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Asymmetric Induction With Cyclodextrins: Photocyclization of Tropolone Alkyl Ethers

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Dedicated to F. Toda on the occasion of his retirement from Ehime University

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Abstract—Employing the photobehavior of tropolone alkyl ethers as the probe, we have established that cyclodextrins could as a serve as a medium to bring about enantioselective photoreactions. The enantioselectivity observed in this study is moderate at best. The enantioselectivity observed in the solid state in comparison to aqueous solution suggests that a rigid environment may be essential to achieve chiral induction during photoreactions of organic molecules. In this context the much higher enantioselectivity observed for the same systems within zeolites is noteworthy.

Introduction

The efforts of chemists during the past few decades have greatly advanced the field of thermal asymmetric synthesis.[1] Even complex molecules can now be synthesized as single enantiomers. Unfortunately, asymmetric photochemical reactions have not enjoyed the same level of success.[2] In the past, chiral solvents, circularly polarized light, and chiral sensitizers have been utilized to conduct enantioselective photoreactions. The highest chiral induction achieved by any of these approaches at ambient temperature and pressure has been ~30% (2–10% enantiomeric excess [e.e.], being common in photochemical reactions under above conditions). The chiral auxiliaries approach, a popular method in solution thermal chemistry, has also been used with success in photochemistry by Scharf and co-workers.[3] Most encouraging results have been obtained using the crystalline state and solid host–guest assemblies. Chiral induction in the crystalline state have been achieved by two methods. In one, by the Weizmann Institute Group, the achiral reactant is crystallized into a chiral space group.[4] The low probability of such crystallization of organic molecules renders this approach less general. The second approach, due to Scheffer using an ionic chiral auxiliary to effect a chiral environment limits it to molecules with carboxylic acid groups that form crystallizable salts with chiral amines or vice versa.[5] The highly successful approach due to Toda using 1,6-bis (*o*-chlorophenyl)-1,6-diphenyl-2, 4-hexadiyne-1, 6-diol as a chiral host is limited to guests that can form solid solutions with the host without any disturbance to the host's macro-structure.[6] Unfortunately, the high cost of the above host ($279.0/gm; Fluka) prevents it from being a routine medium of choice. However, yet another chiral organic host, viz. cyclodextrins (CDs), are inexpensive ($0.12/gm; Wacker Biochem) and readily available. Cyclodextrins are routinely used as a stationary phase in chiral GC and HPLC columns. Their utility as reaction media to effect chiral induction during photochemical reaction remains less explored.[7,8]

Cyclodextrins, one of the most commonly used host systems, possess hydrophobic cavities which in aqueous solution can include a variety of organic molecules whose character can vary from hydrophobic to ionic.[7] The internal diameters and depths of cyclohexaamylose (α-CD), cycloheptaamylose (β-CD), and cyclooctaamylose (γ-CD) provide cavities of various sizes. The oligosaccharide ring forms a torus, with the primary hydroxyl groups of the glucose residues lying on the narrow end of the torus. The secondary glucopyranose hydroxyl groups are located on the wider end. Inclusion complexes of known ratio containing the guest within the cavities of CD can be precipitated from aqueous solutions of CD when the guest is in excess. Such precipitates contain the guest accommodated within the cavities of the CD. An important property of the CD is its chirality: β-CD is dextrorotatory with $[\alpha]_D = +162°$. The selective inclusion of optical isomers by CD has been the underlying factor in its use as a stationary phase in the GC and HPLC chiral columns.[9] Although CD has been the medium of choice to separate chiral isomers, its role as an agent to carry out enantioselective photoreaction has not been established. In this report we present our preliminary results on the use of CD as a chiral reaction medium.

Several reports of chiral induction during irradiation of achiral molecules included in CD have appeared in the

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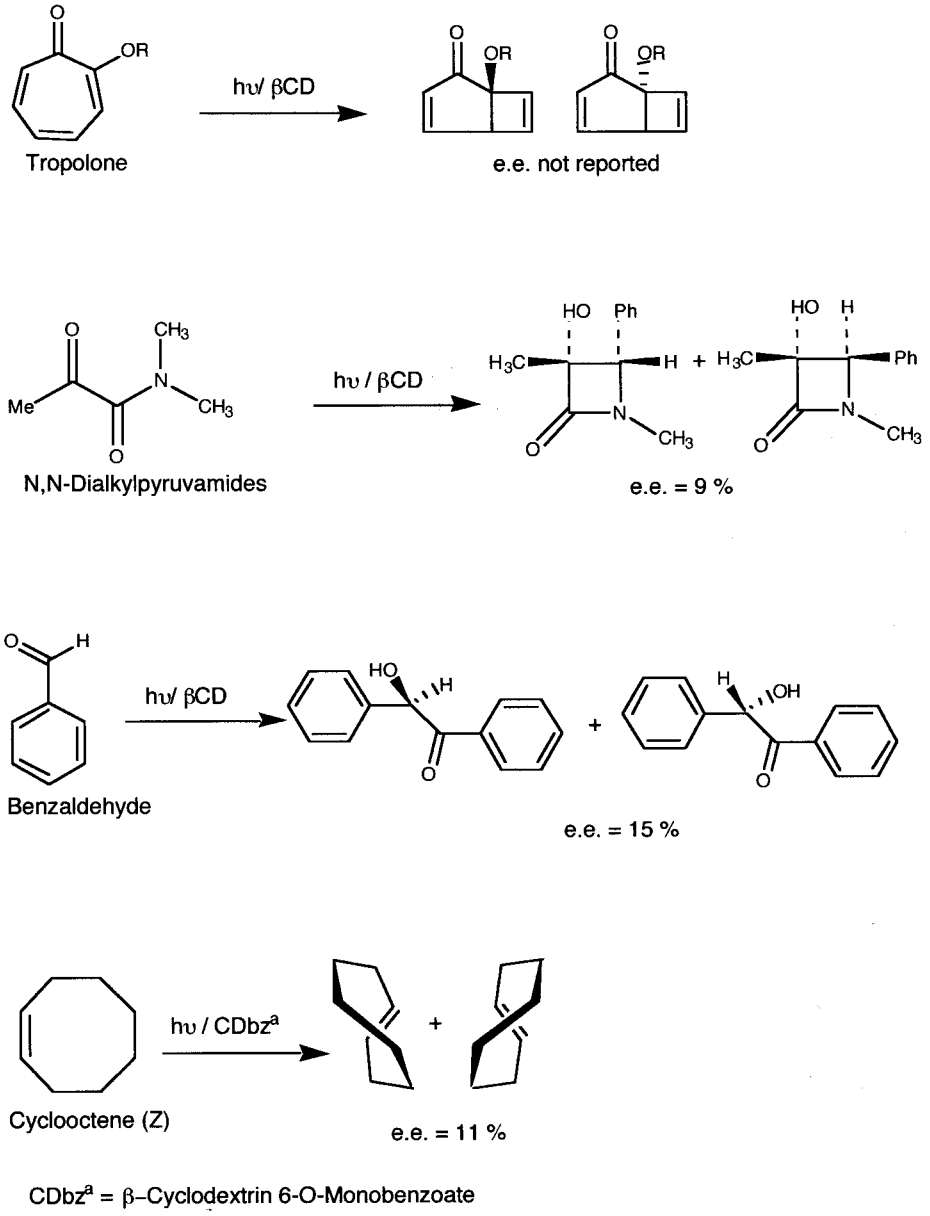
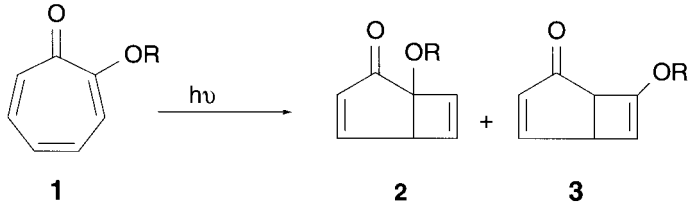


Scheme 1.



1a R =CH_3
1b R =CH_2CH_3
1c R =CH_2Ph
1d R =CH_2CH_2Ph
1e R =$CHCH_3CH_3$
1f R =$CH_2{}^*CH(CH_3)CH_2CH_3$ S(+)
1g R =$CH_2CH_2CH_2Ph$

Scheme 2.

Table 1. Enantioselective photoisomerization of tropolone alkyl ethers as cyclodrextrin complexes in the solid state and as aqueous solution

Tropolone alkyl ether: Alkyl substituent	Cyclodextrin	Host:guest	Irradiation time (min)	Product ratio **2**:**3**	e.e.% solid	e.e.% solution
Methyl	α	1:1	45	1:16	28	0
Ethyl	α	1:1	45	1:7	20	0
Benzyl	β	2:1	180	1:3	20	3
Ethylphenyl	β	2:1	15	1:0.1	25	0
Ethylphenyl	γ	2:1	15	1:0.1	33	4
Propylphenyl	γ	2:1	15	1:0.1	9	3

literature (Scheme 1).[10] One of the earliest reports on the use of CD as a chiral reaction medium for photochemical reactions is by Takeshita and co-workers.[10a] Even though these authors provide no numbers the e.e. obtained during the photocyclization of tropolone methyl ether by them is believed to be small. Aoyama and co-workers recognized the feasibility of chiral induction during the photocyclization of *N*,*N*-dialkylpyruvamides complexed to CD (though the enantiomeric excess obtained in the product was only 9% in β-CD).[10b] By irradiation of benzaldehyde included in β-CD, Turro and Rao have obtained benzoin with an e.e. of about 15%.[10c] Inoue and co-workers obtained an e.e. of 11% in the product *trans*-cyclooctene when the corresponding *cis* isomer was sensitized by β-cyclodextrin 6-*O*-monobenzoate.[10d,e] Although the potential of the CD as a chiral medium has been recognized by several groups, a systematic study is lacking. With this background we have investigated the photochemical behavior of tropolone alkyl ethers within α-, β-, and γ-CD.[11]

Results and Discussion

Probe reaction

Irradiation of tropolone alkyl ether **1** results in a 4 π-electron disrotatory ring closure to yield a bicyclo[3.2.0] product **2** containing two chiral centers (Scheme 2).[11] Prolonged irradiation yields a secondary product **3**. Since the cyclization of tropolone alkyl ether has been investigated earlier in hosts such as zeolite and 1,6-bis (*o*-chlorophenyl)-1,6-diphenyl-2, 4-hexadiyne-1, 6-diol, it seemed to be an appropriate probe to assess the chiral influence of CD on a photoreaction.[12] In this study we focussed on the chiral

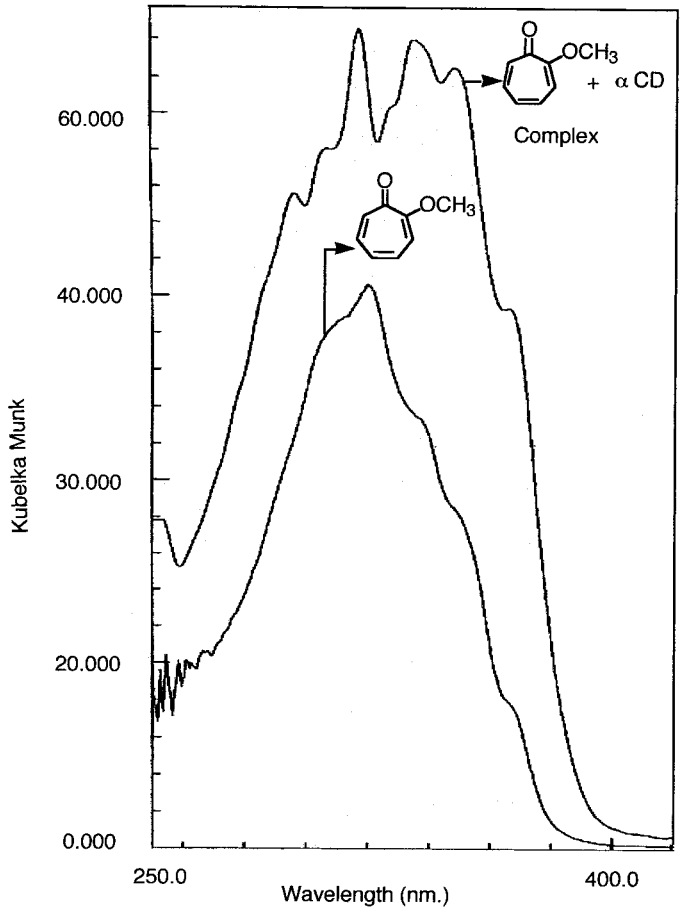


Figure 1. The UV absorption of tropolone methyl ether in solution and diffuse reflectance spectrum of the tropolone methyl ether–α-cyclodextrin complex in the solid state.

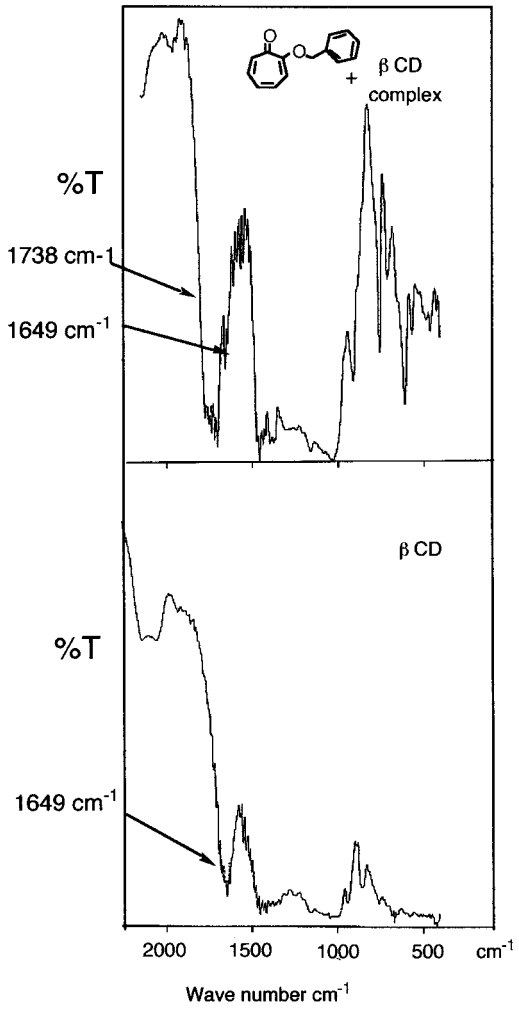


Figure 2. The IR spectra of β-cyclodextrin and tropolone benzyl ether–β-cyclodextrin complex. Both recorded as KBr pellets.

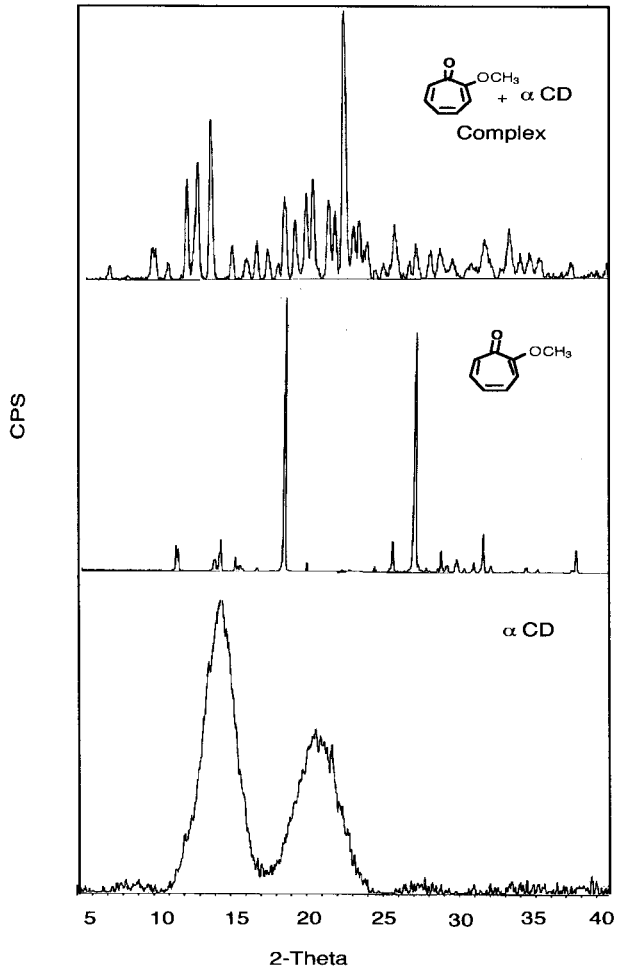


Figure 3. X-Ray powder photographs of α-cyclodextrin, tropolone methyl ether and tropolone methyl ether–α-cyclodextrin complex.

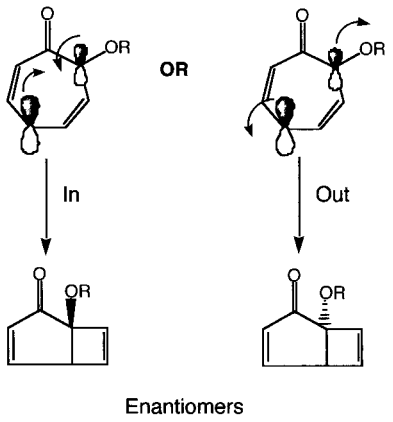
induction in product **2**. The results of studies with four tropolone alkyl ethers (**1a**–**d**) are presented and the results of three others (**1e**–**g**) briefly mentioned in this report. Each one of these ethers were investigated as complexes of all three (α, β, or γ) CD. A moderate chiral induction was observed only in a few cases. Results are summarized in Table 1.

Complexation

Addition of an ether solution of tropolone alkyl ethers **1a**–**g** to a saturated aqueous solution of cyclodextrin (α, β, or γ) and stirring overnight precipitated a white solid in most cases. The precipitate formed was filtered, washed several times with diethyl ether to remove the uncomplexed guest and then dried under vacuum at 50°C for 12 h. The complexes were characterized by their UV and IR absorptions, and X-ray powder photograph (Figs. 1–3). The UV absorption spectrum of the CD complex and the solution spectrum of tropolone methyl ether are identical (Fig. 1). Evidence of absorption corresponding to the carbonyl chromophore in the IR spectra indicated the inclusion of tropolone benzyl ether within the CD (Fig. 2). The X-ray powder pattern of the precipitated white solid complex differed from that of pure CD suggesting the former to be a true complex and not a mechanical mixture of CD and tropolone methyl ether (Fig. 3). The molar ratio of the tropolone alkyl ether and the CD was calculated by estimating the amount of tropolone alkyl ether extracted from a known amount of the complex. Depending on the nature of the alkyl group and the CD a 1:1 or 2:1 (host:guest) complexes were formed (Table 1). Since **1a** and **1b** could not be fully extracted from their CD complexes with diethyl ether the amount that complexed with a known amount of CD was estimated from the knowledge of uncomplexed **1a** and **1b**. We could only speculate on the structure of the tropolone alkyl ether–CD complexes due to difficulty in obtaining crystals suitable for X-ray crystallographic work.

Photochemistry

Irradiation (450 W medium pressure mercury lamp) of complexes were carried out both as solids and aqueous solutions. For solid irradiation, the CD complex made into a fine powder and spread on a petri dish was stirred frequently (every 10 min) with a spatula during the irradiation period to ensure uniform exposure to light. The sample was then dissolved in deionized water and extracted with dichloromethane. Product analysis was carried out using a GC or HPLC (columns used: Supelco β-Dex 325 and Chiralcel



Scheme 3.

OD, respectively). For solution irradiation, the complex was dissolved in distilled water (enough water to obtain a clear solution) and irradiated. Following irradiation, the products were extracted with either chloroform or dichloromethane and analyzed as above. The current study focussed only on the ability of CD to induce chiral induction on the products. The enantioselectivities on product **2** obtained under various conditions are provided in Table 1. The enantiomeric excesses obtained during solid state irradiation although moderate (20–30%) were certainly higher than the numbers reported thus far on other systems (a maximum e.e. of 33% we have obtained as compared to the thus far highest number of 15% e.e. reported by Turro and Rao during the formation of benzoin from benzaldehyde).[10c] Solution irradiations of tropolone alkyl ether-CD complexes gave mostly racemic products.

Correlation between structure and enantioselectivity

The near zero e.e. obtained in solution (Table 1) and the moderate e.e. in solid state (20–30%) suggest the rigidity of the medium to be an important parameter in chiral induction during a photoreaction. Additionally, tight complexation between the reactant and the CD is also found to be a prerequisite for enantioselectivity. Factors affecting the CD–reactant complexation such as the size of cavities in the CD and the bulkiness of alkyl side groups of the reactant alter the e.e. The e.e. obtained in the different CDs such as 28, 5 and 0% in α, β and γ-CD, respectively, with **1a** and 20 and 0% in α and γ-CD, respectively, with **1b** point to the importance of cavity size in chiral induction. The alkyl group on the reactant has to be small enough to sufficiently bury the reactant within the CD. While tropolone methyl ether and tropolone ethyl ether gave moderate e.e., α-CD complexes of tropolone isopropyl ether (**1e**) and tropolone 2-methylbutyl ether (**1f**) gave <5% e.e and d.e. respectively. In view of the fact that chiral centers are present only at the rims of the CD the role of the bulkiness of the alkyl group is understandable.

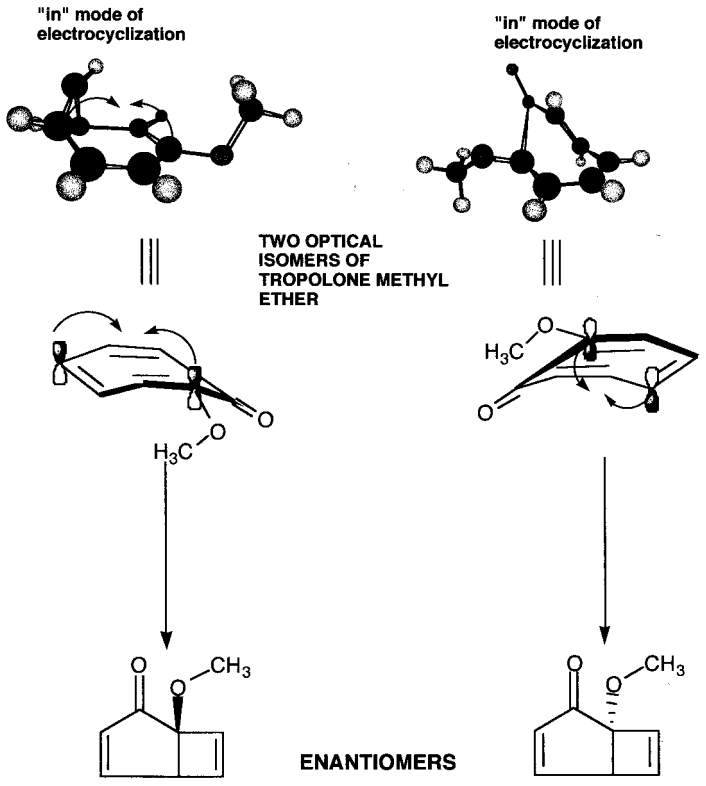
Tropolone alkyl ethers with a phenyl substituent **1c** and **1d** form 2:1 (host:guest) complexes with β-CD (Table 1). In such complexes the tropolone and phenyl moieties of the guest are, most likely, bound to two different CD units. As seen in Table 1 the e.e. is independent of the host:guest ratio; e.e. obtained with the 2:1 complexes of **1c** and **1d** and 1:1 complexes of **1a** and **1b** are in a similar range (25–35%). We believe that even in 2:1 complexes the reactive part of the molecule, namely the tropolone moiety lies close to the rim of CD. At this stage we do not fully understand the lack of chiral induction in the case of CD complexes of tropolone 3-phenylpropyl ether (**1g**). Based on the photochemical behavior of **1a–g** we tentatively conclude that a tight inclusion of the guest coupled with a rigid arrangement of the host favors enantioselectivity during a photochemical reaction within the CD.

A model

Product **2** is formed by the '4e' electrocyclization process from the tropolone alkyl ether. The allowed disrotation could occur in two modes, 'in' or 'out', yielding opposite enantiomers (Scheme 3). The non-planar tropolone alkyl ether can exist in two chiral forms (Scheme 4). In a non-planar molecule the two modes of rotations ('in' and 'out') are unlikely to be equally favored. Even under such conditions only a racemic product mixture is expected. Since by the same mode (e.g. 'in') of rotation the two optical isomers of tropolone alkyl ether would give the opposite optical isomers of the product **2**. In solution a fast equilibrium between the two optical isomers of **1** ensures that the product **2** is racemic even when the rotation occurs in one direction only. In the solid state such a fast equilibrium is less likely. However, in the absence of a chiral medium one would expect **1** to be present as a 1:1 mixture of the two forms (Scheme 4). It is likely that that CD preferentially includes one of the two chiral forms of **1**. Such a preferential inclusion could likely be the origin of the observed enantioselectivity. The fact that chiral induction is not obtained in aqueous solution suggests that the equilibrium between complexed and uncomplexed forms destroys the preferential inclusion by CD. Thus enantioselectivity, as per this model, occurs at the reactant stage itself. We are in the process of seeking experimental support for the proposed model.

A comparison

In the context of chiral induction, achiral tropolone alkyl ethers have been investigated as guests within 1,6-bis (*o*-chlorophenyl)-1,6-diphenyl-2, 4-hexadiyne-1, 6-diol, cyclodextrin and chirally modified zeolites.[12] Since the studies by Takeshita and co-workers have not provided any quantitative data on chiral induction within CD we are unable to compare our data with theirs.[10a] Toda and co-workers have reported that when tropolone methyl ether and tropolone ethyl ether as complexes of 1,6-bis (*o*-chlorophenyl)-1,6-diphenyl-2, 4-hexadiyne-1, 6-diol were irradiated, a single optical isomer of the cyclized product **2** (e.e.=100%) is obtained in 11% yield.[12a] As indicated in the introduction, the drawback with this approach is the prohibitive cost of the host system as well as lack of predictability concerning the success of host–guest complex formation with a given guest molecule. Our own studies with tropolone alkyl ethers within chirally modified zeolites have yielded e.e. in the range of 40–78%.[12e] The e.e. we have obtained with CD as the host though low when compared to the above results with 1,6-bis (*o*-chlorophenyl)-1,6-diphenyl-2, 4-hexadiyne-1, 6-diol and zeolites as hosts, is nevertheless significant.



Scheme 4.

Summary

We have established in this report that cyclodextrins can be used as reaction media to bring about enantioselective photoreactions. The enantiomeric excess obtained thus far by us as well as by others is at best only moderate. The considerable knowledge on cyclodextrins as chiral supports for analytical separation of enantiomers, as models for biological systems, and the low cost of CD are expected to aid in planning and executing experiments that would develop a model capable of predicting the enantioselectivity of a photoreaction. The preliminary results on chiral induction reported here are expected to serve as a starting point for X-ray structural investigation of guest-CD complexes.[13] Unequivocal structures of reactants within the CD will greatly help in understanding chiral induction by cyclodextrins.

Experimental

Synthesis of tropolone alkyl ether derivatives

All tropolone alkyl ethers were synthesized following the general procedure described below.[14] To a stirred mixture of tropolone (1.22 g, 10 mmol; Aldrich), anhydrous potassium carbonate (4.15 g, 30 mmol) and dicyclohexano-18-crown-6 (375 mg, 1 mmol; Aldrich) in dry acetonitrile (50 ml) the corresponding alkyl halide (50 mmol, Aldrich) was added. The suspension was heated to reflux and stirred vigorously for up to 10 h. When reaction was complete as indicated by TLC, the suspension was filtered, the filtrate evaporated and the residue dissolved in methylene chloride. This solution was washed with 2N potassium carbonate to remove any unreacted tropolone, dried using magnesium sulfate and evaporated to give the product, which was purified by column chromatography (silica gel eluted with isopropyl alcohol and petroleum ether).

Complexation of tropolone alkyl ethers with cyclodextrin

A typical procedure adopted for complexation of tropolone alkyl ethers **1a–g** with all three (α-, β- and γ-) CD (American Maze and Co.) is described below.[15] To a saturated solution of cyclodextrin (1.3, 0.17 and 0.7 gm of α, β, and γ-CD, respectively, in 10 ml water) equimolar amount of the tropolone alkyl ether was added as a diethylether solution and left to stir for 24–48 h. The precipitate was filtered and the residue washed several times with diethylether to remove any uncomplexed guest. The complex was dried overnight in a vacuum oven (10^{-2} Torr) maintaining a temperature of 50°C.

Characterization of tropolone alkyl ether cyclodextrin solid complexes

Diffuse reflectance spectra of the solid host–guest complexes were recorded using Shimadzu UV-2101PC spectrometer. IR spectra were recorded as KBr pellets with Perkin–Elmer RXI FT-IR system. X-Ray powder photographs of the host CD, the guest (if solid) and the host–guest complex were recorded on a Scintag XDS 2000 diffractometer.

Irradiation of tropolone alkyl ether cyclodextrin complexes

The complexes were irradiated both as solids and as aqueous solutions. For solid irradiation, a weighed amount of the dried complex was crushed to a fine powder and placed on a petri dish. The sample was then subjected to UV irradiation (450 W medium pressure mercury lamp, pyrex filter) for the required amount of time (30–45 min) with frequent stirring of the sample (every 10 min). Following irradiation, the complex was dissolved in water and extracted at least three times with either chloroform or dichloromethane. The extracts were then dried using magnesium sulfate followed by evaporation of the solvent to get the products. The products were analyzed by HPLC (Chiracel OD) and GC (Supelco β-dex 325). For solution irradiation a weighed amount (~60 mg) of the dried complex was dissolved in distilled water (100 ml) and purged with nitrogen gas and then subjected to UV irradiation for 10 min. The extraction and analysis procedures were the same as with solid irradiation.

Determination of the host–guest ratio

A preweighed amount of the dry complex (450 mg tropolone benzyl ether and 350 mg tropolone ethyl phenyl ether) was dissolved in water and extracted three times with dichloromethane. The dichloromethane extracts were dried using magnesium sulfate, filtered and then evaporated to dryness, which left behind just the compound (the guest). The amount of cyclodextrin present was calculated from the difference in weight of the extracted and the initial weight of the dry complex. The molar ratio of the host cyclodextrin and the guest tropolone alkyl ether represented the complexation ratio. Since tropolone methyl ether and tropolone ethyl ether could not be completely extracted from their CD complexes by either dichloromethane or diethyl ether a different approach was used to measure the host:guest ratio in these two cases. A known amount of cyclodextrin (1 gm α CD for tropolone methyl ether and 1.25 g α CD for tropolone ethyl ether) was used to prepare a saturated solution in water. An equimolar amount of the guest (149 mg tropolone methyl ether and 193 mg tropolone ethyl ether) was added to this saturated solution and left to stir. On completion of the complexation (24–48 h) the slurry was filtered and washed several times with diethyl ether. The filtrate was collected and extracted three times with dichloromethane. The dichloromethane extracts were dried using magnesium sulfate, filtered and then evaporated to dryness to leave behind the guest, which was weighed. This represented the amount of guest that remained uncomplexed, which when subtracted from the guest used for the complexation study gave the amount of guest complexed. The molar ratio of the two, i.e. the host (cyclodextrin) and the complexed guest (tropolone alkyl ether derivative) gave the complexation ratio.

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