), *m/e* (relative intensity) 282 (*M*⁺ + 2, 20.5), 280 (*M*⁺, 19.7), 225 (*M*⁺ - 55, 100), 223 (*M*⁺ - 57, 95.2), 201 (*M*⁺ - 79, 55.1), 151 (*M*⁺ - 129, 25.2), 149 (*M*⁺ - 131, 14.0), 145 (*M*⁺ - 135, 58.0).

Conversion of 2 into 5. General Procedure. A solution of **2** (*R* = *n*-pentyl, 145 mg, 0.516 mmol) in THF/ether/pentane ((4:1:1), 0.5 mL) was added dropwise to a solution of *tert*-butyllithium (0.80 mL of a 1.67 M solution in pentane, 1.30 mmol) in 1.5 mL of THF/ether/pentane (4:1:1) at -120 °C. The resulting solution was stirred for 20 min, followed by addition of the electrophile as a cold THF solution. After 30 min, the reaction mixture was allowed to warm to 20 °C. Water (1 mL) was added, and the mixture was extracted with ether. The combined organic extracts were dried (MgSO₄) and concentrated. Flash chromatography of the crude mixture (silica gel, petroleum ether/ether mixtures) gave **5**. In the case of **5d**, 0.4 mL of HMPA was added before the electrophile was introduced. Yields for each electrophile are shown in Table I.

Spectral Data. **5a:** (oil) IR (neat) 2920, 2560, 2860, 1580, 1420 cm⁻¹; ¹H NMR (CDCl₃) δ 2.83 (m, 4 H), 2.15 (m, 4 H), 1.27 (m, 6 H), 0.86 (t, *J* = 6.7 Hz, 3 H); ¹³C NMR (CDCl₃) δ 134.1, 125.8, 31.4, 30.4, 29.6, 29.3, 28.7, 25.5, 22.5, 14.0; MS (EI, 70 eV), *m/e* (relative intensity) 203 (*M*⁺, 60.2), 146 (*M*⁺ - 57, 100), 129 (*M*⁺ - 74, 16.0). The ratio of 203/202 indicates 94% deuterium incorporation. Calcd for C₁₀H₁₇DS₂ (*M*⁺) *m/e* 203.0912, found *m/e* 203.0905. This product was identical chromatographically with **1**. The ¹H NMR of this product is nearly identical with that of **1** except that the triplet signal at δ 5.95 ppm is ca. 6% of the integration of that in the ¹H NMR of **1**.

5b: (oil) ¹H NMR (CDCl₃) δ 2.90 (m, 4 H), 2.30 (m, 2 H), 2.10 (m, 2 H), 1.30 (m, 6 H), 0.88 (t, *J* = 6.8 Hz, 3 H), 0.20 (s, 9 H); ¹³C NMR (CDCl₃) δ 144.1, 137.2, 34.4, 32.1, 30.6, 29.6, 29.3, 24.8, 22.6, 14.2, 0.6; MS (EI, 70 eV), *m/e* (relative intensity) 274 (*M*⁺, 13.5), 259 (*M*⁺ - 15, 8.87), 217 (*M*⁺ - 57, 56), 200 (*M*⁺ - 74, 11.4), 73 (*M*⁺ - 201, 100). Calcd for C₁₃H₂₆S₂Si (*M*⁺) *m/e* 274.1245, found *m/e* 274.1236.

5c: (oil) IR (neat) 2940, 2860, 1580, 1420 cm⁻¹; ¹H NMR (CDCl₃) δ 2.82 (m, 4 H), 2.32 (m, 2 H), 2.11 (m, 2 H), 1.88 (s, 3 H), 1.28 (m, 6 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (CDCl₃) δ 140.5, 119.3, 36.0, 31.7, 30.3, 30.2, 27.6, 25.2, 22.6, 20.2, 14.0; MS (EI, 70 eV), *m/e* (relative intensity) 216 (*M*⁺, 23.2), 159 (*M*⁺ - 57, 100), 145 (*M*⁺ - 271, 13.2), 85 (*M*⁺ - 131, 15.3). Calcd for C₁₁H₂₀S₂ (*M*⁺) *m/e* 216.1006, found *m/e* 216.1000. This product was identical

spectrally (¹H NMR, IR, MS, and chromatographically (TLC) with an authentic sample.⁶

5d: (oil) IR (neat) 2940, 2860, 1580, 1450 cm⁻¹; ¹H NMR (CDCl₃) δ 2.84 (m, 4 H), 2.30 (m, 4 H), 2.13 (m, 2 H), 2.25-2.50 (m, 8 H), 0.91 (m, 6 H); ¹³C NMR (CDCl₃) δ 145.4, 120.3, 36.1, 34.1, 31.9, 30.5, 28.1, 25.3, 22.6, 21.7, 14.1; MS (EI, 70 eV), *m/e* (relative intensity) 244 (*M*⁺, 36.8), 215 (*M*⁺ - 29, 29.8), 187 (*M*⁺ - 57, 100), 159 (*M*⁺ - 85, 59.3), 85 (*M*⁺ - 159, 19.5). Calcd for C₁₃H₂₄S₂ (*M*⁺) *m/e* 244.1319, found *m/e* 244.1306. This product was identical spectrally (¹H NMR, IR, and MS) and chromatographically (TLC) with an authentic sample.⁶

5e: (oil) IR (neat) 3450, 2940, 2860, 1570, 1470 cm⁻¹; ¹H NMR (CDCl₃) δ 4.90 (m, 1 H), 2.75-3.05 (m, 4 H), 2.29 (m, 2 H), 2.13 (m, 2 H), 1.78 (d, *J* = 4.4 Hz, OH), 1.20-1.60 (m, 14 H), 0.89 (m, 6 H); ¹³C NMR (CDCl₃) δ 145.5, 124.0, 72.6, 35.9, 32.4, 31.9, 30.2, 30.2, 29.8, 29.6, 25.7, 25.1, 22.7, 22.5, 14.1; MS (EI, 70 eV), *m/e* (relative intensity) 302 (*M*⁺, 7.9), 284 (*M*⁺ - 18, 1.6), 245 (*M*⁺ - 57, 2.3), 231 (*M*⁺ - 71, 100), 227 (*M*⁺ - 75, 4.1), 213 (*M*⁺ - 89, 2.0), 203 (*M*⁺ - 99, 7.8). Calcd for C₁₆H₃₀OS₂ (*M*⁺) *m/e* 302.1738, found *m/e* 302.1742.

5f: (oil) IR (neat) 2940, 2860, 1650, 1520, 1250 cm⁻¹; ¹H NMR (CDCl₃) δ 10.0 (s, 1 H), 3.07 (t, *J* = 6.7 Hz, 2 H), 2.98 (t, *J* = 7.1 Hz, 2 H), 2.39 (m, 2 H), 2.23 (m, 2 H), 1.29 (m, 6 H), 0.86 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (CDCl₃) δ 185.5, 161.0, 138.5, 31.9, 29.0, 28.6, 28.3, 27.8, 24.5, 22.5, 14.0; MS (EI, 70 eV), *m/e* (relative intensity) 230 (*M*⁺, 26.5), 173 (*M*⁺ - 57, 100), 145 (*M*⁺ - 85, 19.0), 99 (*M*⁺ - 131, 22.8). Calcd for C₁₁H₁₈OS₂ (*M*⁺) *m/e* 230.0799, found *m/e* 230.0788.

5g: (oil) ¹H NMR (CDCl₃) δ 7.48 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.7 Hz, 2 H), 3.15 (m, 2 H), 2.90 (m, 2 H), 2.38 (s, 3 H), 2.20 (m, 4 H), 2.19 (m, 6 H), 0.78 (t, *J* = 3.4 Hz, 3 H); ¹³C NMR (CDCl₃) δ 141.5, 141.4, 141.1, 140.6, 129.7, 124.3, 32.0, 29.6, 28.7, 26.2, 24.3, 22.3, 21.4, 14.0; MS (CI, 100 eV), *m/e* (relative intensity) 341 (*M*⁺ + 1, 100).

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Registry No. **1**, 73798-32-0; **2**, 100189-87-5; **5a**, 100189-88-6; **5b**, 100189-89-7; **5c**, 73813-65-7; **5d**, 100189-90-0; **5e**, 100189-91-1; **5f**, 100189-92-2; **5g**, 100189-93-3; tolyl menthyl sulfone, 3865-44-9.

Modification of Chemical Reactivity by Cyclodextrins: Observation of Moderate Effects on Norrish Type I and Type II Photobehavior

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The photochemistry and photophysics of organic molecules in organized assemblies are being studied with great interest in order to understand the features controlling the selectivity in the photoreactions brought about by these media.¹ These studies have paved the way to an intriguing number of possibilities by which photoreactivity can be modified. In this connection, we have investigated the photobehavior of a number of phenyl alkyl ketones and α,α-dimethylphenyl alkyl ketones (Scheme I) incorporated in the hydrophobic interior of cyclodextrin cavities. It was

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Table I. 270-MHz ^1H NMR Chemical Shifts^a of β -Cyclodextrin Protons in Complexes

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 valerophenone	1356.0	973.7	1043.1	957.8	993.9	1028.4
β -cyclodextrin complex with α,α -dimethylvalerophenone	1358.1	974.3	1047.9	957.8	1006.6	1031.9

^a Chemical shifts are expressed in Hz with reference to Me_4Si ; solvent, D_2O .**Table II. Product Distribution of Phenyl Alkyl Ketones upon Photolysis in the Presence and Absence of Cyclodextrin**

medium	compound					
	1	2	3	4	5	6
	E/C ^a	E/C	E/C	II/I ^b	E/C	II/I ^b
benzene	6.5	3.8	0.1	1.2	0.1	4.2
<i>tert</i> -butyl alcohol	8.5	5.9	0.2	1.8	0.3	9.0
β -cyclodextrin/ H_2O						
1:1	4.0	2.9	0.3	7.32	0.6	16.6
2:1	3.8	2.9				
3:1	3.8	2.9				
β -cyclodextrin (solid)						
1:1	3.5	3.1	0.40	5.3	0.6	14.0
α -cyclodextrin/ H_2O	4.4	3.8	0.5	7.3	0.8	6.3
γ -cyclodextrin/ H_2O		2.7			0.2	19.0
association constant ^c (β -cyclodextrin) $\times 10^4 \text{ M}^{-1} \text{ L}$	1.53	2.0	1.8		2.0	

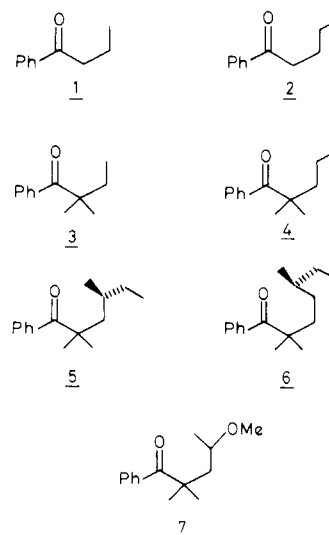
^a Ratio of acetophenone vs. cyclobutanol; products analyzed by GC; error limit $\pm 5\%$. ^b Ratio of type II vs. type I product; products analyzed by GC; error limit $\pm 5\%$. ^c Association constants of phenyl alkyl ketones with β -cyclodextrin in aqueous media measured by UV-absorption spectrophotometry.

anticipated that a cyclodextrin cavity might impose certain constraints on product formation from the type I and type II processes, which these ketones undergo.²

Results and Discussion

Addition of phenyl alkyl ketones 1–7 to saturated aqueous solutions of β -cyclodextrin precipitates a white solid which is soluble in an excess of water. The X-ray powder pattern of the precipitated solid differed from that of β -cyclodextrin. The solid state ^{13}C NMR of the isolated precipitate exhibited peaks corresponding to both ketones and β -cyclodextrin. Both of these results indicate complexation of β -cyclodextrin with aryl alkyl ketones. The molar ratio of the ketone to β -cyclodextrin was calculated by estimating (GC analysis) the amount of ketone extracted from a known amount of the solid complex. The molar ratios of the ketone to β -cyclodextrin for all solid complexes were $\approx 0.85:1$. However, this does not provide any information regarding the stoichiometry of the complexes in aqueous solution. α -Cyclodextrin formed complexes only with 1–3.

Structure of β -Cyclodextrin Complexes. The complexes of β -cyclodextrin with valerophenone (2) and α,α -dimethylvalerophenone (4) were chosen as model systems for the structural analyses in aqueous solution. The 270-MHz ^1H NMR spectra of D_2O solutions of β -cyclodextrin and its complex with 2 and 4 were recorded. The chemical shifts of β -cyclodextrin protons in the uncomplexed and in the complexed forms are utilized for analysis and are tabulated in Table I. If an aromatic nucleus enters the cyclodextrin cavity, protons H_3 and H_5 of cyclodextrin are expected to be shielded since they will be in the magnetic shielding region of the aromatic π cloud.³ Results with

Scheme I. Aryl Alkyl Ketones Investigated

the complexes of 2 and 4 appeared to be similar. Protons H_3 , H_5 , and H_6 are shifted upfield while H_1 , H_2 , and H_4 are virtually unaffected supporting the contention that complexation occurs at the interior of the torus. In both of the systems proton H_5 is shifted upfield to a greater extent than H_3 and H_6 . However, it is to be noted that the difference in chemical shifts observed for the complex of ketone 4 is less when compared to the corresponding protons in the complex of 2 (Table I). This difference may be anticipated on the basis of CPK models which suggest that the presence of the α,α -dimethyl group pushes the aromatic ring toward the side of the cyclodextrin cavity. The geometry is expected to increase the time-averaged distance between the aromatic ring and the interior protons of cyclodextrin. This, in turn would decrease the effective shielding by the aromatic nucleus. Thus, it can be tentatively concluded from both NMR and CPK molecular model analyses that the ketone–cyclodextrin complex possesses a structure such that the phenyl ring is

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Table III. Product Distribution upon Photolysis of Phenyl Alkyl Ketones in the Presence and Absence of β -Cyclodextrin

medium	compound					
	5		6		7	
	E/C ^a	II/I ^b	E/C	II/I	E/C	II/I
benzene	0.77	2.97	0.26	3.29	0.42	6.85
<i>tert</i> -butyl alcohol	3.43	5.00	0.28	6.00	0.63	9.60
β -CD/H ₂ O						
1:1	7.3	7.17	0.33	8.1	3.3	8.6
β -CD (solid)						
1:1	12.45	4.87	0.55	4.9	2.6	2.0
association constant ^c (β -cyclodextrin) $\times 10^4$ M ⁻¹ L	0.87		0.48			

^a Ratio of acetophenone vs. cyclobutanol; products analyzed by GC; error limit $\pm 5\%$. ^b Ratio of type II vs. type I product; products analyzed by GC; error limit $\pm 5\%$. ^c Association constants of phenyl alkyl ketones with β -cyclodextrin in aqueous media measured by UV-absorption spectrophotometry.

inside the cavity and the reactive carbonyl group is at the tip of the broader end of the cyclodextrin.

Stability of the Complexes. UV-vis absorption spectroscopy has been used as an effective tool in determining the stability constants for various cyclodextrin complexes by several groups of workers. The stability constants of the complexes of ketones 1-7 with β -cyclodextrin were determined by using the approach of Benesi and Hilderbrand.⁴ The stability constants for the ketones 1-7 are of the order of 1×10^4 M⁻¹ L (Tables II and III), implying that the complexes are fairly stable in aqueous solution.

Photobehavior. The type II reaction of phenyl alkyl ketones possessing γ -hydrogens has been extensively investigated.² The 1,4-diradical is now well-established to be the primary intermediate in this reaction. The α,α -dimethyl substituted phenyl alkyl ketones undergo α -cleavage (type I reaction) in addition to the type II process. Thus while ketones 1 and 2 upon photolysis, give cyclobutanols and acetophenone as products of type II reaction, 3-7 give benzaldehyde, cyclobutanols, dimethylacetophenone, and the corresponding olefins via type I and II processes. Results obtained upon photolysis (450-W medium pressure mercury lamp with Corning Pyrex filter 0.53; >280 nm) of ketones 1-7 in cyclodextrins (aqueous solution and solid state) along with those in organic solvents are provided in Tables II and III. Perusal of Tables II and III suggests that the inclusion of guest ketones in cyclodextrin does not greatly alter their photobehavior. Nevertheless, the following generalizations emerge from these studies: (a) Cyclodextrins influence the relative yields of type II and type I products. Type II products are favored over type I by cyclodextrins (ketones 3-7). (b) Ratios of products derived from the 1,4-diradical via cyclization and cleavage are slightly altered by cyclodextrin cavity in comparison to organic solvents.

The photoproducts were extracted with chloroform. No products other than those derived from type I and type II reactions were isolated. Importantly, no products derived from the abstraction of cyclodextrin protons by ketones were obtained. Supporting this was the mass balance which showed that isolated type I and type II products correspond to $\approx 90\%$ of the reacted ketones. Addition of more than 1 equiv of cyclodextrin did not produce any significant variation in the product distribution. This suggested that the reaction occurs essentially from an 1:1 complex and further that the observed product distribution was mainly due to complexed material. The latter was indeed expected from the high association constants measured.

It is known that for phenyl alkyl ketones both the type I and type II reactions occur only from the triplet state.²

The radical pair formed from α -cleavage undergoes both disproportionation resulting in type I products and recombination to generate the ground-state ketone. The latter process reduces the efficiency of type I product formation. One could expect that the cyclodextrin cavity may sequester the two radicals produced by the type I process and thus provide an enormous cage effect. We suggest that the enhanced yield of type II products in ketones 3-7 is indeed due to such a process. It is quite likely that the cyclodextrin cavity provides an opportunity for the geminate radical pairs to recombine, thus allowing the competing type II reaction to occur more efficiently. The presence of close to unit cage effect with cyclodextrin has recently been demonstrated in the case of dibenzyl ketones.⁵ The effect of cyclodextrin with phenyl alkyl ketones investigated here is small. This is due to the fact that the formation of type I products (disproportionation) also requires an encounter between the two radicals. Recently, we have found⁶ that with benzoin ethers the type II products can be obtained in quantitative yield by fully suppressing the type I process by cyclodextrin encapsulation. This is indeed remarkable considering the fact that the benzoin ethers do not give type II products in organic solvents. The alternative possibility, namely, that the increased yield of the type II products is due to the conformational feature which enhances the type II reactivity over the type I, cannot be completely ruled out in the absence of quantum yield data, which could not be measured for 1-7 owing to experimental difficulties.

The quantum yield for the type II reaction and the ratio of the products derived from elimination and cyclization are known to be sensitive to the environment.² Solvents that are reasonable Lewis bases prevent the reversion of the triplet-generated biradicals to the ground-state ketones. In this process, they raise the cleavage/cyclization ratio and alter the stereochemistry of cyclization. These effects are explicable by a mechanism involving the hydrogen bonding of the hydroxy biradical to the solvent.

Cyclodextrin influence on type II products needs to be analyzed in terms of three factors: solvent effects on excited state reactivity, solvent (H-bonding) effects on biradical partitioning, and encapsulation effects on biradical partitioning. The cavity of cyclodextrin consists of ether linkages and hydroxyl groups capable of hydrogen bonding to the intermediate 1,4-biradical. The results presented in Tables II and III suggest that the hydrogen bonding and the micromedium effects may not be the only factors controlling the cleavage/cyclization ratio. For all the ketones (1-7), the cyclization yield is reduced in the hydrogen

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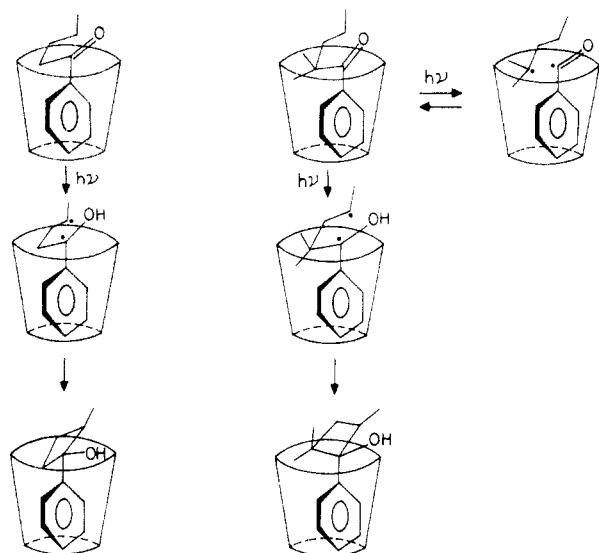


Figure 1. Schematics of type I and II reactions of aryl alkyl ketones in β -cyclodextrin.

bonding solvent *tert*-butyl alcohol compared to that in benzene. However, while the butyrophenone and valerophenone an enhanced yield of cyclobutanols is obtained in cyclodextrin, for ketones 3–7, the cyclization yield is reduced in cyclodextrin. Therefore, we believe that the above results indicate the presence of the conformational control resulting from inclusion within the cyclodextrin cavity. We attribute the variation in the cleavage/cyclization ratio to steric constraints on 1,4-biradicals by the cavity of cyclodextrin.

The basic features which have been well-established² and which we have utilized in understanding the variation in cleavage/cyclization ratio are the following. The elimination reaction from 1,4-biradical requires that the four carbon atoms of the biradical be coplanar so that the *p*-orbitals of the two radicals can continuously overlap with the bond undergoing cleavage. On the other hand, the transition state for cyclization requires the overlap of the two radical centers. Among the two processes, the cyclization is sterically more demanding and appears to require greater motion. While butyrophenone and valerophenone are small and fit completely inside the cavity and the resulting 1,4-biradicals do not experience any constraints, the biradicals from α,α -dimethylbutyrophenone and α,α -dimethylvalerophenone may experience considerable steric constraints during closure to cyclobutanols. This factor may be responsible for the decreased efficiency of cyclobutanol formation in α,α -dimethyl phenyl alkyl ketones. ¹H NMR studies and CPK molecular models reveal that α -substitution forces the molecule to move closer to the rim of the cavity and thus exposes them to large steric constraints during the closure to cyclobutanol (Figure 1). Substitution at the δ -position should enhance the steric constraints which is indeed found to be the case with ketones 5–7.

The above interpretation of the results is based on the assumption that the stoichiometry of the complexes in aqueous solution is 1:1 and the excited ketone and the intermediate biradical react by remaining within the torus. We assume that the association constants for the biradical intermediate and the excited ketone are virtually the same as for the ketone in the ground state. Although information on these are highly desirable, they are not presently available. We are currently extending our studies of photoreactivity in inclusion complexes to other host systems as well as to other reactions.

Experimental Section

Materials. Phenyl alkyl ketones 1–7 were prepared by reported procedures.⁷ Cyclodextrins were procured from Aldrich and used as received. Doubly distilled water was used for all the experiments. All the solvents were distilled twice before use.

Preparation of Cyclodextrin Complexes. Addition of ketones (1 equiv, 20 mg) to saturated solutions of cyclodextrin (1 or 2 equiv, 125 or 250 mg) resulted in precipitation of the inclusion complex. The solutions were stirred (magnetically) well for completion of complexation and then dissolved in excess of water. Aqueous solutions of α - and β -cyclodextrin complexes were also prepared in a similar manner. The solid complexes of β -cyclodextrin were prepared by stirring the saturated aqueous solution of β -cyclodextrin with equivalent amounts of 1–7. The precipitated complexes were filtered, washed with cold ether, and dried in a desiccator at 60 °C for 12 h. The molar ratio of the host to guest was determined as follows. The solid complex which was dried to constant weight at about 60 °C after washing with water and ether was redissolved in water. The guest ketone was extracted thoroughly with chloroform, and the amount of ketone present in the complex was estimated by GC. The molar ratio of β -cyclodextrin to the ketone was then calculated.

Identification of Cyclodextrin Complexes. (a) **Powder Diffraction of Solid Complexes.** X-ray powder photographs of β -cyclodextrin and β -cyclodextrin complexes with 1–7 were taken by using a Phillips powder diffractometer employing monochromated Cu K α radiation. Powder patterns of β -cyclodextrin and of the complexes were different.

(b) **¹H NMR of Complexes.** The solid-state ¹³C NMR spectra were run at the National Research Council of Canada, Ottawa, by Dr. J. Ripmeester on a Bruker FT CXP-200 instrument. The spectra revealed the presence of peaks corresponding to both cyclodextrin and ketones.

¹H NMR spectra of the D₂O solutions of the complexes were recorded on a Bruker WH-270 MHz FT NMR spectrometer. About 6–7 equiv of the ketones 2 and 4 were added to solutions of β -cyclodextrin (2 mg) in 1 mL of D₂O. The solutions were stirred well, and the spectra were recorded.

(c) **UV-Spectral Measurements.** A stock solution of 0.01 M of ketones 1–7 was prepared in methanol and 50- μ L portions of these were added to 10-mL standard flasks containing varying amounts of β -cyclodextrin solutions (0.5–5 mL of concentration 10^{–3} M). The solutions were made up to 10 mL and stirred well for 2–3 h. UV spectra of these solutions were recorded on a Shimadzu-UV-180 spectrophotometer. Optical density values were measured at a wavelength where a maximum shift is noticed (250 nm). Plots of $a_0b_0/\Delta OD$ vs. ($a_0 + b_0$) were linear. From the slopes and intercepts of these plots, K_s , the stability constants were determined.⁴

Photolysis of β -Cyclodextrin Complexes. The aqueous solutions of the complexes were irradiated in Pyrex tubes after bubbling with oxygen-free dry nitrogen for 20 min by using a 450-W Hanovia medium pressure mercury lamp (Corning 0.53 filters) for about 10% conversion. The products were extracted with chloroform and analyzed using a Chemito analytical gas chromatograph (5 ft \times 1/8 in. SE-30 or Carbowax on Chromosorb P column). Products of the photolysis were benzaldehyde, acetophenone, dimethylacetophenone, and cyclobutanols, and these were identified by coinjection with the authentic samples. Care was taken so that benzaldehyde and acetophenone were not removed along the chloroform. The product ratios were obtained by comparing the peak areas. No corrections for detector response were made.

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