CHEMISTRY IN CAVITIES

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ABSTRACT

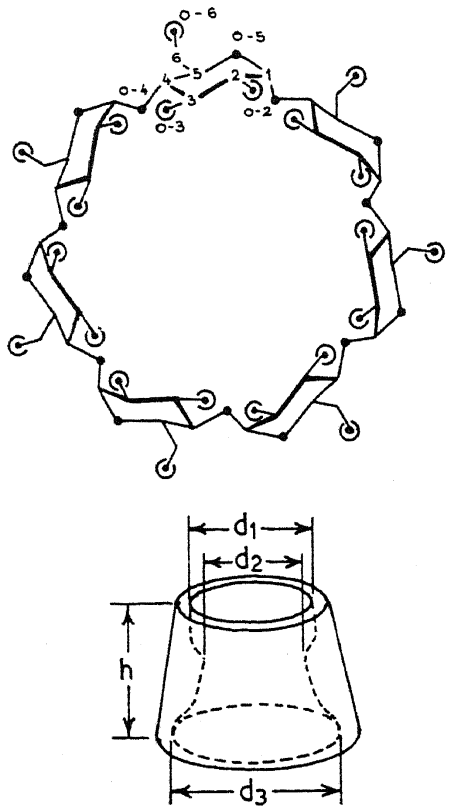
Cyclodextrin as a host, in solution and solid state, can exert remarkable influence on the course of chemical reactions. Cyclodextrin complexation can bring about stereo, regio and optical selectivity on the product distribution. Such selectivities arise due to the restriction brought about by the host cyclodextrin on the rotational and translational movements of the guests or intermediates derived from them. Further, the complexation process is selective resulting in geometrical and conformational control on chemical reactions. Examples of photochemical reactions investigated in our laboratory discussed here highlight the emerging role of chemically inert cavities in selective organic transformations.

INTRODUCTION

One of the greatest challenges to the organic chemist has been to mimic the remarkable catalyses and selectivities of biotic molecular transformations brought about by the enzymes. Considerable amount of effort has been put into the design and the study of 'enzyme models'[1]. One of the most promising fields of study in achieving this goal is the area of 'host-guest chemistry', also termed 'the chemistry of inclusion complexes'. A host molecule is one which is able to accommodate guest units of suitable dimensions into cavities or channels present in its molecular framework. Examples of organic host molecules include urea, deoxycholic acid, Dianin's compound, tri-o-thymotide, hydroquinones and the cyclodextrins. The host-guest fit in these complexes occurs without the formation of covalent bonds, the driving force for complexation being a combination of hydrogen bonding, van der Waal's interactions, hydrophobic effect and solvent liberation forces. Of the host species mentioned above, all but the cyclodextrins form inclusion complexes only in the solid state, the cavities and channels being provided by the specific mode of packing of the host lattice in the presence of the guest. The cyclodextrins are unique in that they possess a rigid molecular cavity that enables them to form inclusion complexes in the solution phase as well as in the solid phase and hence the desired guest orientations can be engineered in the aqueous phase itself. This uniqueness has made the cyclodextrins the most attractive for 'enzyme modelling' studies. Much work on 'enzyme modelling' has been done with the cyclodextrins with the achievement of a remarkable catalytic effect[2].

α, β and γ cyclodextrins are chiral cyclic oligosaccharides comprising of six, seven and eight glucose units respectively, that are connected by 1,4 linkages in a cyclic array, leaving a cavity in the centre, which can accommodate the guests of suitable dimensions[3] (figure 1). The encapsuling effect of cyclodextrins in bringing about selective molecular transformations in the aqueous phase is exemplified by studies on the chlorination of anisole[4] and on the carboxylation of phenols[5]. In both these cases selective attack occurred at the para-position of the aromatic ring. Despite the selectivity achieved in the above thermal reactions, the utility of the cyclodextrins in thermal chemistry has been limited to reactions that proceed with a moderate activation energy. On the other hand, cyclodextrins are the best candidates for utilization in excited state chemistry.

The prime of photochemistry having been completed, with extensive investigations of all types of chromophores yielding less exciting



Cyclo-dextrin	d_1 (Å)	d_2 (Å)	d_3 (Å)	h (Å)
α	5.6	4.2	8.8	7.8
β	6.8	5.6	10.8	7.8
γ	8.0	6.8	12.0	7.8

Figure 1. Structure and dimensions of cyclodextrin cavity.

results, one of the most rewarding goals, for the present-day photochemist would be to attain selectivity in photochemical transformations which would increase their utility in organic synthesis. Our goal, when we entered the arena of 'photochemistry in cyclodextrins' was not only the attainment of selective photochemistry, but also to improve our understanding of the cyclodextrins themselves, by conducting well studied photoreactions in them. In order to achieve the best host-guest fit that is required to achieve maximum selectivity, a suitable choice of the guest is essential and this calls for a thorough knowledge of the host complexation. In this regard, a well-understood photoreaction could aid one, in understanding how exactly the host influenced the course of the reaction.

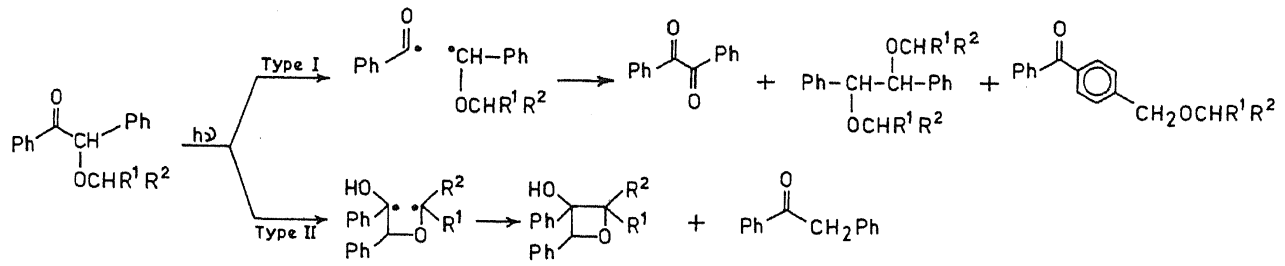
In all our studies, photoreactions were carried out in the aqueous phase in the presence of excess cyclodextrin, and also in the solid cyclodextrin complexes. While in the aqueous phase, the included molecule enjoys a certain amount of flexibility, this is totally refused in the solid complexes due to the tight packing of the surrounding complex molecules. Hence, studies in the aqueous phase should reveal the effect of the cavity alone, while those in the solid complexes show the effect of the cavity as well as the rigid surroundings, on the guest molecules. In the present article we summarize our achievements in the exploration of 'cyclodextrin chemistry' with some phototransformations.

Cyclodextrin complexation is expected to modify the photoreactivity of a substance in the following ways:

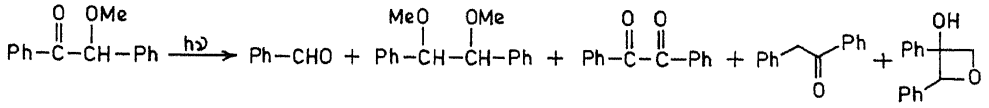
(i) The preferable complexation of one of the many conformations possible for a substrate, to bring about selective transformations that may not be observed in organic solvents.
(ii) Complexation of the substrate in a certain orientation, to protect certain sites from attack by the reactive species.
(iii) Steric restriction on the rotational motions of the reactive intermediates, thus preventing certain modes of decay of the intermediates.
(iv) A 'super cage-effect' preventing the initially formed radicals of a reaction from diffusing away from each other, by holding them together in the cavity.

Conformational control via β-cyclodextrin complexation[6, 7]:

A remarkable effect was observed on the photoreactivity of benzoin alkyl ethers and alkyl deoxy benzoins upon cyclodextrin complexation. Benzoin alkyl ethers are known to undergo Norrish type I reaction as the only photo-process in organic solvents (scheme 1). The competing (type II) hydrogen abstraction process, though



1 $R^1 = R^2 = H$
2 $R^1 = CH_3$; $R^2 = H$
3 $R^1 = R^2 = CH_3$



Benzene	18	58	24	—	—
Methanol	26	62	10	1	—
β-Cyclodextrin/solid (degassed)	8	—	—	69	22
β-Cyclodextrin /solid/O_2	Ph–COOH Ph–COOMe	32 40		16	11
β-Cyclodextrin (soln. 1 : 1)	23	54	7	12	4
β-Cyclodextrin (soln. 1 : 5)	14	53	14	15	4

Scheme 1

feasible in these substrates, is not observed at all in organic solvents. Quite interestingly, the solid β-cyclodextrin complexes of the substrates 1–3, upon irradiation, are found to yield only the type II products in quantitative yields (scheme 1). The control irradiations of crystalline benzoin ethers and of a mixture of benzoin ethers and β-cyclodextrin did not yield any type II products and led to the recovery of the starting materials only. An examination of figure 2 reveals that out of the two possible extreme conformations A and B for these substrates, only B is capable of undergoing the type II process. The preferable complexation of this conformation in the cyclodextrin cavity would account for the remarkable difference in the photoreactivity. Upon prolonged irradiation, the solid β-CD complexes of the benzoin alkyl ethers afford the type II products in more than 60% yield, at which stage the competitive absorption by one of the products, deoxybenzoin acts as internal fitter and slows-down the reaction, suggesting that almost all the substrate molecules are complexed in conformation B. The observation of the type II process from conformation B, trapped inside the cyclodextrin cavity, is possible only when the competing (much faster) type I process is suppressed by the 'cage effect' of the cyclodextrin cavity. This phenomenon is indeed found to be occurring, as shown by the results of the photolysis of solid β-CD complexes of these substrates in an aerated atmosphere, which yielded oxygen trapped products of the initially formed type I radicals. Thus the remarkable difference in photoreactivity of benzoin alkyl ethers in β-cyclodextrin can be attributed to a combination of the 'cage effect' and 'conformational control' afforded by the cyclodextrin cavity. The photolysis of aqueous solutions of the above complexes afforded a mixture of type I and type II products which could be arising due to reactions from the complexed as well as uncomplexed species in the aqueous phase. An increase in the amount of β-cyclodextrin from one to five equivalents which is

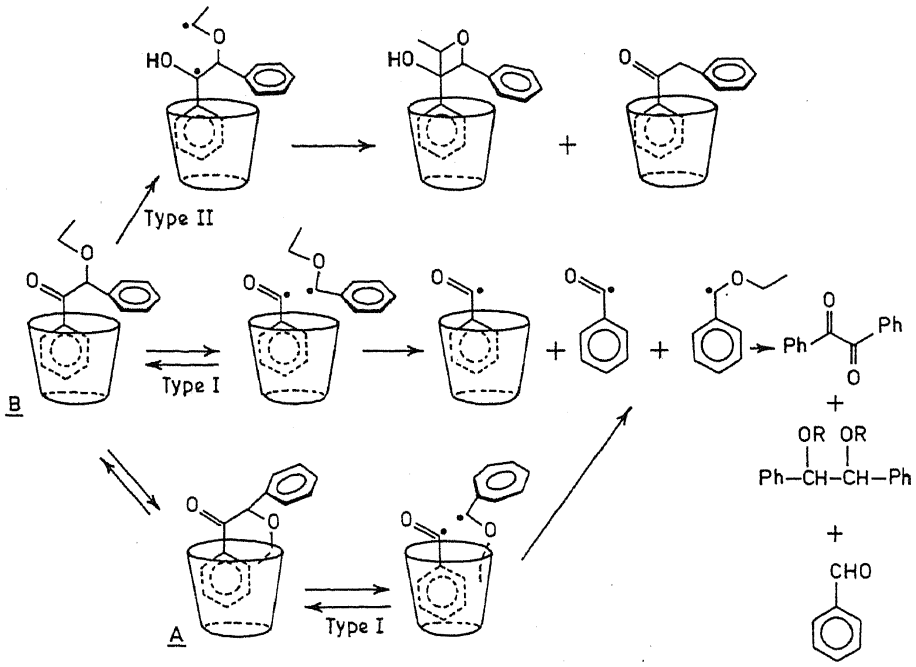
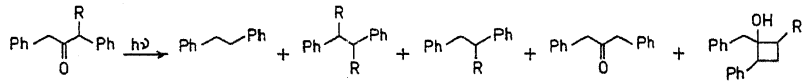


Figure 2. Mechanism of selectivity in product formation during the photolysis of cyclodextrin bound benzoin ethyl ether.



	AA	BB	AB		
4 R = CH_2–CH_3					
Benzene	21	21	45	13	—
Methanol	23	21	44	13	—
β-Cyclodextrin (solid)	<0·5	<0·5	99	—	—
5 R = CH_2–CH_2–CH_3					
Benzene	23	22	45	4	7
Methanol	21	19	39	4	8
β Cyclodextrin (solid)	<0·5	<0·5	99	—	—
6 R = CH_2-CH_2-CH_2-CH_3					
Benzene	17	17	38	14	19
Methanol	17	17	35	15	19
β-Cyclodextrin (solid)	<0·5	<0·5	99	—	—

Scheme 2

expected to suppress the dissociation of the complex, leads to an increase in the yield of type II product, supporting the above contention.

The conformation that is preferred by cyclodextrin may vary from one system to another, depending upon the nature of the included molecule. This is exemplified by the behaviour of α-alkyl dibenzyl ketones in β-cyclodextrin. The substrates 4–6, which undergo both type I and type II processes in organic solvents, upon complexation into the cavity of β-cyclodextrin, give rise to the exclusive formation of the α-cleavage (type I) cage product AB (scheme 2) upon irradiation of the solid complexes. Out of the two possible conformations shown in figure 3 C and D, if the molecule is trapped in conformation C in β-cyclodextrin cavity, the only possible photoreaction is the type I process, the type II being impossible in this conformation. The radicals resulting from α-cleavage, after facile decarbony-

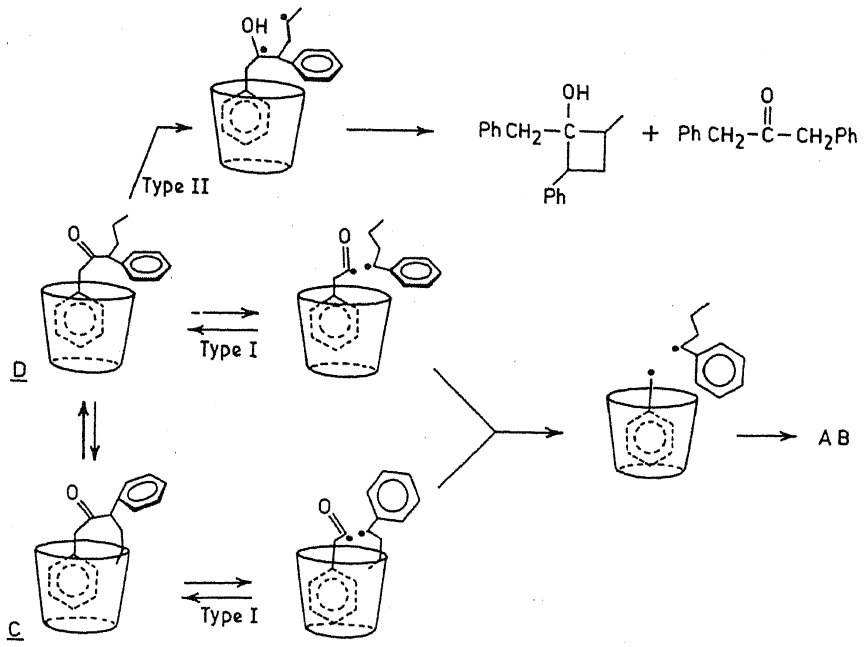


Figure 3. Photo behaviour of α-propyl dibenzyl ketone in cyclodextrin.

lation would readily recombine within the cavity to form the cage product AB, exclusively. It may be noted that the preferred conformation in this case is the reverse of what was observed in benzoin ethers. Thus interesting conformational preferences are observed in β-cyclodextrin.

Molecular traffic control[8–10]:

One of the most striking features of cyclodextrin complexation is the geometrical difference between the complexes of the ortho, meta and para isomers of disubstituted aromatic compounds (figure 4). This has been exploited to the full extent in the enzyme modelling studies by Bender[11], Breslow[12] and co-workers. A remarkable catalysis of the hydrolysis was observed when the meta-substituted esters were studied in comparison with the unsubstituted and the para-substituted esters. This has been attributed to the orientation of the meta-isomer in the cyclodextrin cavity in a suitable manner that brings the carboxylate moiety in close proximity for the cyclodextrin hydroxyls to attack. As can be noticed, such a complexation protects all but one ortho position of the aromatic ring from attack

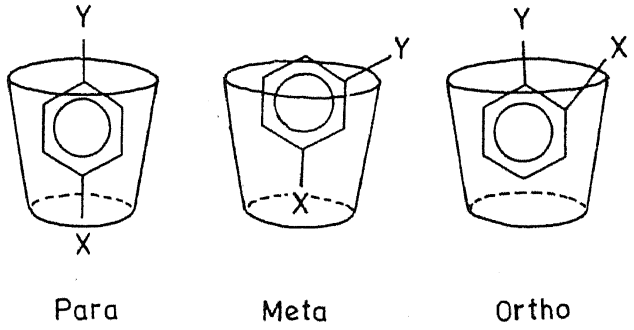


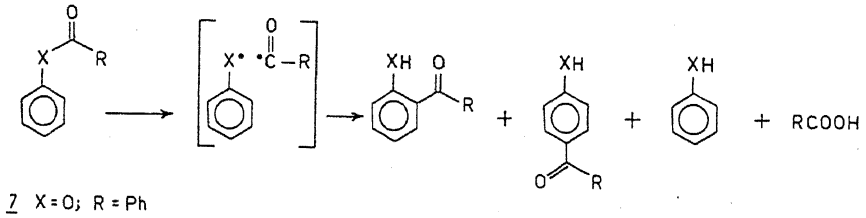
Figure 4. Proposed geometries of the guest (di-substituted benzenes) in cyclodextrin cavity.

by any species. Such a geometrical restriction can control the molecular movement of the attacking reagent. This effect is termed as 'molecular traffic control'. We have succeeded in exploiting this unique feature of cyclodextrin complexation in the photo-Fries rearrangement of phenyl esters and anilides and in the photo-Claisen rearrangement of *m*-alkoxyphenyl allyl ethers.

The well-known photorearrangement of phenyl esters and anilides in organic solvents yields a mixture of the ortho- and para-phenolic

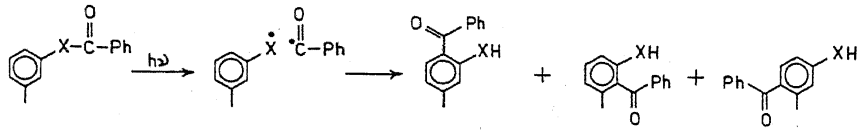
or anilinic ketones with the formation of small amounts of phenol or aniline. Selective attack of the initially formed acyl radical at the ortho position of the aromatic ring, with a complete prohibition of the para attack, could be achieved by irradiating substrates 7 and 8 as their solid β-cyclodextrin complexes or in aqueous solutions containing an excess of β-cyclodextrin (scheme 3). This was interesting, but more so were the results of the corresponding *m*-methyl esters and anilides. Compounds 9 and 10, which form a mixture of two ortho- and a para-rearranged products when photolyzed in organic solvents, upon encapsulation by β-cyclodextrin, revealed not only a complete prohibition of the para-rearrangement, but also a remarkable preference for one among the two ortho-isomers (scheme 4). This demonstrates how the traffic of the acyl radical could be regulated towards the only exposed ortho position of the aromatic ring, in a suitably designed complex (scheme 5).

A tight fit between the host and the guest molecules would be expected to be necessary to bring about maximum selectivity in photoreactions. To fulfil this criterion a suitable choice of the host system and the guest would be needed. Interesting results obtained in the photo-Claisen rearrangement of *m*-alkoxyphenyl allyl ethers highlight the importance of this criterion. Out of the two possible ortho isomers and the para isomer that are formed during photolyses of 11 and 12 in organic solvents, only one ortho isomer was obtained with a remarkable selectivity upon irradiation of the α-cyclodextrin complexes of these substrates (scheme 6). At the same time, the β-cyclodextrin complexes of the same substrates did not yield any significant selectivity. While, α-cyclodextrin, with a smaller cavity was able to



7 X=O; R=Ph					
	MeOH	48	30	14	8
	C_6H_6	55	30	15	—
	β-CD-H_2O (1:10)	~99	≃1	—	—
	β-CD solid	~99	≃1	—	—
8 X=NH; R=Ph					
	EtOH	65	35	—	—
	β-CD-H_2O (1:10)	96	4	—	—
	β-CD solid	100	—	—	—

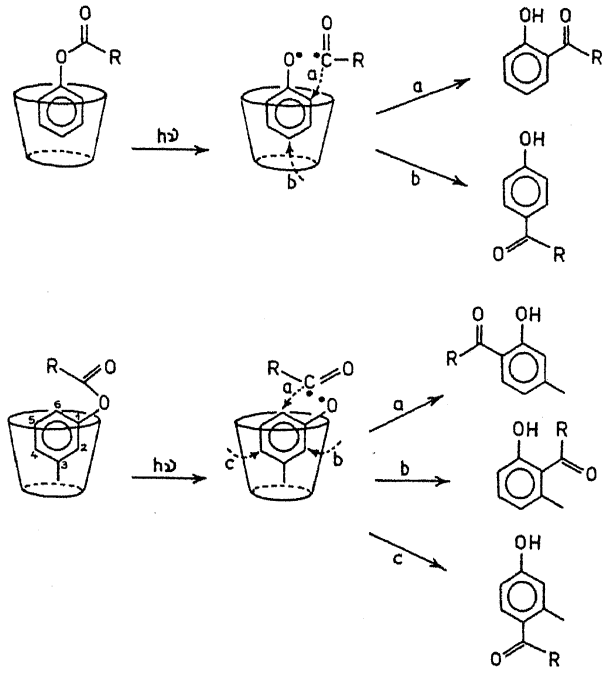
Scheme 3



9 X=O	Methanol	26	21	26
	β-CD soln. (1:10)	66	34	—
	β-CD solid	97	3	—
10 X=NH	Ethanol	41.7	41.7	16.6
	β-CD soln. (1:10)	64	36	—
	β-CD solid	100	—	—

Scheme 4

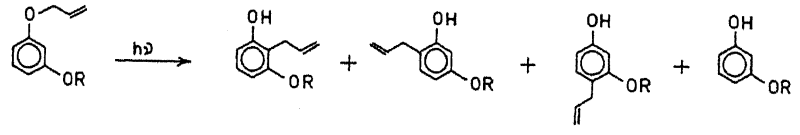
bring about selectivity, the larger cavity of β-cyclodextrin probably failed to hold the molecule tightly. Introduction of an intramolecular filling by a lengthening of the alkoxy substituent chain apparently provided the tight fit necessary for achieving selectivity in β-cyclodextrin. Thus, with increasing chain length of the substituent the selectivity observed in β-cyclodextrin increased.



Scheme 5

At the same time, it might be expected that the presence of too long an alkyl chain that would occupy most of the cavity, pushing the aromatic ring outside, thus exposing both its ortho positions for attack, would not lead to any selectivity at all in the cases of both α and β cyclodextrin complexation. This was indeed the case with *m*-dodecycloxyphenyl allyl ether (figure 5) which did not give rise to significant selectivity upon complexation. Thus a manipulation of the substituents to achieve tight complexation helps to bring about selectivity.

An underlying assumption in the above discussion, which cannot be overlooked, was that the transition state or the intermediate of a reaction prefers to remain in the same complexed geometry as the reactant. This assumption seems to have carried off quite well with the above examples although certain other cases can be categorized in a different manner. The cavity bound intermediate, once formed can relax to a better geometry and hence bring about a different pattern of selectivity that cannot be predicted on the basis of the starting materials' complexed structure. The photobehaviour of α-alkyl DBK's in aqueous β-cyclodextrin is an example of this category. The para rearranged product 13 (figure 6) of the alkyl DBK's, 4–6 which are not formed when photolyzed in organic solvents is obtained



11 R = CH_3	Ethanol	22	28	31	19
	Water	41	41	14	4
	α-cyclodextrin (1 : 10, aqueous)	23	69	8	—
	α-cyclodextrin (solid)	—	100	—	—
	β-cyclodextrin (solid)	62	30	8	—
12 R = $CH_2CH_2CH_3$	Ethanol	38	42	14	6
	Water	36	44	9	11
	α-cyclodextrin (1 : 10, aqueous)	18	72	5	5
	α-cyclodextrin (solid)	5	95	—	—
	β-cyclodextrin (solid)	51	49	—	—

Scheme 6

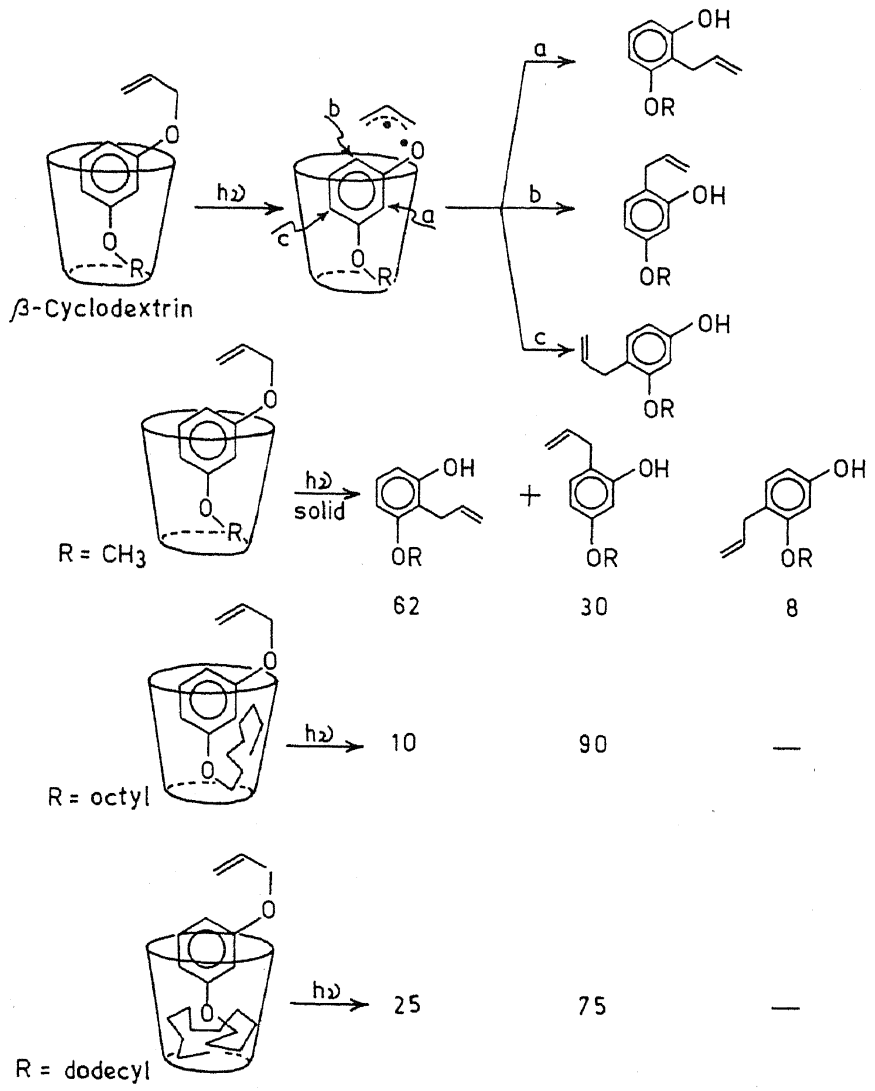


Figure 5. Selective photo-claisen rearrangement of *m*-alkoxy phenyl allyl ethers bound to cyclodextrins.

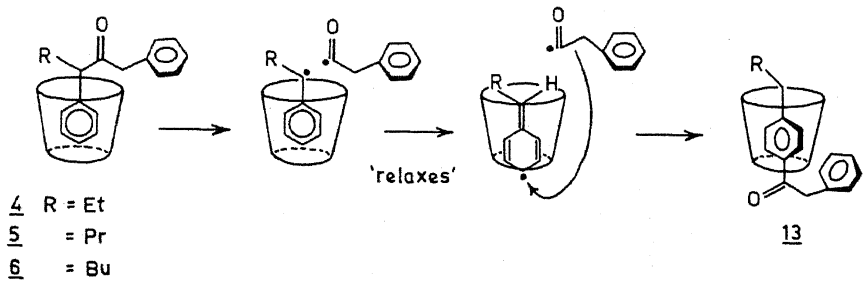


Figure 6. Photo behaviour of α-alkyl dibenzyl ketones complexed to cyclodextrin in aqueous solution.

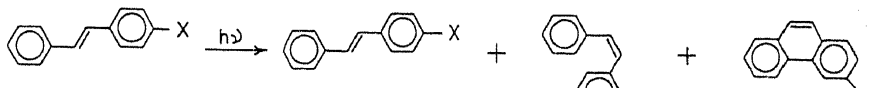
in ~ 60% yield in aqueous β-cyclodextrin. This requires that the para position of the aromatic ring be exposed for attack by the acyl radical, probably by a sinking down of the benzyl radical well into the cavity, presumably due to its hydrophobicity, thus blocking the ortho positions from attack (figure 6). This behaviour would be in contrast to that of the phenoxy

radical in the cases of photo-Fries and photo-Claisen rearrangements in aqueous β-cyclodextrin, where only the ortho product was formed. The apparent relaxation to a stabler form of complexation undergone by the hydrophobic benzyl radical is probably not required by the hydrophilic oxygen radical in the latter cases.

Restriction on rotational and translational motions[13–15]:

The cyclodextrin sleeve that surrounds the guest molecule, does not remain physically inert during a photoreaction, though it does chemically. When a certain mode of decay of an intermediate demands a large degree of parturbation via rotational motion, the inflexible wall of cyclodextrin can, in principle, sterically hinder that reaction from taking place. Impressive selectivities obtained in the photoisomerization of stilbenes and β-ionone and in the Norrish type II reaction of arylalkyl ketones belong to this category. Stilbenes, undergo facile trans ⇄ cis isomerization in organic solvents to afford a photostationary state rich in (~ 85%) the cis isomer (scheme 7). Retardation of the trans → cis isomerization was observed in aqueous solution of the β-CD complexes of the stilbenes 14–17. In all the cases examined, the trans isomer was formed in ~ 70% yield. Interestingly, the cis → trans isomerization proceeded unhindered. This behaviour of the stilbenes was in contrast to that of the alkyl cinnamates 18–20, which behaved in the same manner in organic solvents and in aqueous β-cyclodextrin. The restriction of the geometrical isomerization in the case of stilbenes can be attributed to the effect of the cyclodextrin wall, on the 90° twisted intermediate, sterically preventing it from undergoing further rotation to the cis-isomer. In the case of cinnamates, the carbonyl moiety of smaller dimensions, probably does not experience any retardation to isomerization in cyclodextrin. The facile cis → trans isomerization of the stilbenes in β-cyclodextrin could be attributed to a different mode of complexation of the cis-stilbene (figure 7).

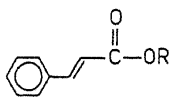
In the case of β-ionone (21) and its derivatives, there is a competition between isomerization and H-abstraction when photolyzed in organic solvents. In β-cyclodextrin, however, there was a remarkable preference for H-abstraction over isomerization (scheme 8). Although β-ionolydene aldehyde (22) abided by the above observation, β-ionone derivatives 23 and 24 formed an exception by behaving similarly in organic solvents and in aqueous β-cyclodextrin. Thus, a phenomenon similar to the stilbenes may not be occurring unless there is a difference in the geometry of the



14 X = H 15 X = CH_3
16 X = F 17 X = OCH_3

Product distribution at photostationary state

X = H			
Benzene	5	91	4
β-CD/ H_2O (10 : 1)	71	29	—



18 R = CH_2CH_3
19 R = $(CH_2)_3CH_3$
20 R = $(CH_2)_5CH_3$

Scheme 7

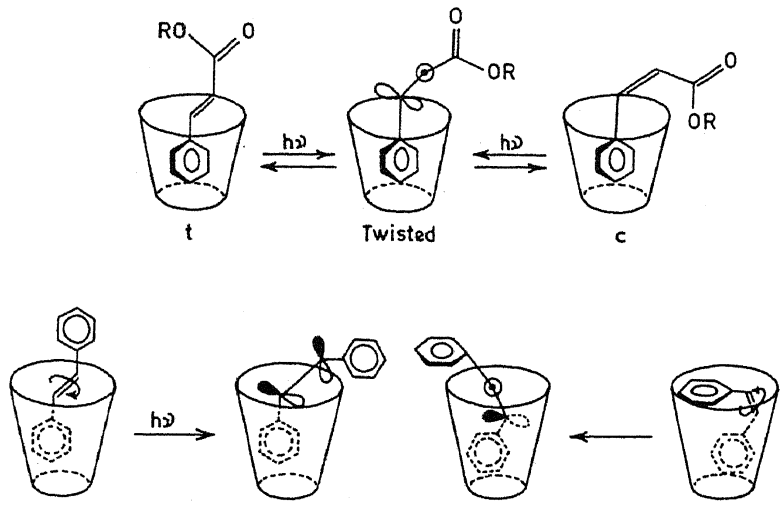
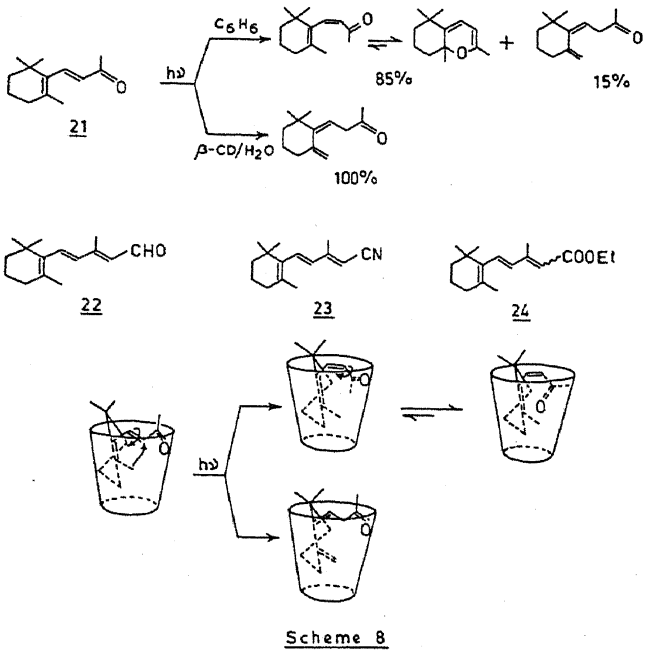


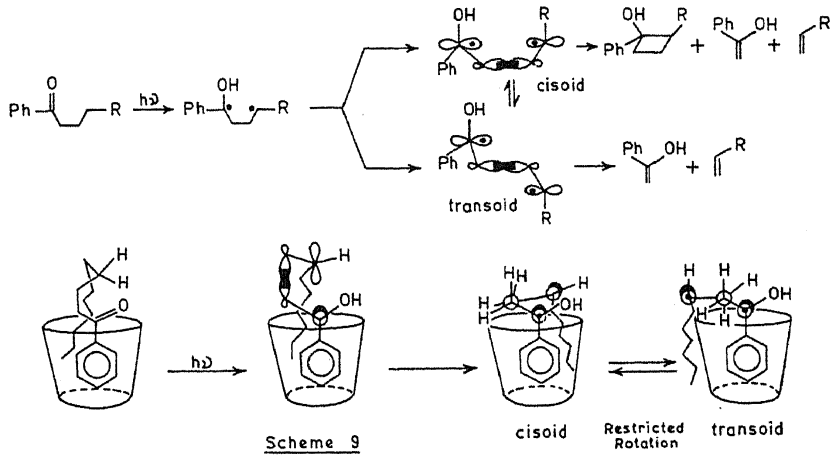
Figure 7. Geometrical isomerization of disubstituted olefins in cyclodextrin cavity.



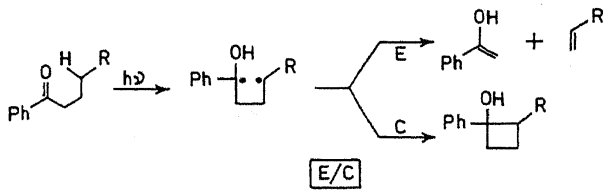
Scheme 8

complex for the two sets of compounds. A point of interest in this reaction is that the two products arise from two different excited surfaces, namely, $^1\pi\pi^*$ and $^1n\pi^*$. A close examination of the UV spectra of the complexes of 21 and 22 shows that a possible switch between $^1\pi\pi^*$ and $^1n\pi^*$ could have occurred in β-CD due to the polarity experienced by the molecule inside the cavity. The above example is thus an interesting illustration of the polarity effect of β-cyclodextrin in bringing about selectivity.

The 1,4-biradical that forms an intermediate in the Norrish type II reaction, has two modes of further reaction, namely, fragmentation and cyclization, apart from returning to the starting ketone (scheme 9). The triplet biradical, that is formed in the cisoid form, readily equilibrates with the transoid geometry, the transoid being favoured in hydrogen bonding solvents like tert-butanol or water. Intersystem crossing generates the singlet biradical that remembers the conformation of the corresponding triplet, and hence the ensuing products reflect the conformation of the triplet biradical. It may be noted that the transoid form can undergo only fragmentation while the cisoid form can also cyclise to give the corresponding cyclobutanol. The equilibrium between the cisoid and the transoid geometries which lies in favour of the transoid in organic solvents can be shifted in favour of the cisoid in β-cyclodextrin by the introduction of a long alkyl tail to the molecule, that would anchor the molecule inside the cavity in the cisoid form, the cisoid → transoid conversion being highly restricted by β-cyclodextrin. Such a trapping of the cisoid form of the 1,4-biradical by the β-cyclodextrin cavity should bring about an increased cyclization yield at the expense of the fragmentation process. This was observed in the



Scheme 9



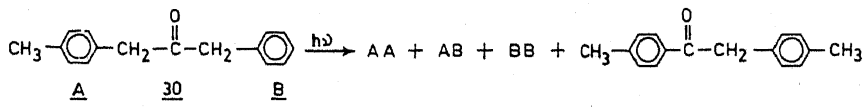
	Benzene	t-Butanol	β-CD soln. (1:1)	β-CD solid
25	6.56	8.55	3.88	3.5
26	3.03	4.22	3.82	2.65
27	1.2	2.55	1.76	0.79
28	2.48	3.28	1.64	0.69
29	1.58	2.88	1.42	0.35

Scheme 10

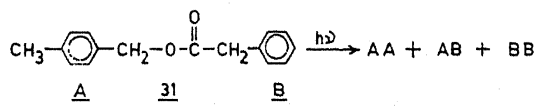
type II reaction of arylalkyl ketones 25–29 in the solid β-cyclodextrin complexes (scheme 10). Based on the above arguments, an increase in the alkyl chainlength should bring about an increased yield of the cyclised product, by arresting the cisoid → transoid conversion further to increasing extents, and this was indeed observed.

Super cage effect[16]:

The important role of 'cage effect' of cyclodextrin was mentioned in the photoreaction of benzoin-alkyl ethers and alkyl DBK's. A full demonstration of this cage control of a radical reaction in β-cyclodextrin was made in the photolysis of dibenzyl ketones and benzylphenyl acetates. The substrates 30 and 31 are known to form benzyl radicals A and B upon photolysis and these in organic solvents undergo coupling to give a statistical mixture of the products AA, AB and BB. Photolysis in β-cyclodextrin produces a single product AB in all the cases in



Benzene	25	50	25%	—
β-Cyclodextrin (solid complex)	1	86	1.5	12



Benzene	20	60	20%
β-Cyclodextrin (solid complex)	<1	99	<1%

Scheme 11

quantitative yields (scheme 11). This demonstrates the efficiency of the supercage provided by the cyclodextrin in keeping the two benzyl radicals together, to generate the coupling product AB.

In conclusion, it can be realized that the study of 'host-guest chemistry' has opened up a new pathway for the photochemist to trek into. The results of the above investigation only expose the fertility of the field of 'inclusion-complexes' for further investigation and utilization to suit the interests of the aspiring organic chemist.

20 June 1986

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ANNOUNCEMENTS

NATIONAL SYMPOSIUM ON 'USE OF NUCLEAR AND ALLIED TECHNIQUES IN RESEARCH ON SOIL FERTILITY AND FERTILIZER USAGE'

A National Symposium on 'Use of Nuclear and Allied Techniques in Research on Soil Fertility and Fertilizer Usage' organized by the Department of Atomic Energy will be held at Tamil Nadu Agricultural University, Coimbatore during *January 21–23, 1987*. For further details contact Dr T. J. D'Souza, Nuclear Agriculture Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085.

KAAS AWARDS FOR 1986

This has reference to the announcement about the above awards—vide *Curr. Sci.*, Vol. 55, No. 16, p. 814, 1986. The last date for the receipt of the applications for the Awards has been extended to **15th October 1986.**