Tetrahedron Vol. 44, No. 23, pp. 7223 to 7233, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00

MODIFICATION OF PHOTOCHEMICAL REACTIVITY BY CYCLODEXTRIN COMPLEXATION: SELECTIVITY IN PHOTO-CLAISEN REARRANGEMENT

M.S. Syamala and V. Ramamurthy *#

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, India

(*Received in UK* 28 *September* 1988)

Abstract: Photorearrangements of *meta*-alkoxyphenylallyl ethers 1-5 in ethanol, in water and as complexes of α and β-cyclodextrins have been investigated. The ratio of the two ortho rearrangement products was dependent both on the length of the alkoxy substituent and on that of the host cavity suggesting that, subtle and rationale engineering manipulation is required to achieve exclusive obtention of only one ortho isomer. It is speculated that α-cyclodextrin provides a "tight fit" while β-cyclodextrin offers a "loose fit". This tightness of binding is suggested to be responsible for the selectivity among the ortho isomers with α-cyclodextrin as the host. Further, the results indicate that "loose cavity" can be tightened by incorporating a "molecular spacer" such as a long hydrocarbon chain as an intramolecular appendix.

The ability of cyclodextrins to include aryl units to form inclusion complexes has been well established and this phenomenon has been successfully utilised to bring about remarkable catalyses and selectivities in a number of thermal reactions [1]. We envisioned that cyclodextrins, in principle, can play a useful role in regulating the traffic of molecualr species towards certain accessible positions, by encircling and hence protecting the rest of the potential reactive sites with its molecular network. Hence it can be expected that unimolecular photorearrangements which involve an initial cleavage followed by reorganisation of the fragments, when conducted in cyclodextrins, will give rise to one particular isomer specifically. To demonstrate the occurrence of such a geometric control, we have investigated the photo-Claisen rearrangement of *meta*-alkoxyphenylallyl ethers as complexes of α and β-cyclodextrins. The photochemical analogue of the well known Claisen rearrangement, produces in the case of *meta*-alkoxyphenylallyl ethers, a mixture of two ortho and a para rearranged isomeric phenols alongwith the cleavage product, namely, *meta* -alkoxy phenol (Scheme 1) [2]. We have attempted to regulate the rearrangement process by complexation with the cyclodextrins into giving selectively one rearranged isomer as the product. The present paper describes the results of such an investigation.

RESULTS

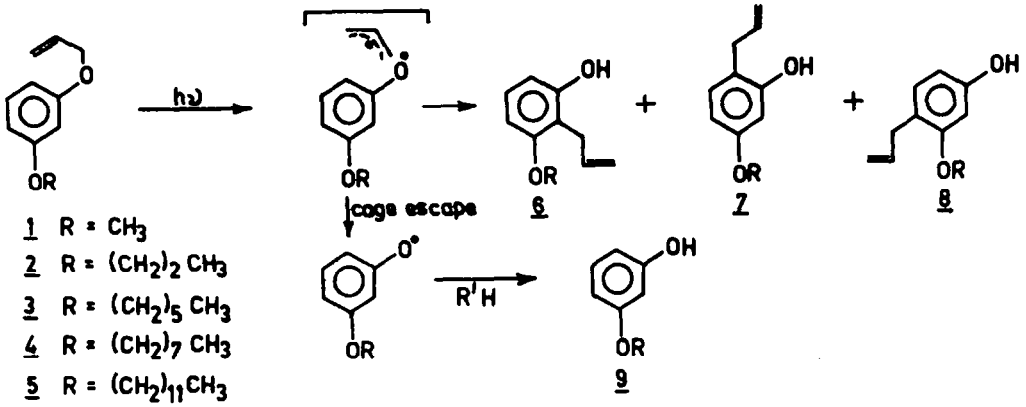
Addition of one equivalent of allyl ethers 1-5 to saturated aqueous solutions containing either α or β-cyclodextrin precipitated a white solid, which was either dried to get a solid complex or dissolved in an excess of water to get aqueous solutions and both of these were used for irradiations. The presence of an inclusion complex between the substrate and the

cyclodextrin in the solid state was inferred from the X-ray powder diffractograms of the solid samples. The X-ray powder diffractograms showed noticeably different patterns for the complexes and for free cyclodextrins, suggesting the formation of microcrystalline inclusion complexes. Furthermore, the determination of the host:guest ratio revealed the stoichiometry of the complexes to be 1:1.

Indications regarding the formation of inclusion complexes in aqueous cyclodextrin solutions came from 270 MHz H^1-nmr spectra and the dissociation constants of the complexes. In the cases of both 1 and 2, the spectra of α-cyclodextrin solutions showed a downfield shift of H_3 alone (1: -16 Hz; 2: -11 Hz) while those of β-cyclodextrin solutions showed upfield shifts for both the H_3 and H_5 protons (1: H_3 +3.3 Hz and H_5 +18.7 Hz; 2: H_3 +13.6 Hz and H_5 +24.5 Hz). Such changes in the chemical shift values are known to be the consequence of the diamagnetic anisotropic effect of the aromatic ring residing inside the cavity and are taken to be evidence for the formation of inclusion complexes in aqueous cyclodextrin solutions [3]. Dissociation constants for α and β-cyclodextrin complexes of substrates 1 and 2 were determined spectrophotometrically by the method of Benesi and Hildebrand [4]. Along with these K_D values also given in Table 1 are the K_D values for 1-adamantanol in α and β-cyclodextrins, determined by using the competitive inhibitory effect of 1-adamantanol on the cyclodextrin complexes of substrate 2. These, as seen from Table 1, match well with the K_D values reported for 1-adamantanecarboxylic acid in α and β-cyclodextrins [5].

Photolyses of 1 and 2 in isotropic media such as ethanol and water produced a mixture of three rearranged products, namely, 2-allyl,3-alkoxyphenol, 6, 6-allyl,3-alkoxyphenol, 7 and 4-allyl,3-alkoxyphenol, 8, along with the fragmentation product, 3-alkoxyphenol, 9 (Scheme 1). The relative percentages of these products are given in Tables 2 and 3. These products were characterised on the basis of their spectral and elemental analysis data. Photolyses of the solid α and β-cyclodextrin complexes of substrates 1-5 revealed interesting variations in the distribution of products in comparison to the homogeneous solution. In all the cases, it can be noticed that the fragmentation product 9, and the para isomer 8, are absent in the cyclodextrin irradiations. Moreover, an interesting trend was observed in the distribution of the two ortho isomers 6 and 7, as the length of the alkoxy chain was increased, namely as we moved from substrates 1 to 5 (Table 4). As the length of the chain increases there is a gradual decrease in the selectivity observed, with an increased formation of 6 in all the cases. The results of the photolyses of the corresponding β-cyclodextrin complexes, in contrast, showed exactly the reverse trend. The photolysis of 1 as solid β-cyclodextrin complexes led to a mixture of the two ortho rearranged products with a slight predominance for 2-allyl,3-methoxyphenol (6 R=CH_3), along with a minor amount of the para rearranged product. This is in contrast to the exclusive formation of 6-allyl,3-methoxyphenol in the corresponding α-cyclodextrin complex. Remarkably, as the alkoxy chain length was increased from 1 to 4, the photoproducts of solid β-cyclodextrin complexes showed an increasing selectivity, with the ortho isomer, 6-allyl,3-octyloxyphenol, forming >90% of the product mixture in the case of 4. Interestingly, as the chain length was further increased from octyl to dodecyl, a drop in selectivity was observed.

In order to confirm that the above alteration in the photochemical product distribution is indeed due to the inclusion of 1-5 in the cavity of cyclodextrin the following control experiments were conducted. A mechanical mixture of 1 and β-cyclodextrin was photolysed. The rearranged isomer, in these cases, were formed in low yields along with some polymeric material (Table 2). Further, irradiation of a mixture of 1 and α-methylglucoside (the monomer unit of cyclodextrin) did not produce any selectivity. These two experiments suggest that cyclodextrin inclusion is required to bring about the alteration.



Scheme 1

Table 1: Dissociation Constants of Cyclodextrin Complexes in Aqueous Medium

Substrate (guest)	*Dissociation constants (ML^{-1})* [a] *α-Cyclodextrin*	*β-Cyclodextrin*
m-Methoxyphenylallyl ether 1	3.8×10^{-4}	1.05×10^{-3}
m-Propyloxyphenylallyl ether 2	4.4×10^{-4}	7.52×10^{-4}
1-Adamantanol	1.15×10^{-3}	6.31×10^{-4}
1-Adamantanecarboxylic acid [b]	8.2×10^{-4}	5.2×10^{-4}

[a] : Measued at 23°C; Error limit : ±5%.
[b] : Reported values from the literature (Ref. 7).

Table 2 : Photoproducts of *m*-Methoxyphenylallyl ether (1) in Various Media

Medium	*Percentages of products* [a]			
	9	6	7	8
Ethanol	18	22	28	31
Water	4	41	41	13
α-Cyclodextrin/Water[e] (1:1)[b]	1	37	51	9
α-Cyclodextrin/Water (10:1)	-	23	69	7
α-Cyclodextrin/Solid[f] (1:1)	-	-	100	-
β-Cyclodextrin/Water (1:1)	6	43	35	5
β-Cyclodextrin/Water(10:1)	5	35	55	5
β-Cyclodextrin/Solid (1:1)	-	62	29	8
Mixture with α-cyclodextrin[d] (1:1)	-	45	24	30
Mixture with methyl glucoside[d](1:1)	-	50	24	25
β-Cyclodextrin/hexanol/substrate complex(1:1:1)[c]	-	51	40	8
β-Cyclodextrin/octanol/substrate complex (1:1:1)	-	31	63	5

a: For structure of products see Scheme 1 (R=CH_3); Products analysed by gc; error limit ±5%.
b: Ratio of cyclodextrin to the guest.
c: Ratio of cyclodextrin to alcohol to the guest.
d: Mechanical mixture of cyclodextrin/methyl glucoside and the guest prepared by grinding the host and the guest
e: Cyclodextrin complex irradiated in aqueous medium.
f: Cyclodextrin complex irradiated in the solid state.

Table 3: Photoproducts of m-Propyloxyphenyl allyl ether

Medium	*Percentages of products* [a]			
	9	6	7	8
Ethanol	5	37	41	14
Water	11	36	43	8
α-Cyclodextrin/Water (1:1)[b]	7	30	56	6
α-Cyclodextrin/Water (10:1)	5	17	72	5
α-Cyclodextrin/Water (10:1) in presence of 1-adamantanol (10 eq)	5	34	53	6
β-Cyclodextrin/Water (1:1)	4	39	48	7
β-Cyclodextrin/Water (10:1)	-	34	63	3
β-Cyclodextrin/Water (10:1) in presence of 1-adamantanol (10 eq)	7	41	41	10

a : See Scheme 1 for structure of products (R=$(CH_2)_2$-CH_3); Products analysed by gc; error limit ± 5%.
b : Ratio of cyclodextrin to the guest.

Ternary complexes of β-cyclodextrin and 3-methoxyphenylallyl ether 1 with 1-hexanol and 1-octanol, which can be considered to be the intermolecular analogues of 3 and 4 were prepared as described in the experimental section. Photolysis of these solid complexes, as shown in Table 2 reveal a marginal preference for the formation of the ortho isomer 7, but the selectivity observed in these cases was much inferior and was not comparable with those of 3 or 4.

The results of photolyses of the aqueous solutions of 1 and 2 containing varying amounts of α and β-cyclodextrins are given in Tables 2 and 3. It can be seen that, there is an increased preference for the formation of the ortho isomer 7 (R=CH_3 or R=n-C_3H_7), as the amount of cyclodextrin present in the aqueous medium is increased. The selectivity observed in α-cyclodextrin solutions are, in general greater than that of the corresponding β-cyclodextrin solutions. The addition of ten equivalents of 1-adamantanol, which acts as a competitive inhibitor in aqueous cyclodextrin solutions, due to its ability to form strong complexes, brings down the selectivity observed in β-cyclodextrin solutions of 2, while only a marginal drop in selectivity is observed in the α-cyclodextrin solutions. This is in line with the reported K_D values for 1-adamantanecarboxylic acid and those determined for 1-adamantanol itself [5] (Table 1). The inhibitory effect supports the occurrence of inclusion complexes in aqueous solutions and their role in bringing about selectivity.

DISCUSSION

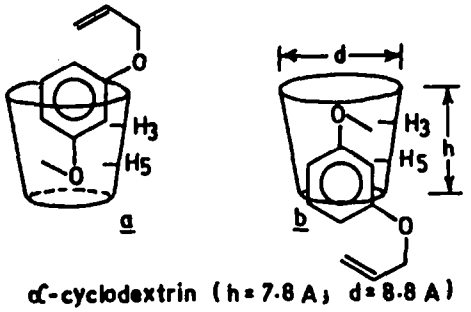
Speculations on the Structure of the Complexes: In order to understand the above observations on the product distribution in the presence of cyclodextrin, a good knowledge of the structure of the complex is essential. In the absence of this, an intuitive approach supported by qualitative experimental data and literature on related systems should be of some value. In the following paragraphs, we speculate on a model that has been of some help to us in understanding the role of cyclodextrin in bringing about selectivity in photo-Claisen rearrangement.

Analyses of the H^1-NMR spectra of the α-cyclodextrin complexes of both 1 and 2 reveal that out of the three inner protons of the cavity, only H_3 is shifted downfield in comparison to the chemical shifts of the uncomplexed host protons. One of the ways in which this can be understood is by visualising the inclusion of the aromatic ring from the secondary hydroxyl side, namely, from the wider mouth of the torus with the alkoxy portion occupying the bottom of the cavity, leading to an incomplete penetration by the aromatic ring (Fig.1). This picture is consistent with the orientataion proposed for several *meta* -substituted aromatics by Bender and co-workers, on the basis of their ester hydrolysis studies [6]. In the case of β-cyclodextrin complexes of 1 and 2, however, the 270 MHz H^1-NMR spectra reveal that both the H_3 and H_5 protons of the cyclodextrin have shifted upfield in the complexed state, with the H_5 shifting to a greater extent than the H_3. This could be due to one of the following reasons. The aromatic ring could probably have penetrated deeper into the β-cyclodextrin cavity due to its larger size, thus enabling both H_3 and H_5 to feel its diamagnetic shielding effect. The orientation of the substrate molecule, in this case, would remain similar to that of the α-cyclodextrin complexes. Another mode of orientation would require the aromatic ring to enter into the cavity in such a way that its allyloxy moiety is located near the bottom of the cavity (Fig.1). Such an orientation would make the H_5 protons feel a cumulative effect of the diamagnetic anisotropy of the allylic double bond and the phenyl ring. Such an orientation also finds support in the reported hydrophobicity parameters for various substituents [7].

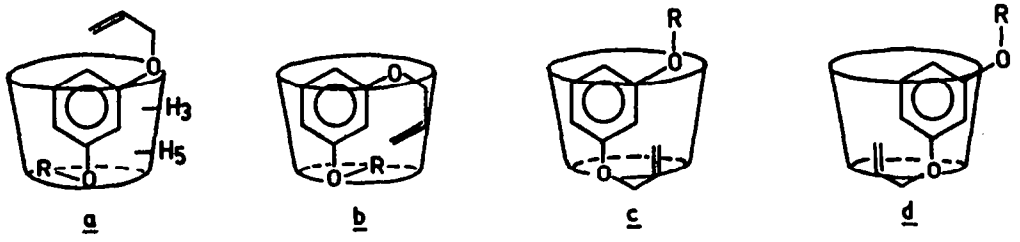
Table 4: Photoproducts of 1-5 in Solid Cyclodextrin Complexes

Substrate	Percentages of products a		
	6	7	8
α-Cyclodextrin			
1	-	100	-
2	5	94	-
3	12	87	-
4	12	88	-
5	36	64	-
β-Cyclodextrin			
1	62	29	8
2	50	49	-
3	24	76	-
4	10	90	-
5	25	75	-

a : For structure of products see Scheme 1; Products analysed by gc; error limit ± 5%.



α-cyclodextrin (h = 7·8 Å; d = 8·8 Å)



β-cyclodextrin (h = 7·8 Å; d = 10·8 Å)

Figure 1

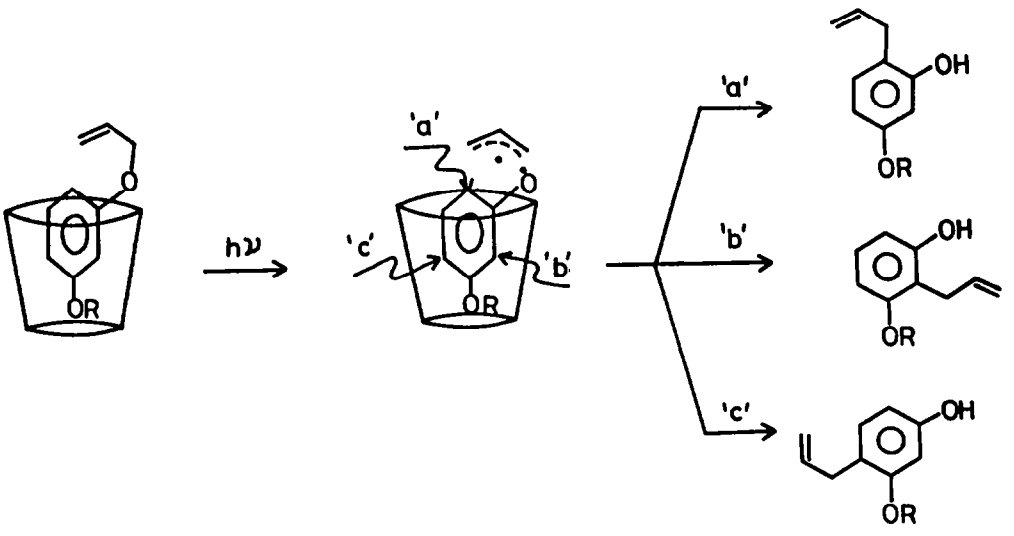
In the case of 2, however, the hydrophobicity parameter for propyl group being greater than that of the allyl, a slight preference for structure a or b (Fig 1) is likely. In this case also, the co-existence of more than one type of complex is probable. Proceeding along the same line, one can predict that as the length of the alkoxy chain increases, due to its greater hydrophobicity, the alkoxy moiety would prefer to reside inside the cavity with the allyloxy moiety oriented near the secondary hydroxyl end of the torus. The increasing chain length would also act as a spacer to induce a tight fit between the host and the guest. However, the presence of too long a chain would lead to a situation where, the cavity would be mostly occupied by the chain with the aromatic ring exposed to the exterior.

Photolysis General: Claisen rearrangement is one of the most widely studied sigmatropic rearrangements [8]. Its photochemical analogue, however, has received very scant attention mostly due to the extensive polymerisation of the allyl ethers upon photolysis, yielding the rearrangement products in low yields. Isotopic labelling studies and crossover experiments on the photo-Claisen rearrangement have shown that the reaction proceeds by an initial cleavage to produce a radical pair in the solvent-cage, which then rearranges to produce a mixture of the ortho and para allylic phenols. A fraction of the radicals that escape from the solvent-cage undergo hydrogen abstraction to give the fragmentation product, namely, the corresponding phenol (Scheme 1).

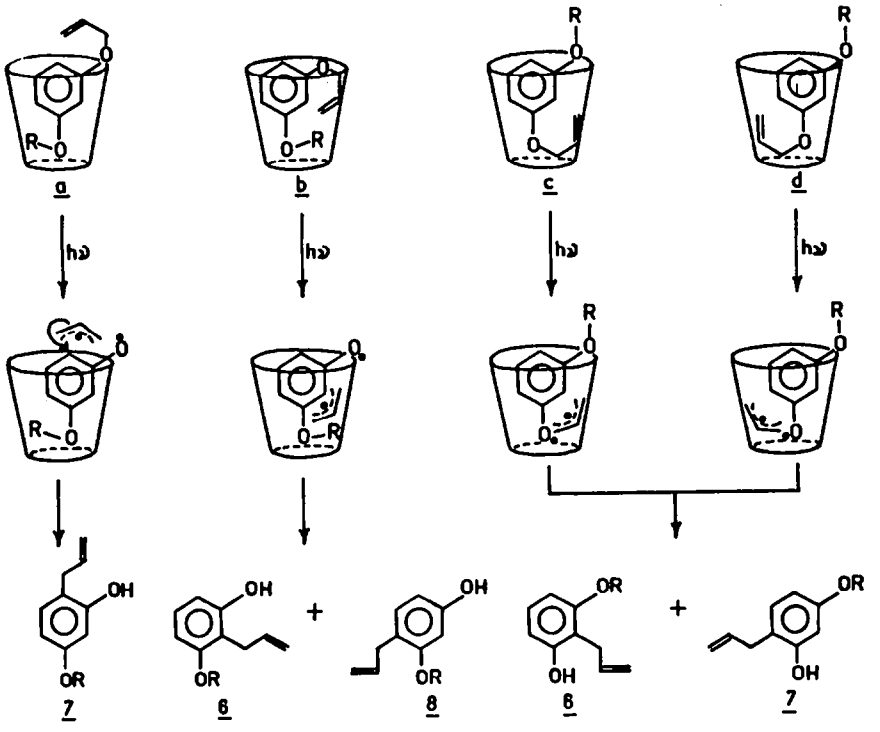
Photolysis of Complexes in the Solid State : The selectivity observed in the photolysis of the α-cyclodextrin complex of 1 in the solid state can be expected on the basis of the orientation of the substrate 1 in the α-cyclodextrin cavity in a manner shown in Scheme 2. It can be seen from Scheme 2 that the α-cyclodextrin sleeve encircles the molecule in such a way as to protect all but the 6-position for attack by the allyl radical produced by the initial cleavage. The gradual drop in selectivity, as we move from 1-5, can be viewed as a consequence of the increased exposure of the aromatic ring from within the cavity due to the longer chain occupying most of the cavity.

The results of irradiations of the β-cyclodextrin complexes, similarly, can be understood on the basis of the proposed structures. In the case of substrate 1, out of the four possible structures a-d, while c and d can give a mixture of the two ortho isomers, b can give the 2-allyl,3-methoxyphenol, 9 ($R=CH_3$) and the para isomer (8, $R=CH_3$), a can form only the 6-allyl,3-methoxyphenol, 7 ($R=CH_3$) (Scheme 3). The observed distribution of products probably is the result of the co-existence of all the four types of complexes in the case of 1. As the chain length of the substituent increases, however, an increased preference for type a complexation is probable, with the alkyl chain acting as a spacer[9] to orient the molecule in a rigid fashion suitable for selective attack at the 6-position to produce selectively the isomer 7. In fact, in the case of the substrate 4, 6-allyl,3-octyloxyphenol 7 ($R=C_8H_{17}$) forms >90% of the products in accordance with the model described above. In the case of substrate 5, however, the dodecyl chain is probably too long and hence occupies most of the cavity leading to an exposure of both the ortho positions of the aromatic ring for attack .

Photolysis of Complexes in Aqueous Solution: Photolysis of substrates 1 and 2, in water, produces a mixture of all the four products 6-9 ($R=CH_3$ or $R=C_3H_7$). As cyclodextrin (α or β) is added to the system, the formation of 3-alkoxyphenol, 9 and the para rearranged isomer 8 are retarded and among the two ortho isomers 6 and 7, an increased preference for 6-allyl,3-alkoxyphenol, 7, is observed. The solubility factor prevented the investigation of substrates 3-5 as their cyclodextrin complexes in the aqueous phase. The results obtained for substrates 1 and 2 seem to indicate that there is a dynamic equilibrium between the complexed and uncomplexed molecules. This leads to the occurrence of reaction from the free as well as bound substrates, which explains the poorer selectivity in aqueous solutions when compared



Scheme 2



Scheme 3

with the solid state. The addition of cyclodextrin suppresses the dissociation of the substrate from the cavity to increasing extents, leading to improved selectivities.

Conclusion: While α-cyclodextrin, with a smaller cavity was able to bring about selectivity, the larger cavity of β-cyclodextrin probably failed to hold the molecule tightly. Introduction of an intra-molecular filling by a lengthening of the alkoxy substituent chain apparently provided the tight fit necessary for achieving selectivity in β-cyclodextrin. At the same time, it became clear that the presence of too long an alkoxy chain that would occupy most of the cavity, pushing the aromatic ring outside, thus exposing both its ortho positions for attack leads to poor selectivity both in α and β-cyclodextrin cavities. Thus, a manipulation of the substituents to achieve tight complexation helps to bring about selectivity. What is needed at this stage are systems that can be described in firm quantitative terms, with limited 'handwaving' in the form of speculative figural representations of complex structures. It is desirable to have systems where it is possible to obtain measured dissociation constants and product distribution as a function of complexation.

EXPERIMENTAL

α and β-cyclodextrin (Sigma) were used as received. The *meta*-alkoxyphenylallyl ethers 1-5 (R=methyl, propyl, hexyl, octyl and dodecyl) were prepared by reported procedures[10] and purified by repeated column chromatography (silica gel/chloroform). The purity of the substrates was ascertained by gas chromatographic analyses. Distilled water and distilled solvents were used for irradiations and extractions.

Preparation of Complexes : α and β-cyclodextrin complexes of 1-9 were prepared as described earlier [11]. The ternary complexes of β-cyclodextrin, *meta*-methoxyphenylallyl ether and alcohols (hexanol or octanol) were obtained by adopting two procedures: (i) A mixture of one equivalent each of the alcohol and *meta*- methoxyphenylallyl ether was added to a saturated aqueous solution containing 0.5 equivalents of β-cyclodextrin and stirred magnetically. The resulting white precipitate was filtered, washed, dried and used for irradiation. (ii) An inclusion complex of the alcohol with β-cyclodextrin was prepared by mixing one equivalent of each in a limited amount of water and to the resulting curdy solution, two equivalents of *meta*-methoxyphenylallyl ether were added and stirred for 12 h. The resulting precipitate, after washing and drying was used for irradiation. The latter procedure which yielded better results was adopted for repetitive irradiations.

Aqueous solutions of the complexes for irradiations were prepared by adding 20 mg of the substrate to a saturated aqueous solution containing ten equivalents of cyclodextrin and stirring magnetically for ten hours. The resulting turbid solution was dissolved in an excess of water and stirred magnetically to get a transparent solution for irradiation. A set of experiments were conducted by adding ten equivalents of 1-adamantanol to the above aqueous solutions and stirring for 12 h to obtain clear solutions for irradiation.

Identification of Complex Formation: Procedures adopted to measure dissociation constants, host-guest ratios and to record X-ray powder photographs and H^1-NMR spectra have been described earlier[11] and the same were adopted.

In order to study the inhibitory effect of 1-adamantanol upon the complexation of phenylallyl ethers with α and β-cyclodextrin spectrophotometric studies were carried out with 2. A stock solution of 10^{-2} M of 2 in methanol was prepared and 100 μL alliquots from that were added to 10 mL standard flasks. From a stock solution of 10^{-2} M of α or β - cyclodextrin, 1mL alliquots were also added to the same flasks. Varying amounts of 1-adamantanol from a stock solution of 0.52 M in methanol were added and the solutions, after adjusting for an equal volume of methanol in each, were made upto 10 mL with water. The absorption spectra of these solutions were recorded in the range 350-220 nm after stirring magnetically for 12 h. The spectra showed a decrease in the absorbance upon addition of 1-

adamantanol. The gradual decrease in absorbance at 280 nm and 270 nm was used to calculate the dissociation constants of the CD-AdOH system, using the K_D values of 2 with α and β-cyclodextrin determined as described above. The K_D values obtained for 1-adamantanol with α and β-cyclodextrins were compared with those reported for 1-adamantanecarboxylic acid with α and β-cyclodextrins.

Photolysis: The solid α and β-cyclodextrin complexes of the substrates, prepared as described above were irradiated in petri-dishes covered with quartz plates in a Rayonet reactor fitted with 254 nm mercury lamps. Aqueous cyclodextrin solutions were irradiated in quartz tubes in a similar reactor. Solutions of the substrates 1-5 in ethanol were also irradiated simultaneously in quartz tubes. The cyclodextrin complexes, after irradiation were worked up in the following manner. The solid complexes were dissolved in an excess of water and the resulting solutions were extracted with warm chloroform. The aqueous cyclodextrin solutions were also extracted in a similar manner and the products obtained after evaporation of solvent were analysed by gas chromatography with a Chemito-3800 gas chromatograph. The analyses were done by employing a 5% SE-30 column (8' x 1/8") in the temperature range of 125-280°C programmed at the rate of 10°C/min. In all the cases studied the gas chromatographic pattern consisted of the following products eluted in their respective order; the phenol (cleavage product) 9, the starting material, 2-allyl,3-alkoxyphenol 6, 6-allyl,3-alkoxyphenol, 7, and 4-allyl,3-alkoxyphenol, 8.

Preparative Photolysis: Solutions of 500 mg of substrates 1-5 in 50 mL of ethanol were irradiated in quartz tubes with 254 nm radiation for 12 h. The resulting mixture after removal of the solvent was subjected to thin layer chromatography (silica gel-hexane/chloroform). The products 6-9 were isolated in their pure form and were characterised by H^1-NMR and IR data. Representative H^1-NMR and IR data are given for the products 6-8 (R=CH_3) below. For products from the substrates 2-5 the H^1-NMR (270 MHz) and IR data were similar and hence are not provided.

6 IR (Neat) cm^{-1} : 3600-3200(b), 2950,1640,1600,1475,1280,1120.
H^1-NMR ($CDCl_3$) : δ 7.188,t, (1H) J=8 Hz, 6.498,d(1H) J=8 Hz, 6.508,d(1H) J=8Hz, 5.988,m(1H), 5.108,m(2H), 3.88,s, (3H), 3.468, dt (2H) J_1=6Hz, J_2=1.5 Hz

7: IR (Neat) cm^{-1} : 3400-3150(b),2950,1620,1600,1510,1300,1180
H^1-NMR ($CDCl_3$) : δ 7.018,d(1H) J=8.2 Hz, 6.478,dd(1H), J_1=8.2 Hz, J_2=2.5 Hz, 6.428,d(1H) J=2.5 Hz, 6.018,m(1H), 5.148,m(2H), 3.768,s(3H), 3.358,d(2H) J=6.25 Hz.

8: IR (Neat) cm^{-1} : 3400-3100(b),2950,1620,1600,1510,1470,1160
H^1-NMR ($CDCl_3$) : δ 6.948,d(1H) J=9Hz, 6.48,d(1H), J=2.5 Hz,6.358,dd(1H) J_1=9Hz, J_2=2.5 Hz, 5.988,m(1H), 5.048,m(2H), 3.7958,s (2H), 3.318,d(2H) J=6.5 Hz.

Thermal Rearrangement: Solutions of substrates 1-5 in diethyl aniline were heated at 200°C for 2 h, in order to effect their thermal rearrangement. The resulting mixture was freed from the solvent by treatment with HCl, and the products were subjected to thin layer chromatography (silica gel-hexane/$CHCl_3$). From their spectral data, the two products of rearrangement were characterised to be 6 and 7, namely, the two ortho rearrangement products. The spectral data of these were identical with those obtained upon photolysis. The cleavage product 9 and the para rearrangement product 8 were not formed in the thermal rearrangement.

Control Experiment: In order to check the possibility of interconversion between the two ortho isomers 6 and 7 during photolysis of the solid cyclodextrin complexes, an inclusion complex of 6 (R=CH_3) was made with α-cyclodextrin and this was photolysed in the same manner as described above. The initial isomer was found to be photostable after irradiation for a week.

REFERENCES

Present address: Central Research and Development Department, Experimental Station, E. I. Du Pont & Co, Wilmington, Delaware 19898, U. S. A.

1. Griffiths, D.W.; Bender, M.L. *Adv. Catalysis* ., 1973, 23, 209.
Bender,M.L.; Komiyama,M. "*CyclodextrinChemistry* ", Springer, Berlin, 1978.
Tabushi, I.; Kuroda, Y. *Adv. Catalysis* .,1983, 32, 417.

2. Koga, G.; Kikuchi, N.; Koga, N. *Bull. Chem. Soc. Japan.*, 1968, 41, 745.
Kelly, D.P.; Puihey, J.T.; Rigby, R.D.G. *Aust. J. Chem* ., 1969, 22, 977.
Hammond, G.S.; Carrol, F.A. *Israel. J. Chem* ., 1972, 10, 613.

3. Demarco, P.V.; Thakkar, A.L. *J. Chem. Soc. Chem. Commun.*, 1970, 2.

4. Benesi, H.A.; Hildebrand, J.H. *J. Am. Chem. Soc* ., 1949, 71, 2703.

5. Komiyama, M.; Bender, M.L. *J. Am. Chem. Soc* ., 1978, 100, 2259.

6. Van Etten,R.L.; Sebastian,J.F.; Clowes,G.A.; Bender,M.L. *J. Am. Chem. Soc.*, 1967, 89, 3242.
Van Etten, R.L.; Clowes, G.A.; Sebastian, J.F.; Bender, M.L. *J. Am. Chem. Soc* ., 1967, 89, 3253.

7. Menger, F.M.; Venkatram, U.V. *J. Am. Chem. Soc* ., 1986,108, 2980.

8. Rhodas, S.J.; Rudins, N.R. *Organic Reactions* , 1975, 22, 1.

9. Ueno, A.; Suzuki, I.; Hino, Y.; Suzuki, A.; Osa, T. *Chem. Lett* ., 1985, 159.

10. Kaufman, K.D.; Russey, W.E. *J. Org. Chem* ., 1965, 30, 1320.

11. Ramamurthy, V.; Eaton, D.F. *Acc. Chem. Res* ., 1988, 21, 300.
Arjunan, P.; Ramamurthy, V. *J. Photochem* .,1986, 33, 123.
Syamala, M.S.; Devanathan, S.; Ramamurthy, V. *J. Photochem* ., 1986, 34, 219.

Sharat, S.; Usha, G.; Tung, C.H.; Turro, N.J.; Ramamurthy, V. *J. Org. Chem* ., 1986, 51, 941.
Nageswara Rao, B.; Turro, N.J.; Ramamurthy, V. *J. Org. Chem* ., 1986, 51, 460.
Dasaratha Reddy, G.; Usha, G.; Ramanathan, K.V.; Ramamurthy, V. *J. Org. Chem* .,1986, 51, 3085.
Syamala, M.S.; Dasaratha Reddy, G.; Nageswara Rao, B.; Ramamurthy, V. *Curr. Sci* ., 1986, 55, 875.
Devanathan, S.; Dasaratha Reddy, G.; Ramamurthy, V. in " *Surfactants in Solution :* Modern Aspects " ; Mittal, K.L. Ed.; Plenum: New York, In the press.
Dasaratha Reddy, G.; Jayasree, B.; Ramamurthy, V. *J. Org. Chem.* 1987, 52, 3107.
Dasaratha Reddy, G.; Ramamurthy, V. *J. Org. Chem* ., 1987, 52, 3952.
Dasaratha Reddy, G.; Ramamurthy, V. *J. Org. Chem* ., 1988, 52, 5521.
Nageshwer Rao, B,; Syamala, M.S.; Turro, N.J.; Ramamurthy, V. *J. Org. Chem* ., 1987, 52, 5517.
Nageswer Rao, B.; Syamala, M. S.; Ramamurthy, V. *Tetrahedron* , Accompanying paper.