PINSA, **68, A**, No. 5, September 2002, pp. 453-463

ASYMMETRIC INDUCTION WITH β CYCLODEXTRIN: *CIS-TRANS* PHOTOISOMERIZATION OF DIPHENYL-CYCLOPROPANE AND ITS DERIVATIVES

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(Received 17 June 2002; Accepted 16 August 2002)

Cyclodextrins due to their inherently chiral nature can bring about moderate enantio and diastereoselectivity during the photoreactions of included guest molecules. Photoisomerization of diphenylcyclopropane and its derivatives have been used as a useful probe for this purpose. Interestingly, the optical isomers that are favoured by β-CD during the photoisomerization of diphenylcyclopropane and its derivatives are the same one that are selectively included when a racemic mixture is equlibrated with β-CD.

Key Words : Asymmetric Induction; Cyclodextrins; Photochemistry; Cyclopropanes

Introduction

Recently several groups including authors have actively pursued asymmetric induction of products during photochemical reactions[1]. Zeolites, host-guest complexes and crystals have been used as suitable media to carry out asymmetric photochemical reactions[2]. Cyclodextrin (CD) is another host capable of carrying out such reactions[3]. They are inexpensive ($0.12/gm; Wacker biochem) and readily available. 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[4]. Recently, we showed that using cyclodextrins moderate enantiomeric excesses could be obtained during photocyclization of tropolone ethers[5]. In spite of random attempts, their utility as reaction media to effect chiral induction during photochemical reaction remains less explored[6,7]. To further probe the utility of cyclodextrin as a chiral medium we have investigated the photoisomerization of *meso cis*-diphenyl-cyclopropane and its derivatives to the optically active *trans* form[8]. Results of this study are presented in this report.

1,2-Diphenylcyclopropane has played a central role in the quest for new methods of asymmetric induction in organic photochemistry[8]. *cis*-1,2-Diphenylcyclopropane, which is achiral, can be transformed into its chiral *trans* isomer by both singlet and triplet-photosensitized irradiation. Following the original report by Hammond and Cole (ee 6.7%), the chiral induction on this isomerization process has been investigated by at least five independent research groups and the best ee obtained thus far is only 10% (Scheme 1). We have chosen *cis*-diphenylcyclopropane **1** and *cis*-diphenylcyclopropane-1-carboxylic acid derivatives (ester **3** and two of its amide **4** and **5**, Scheme 2) as substrates to examine the potential of CD as a medium to perform chiral induction during photochemical reactions. Results presented in this report show an improvement in optical selectivity over previous attempts during the geometric isomerization of *cis*-1,2-diphenylcyclopropane systems. Compounds **1** and **3** were studied for enantioselectivity and compounds **4** and **5** for diastereoselectivity within cyclodextrins. It must be mentioned here that attempts were made to complex all five compounds with all three cyclodextrins (α, β, γ) but the results presented in this report are mainly of those with β-CD because either α and γ-CDs do not form complexes or the stereoselectivity is insignificant. Photochemistry of compounds **3**, **4** and **5** did not require any sensitizer whereas the isomerization of compound **1** was effected with the help of a triplet sensitizer (4′ methoxyacetophenone).

Results and Discussion

Complexation and Characterization

Addition of ether solution of *cis*-diphenyl cyclopropane and its derivatives (**1**, **3**, **4** and **5**) to a

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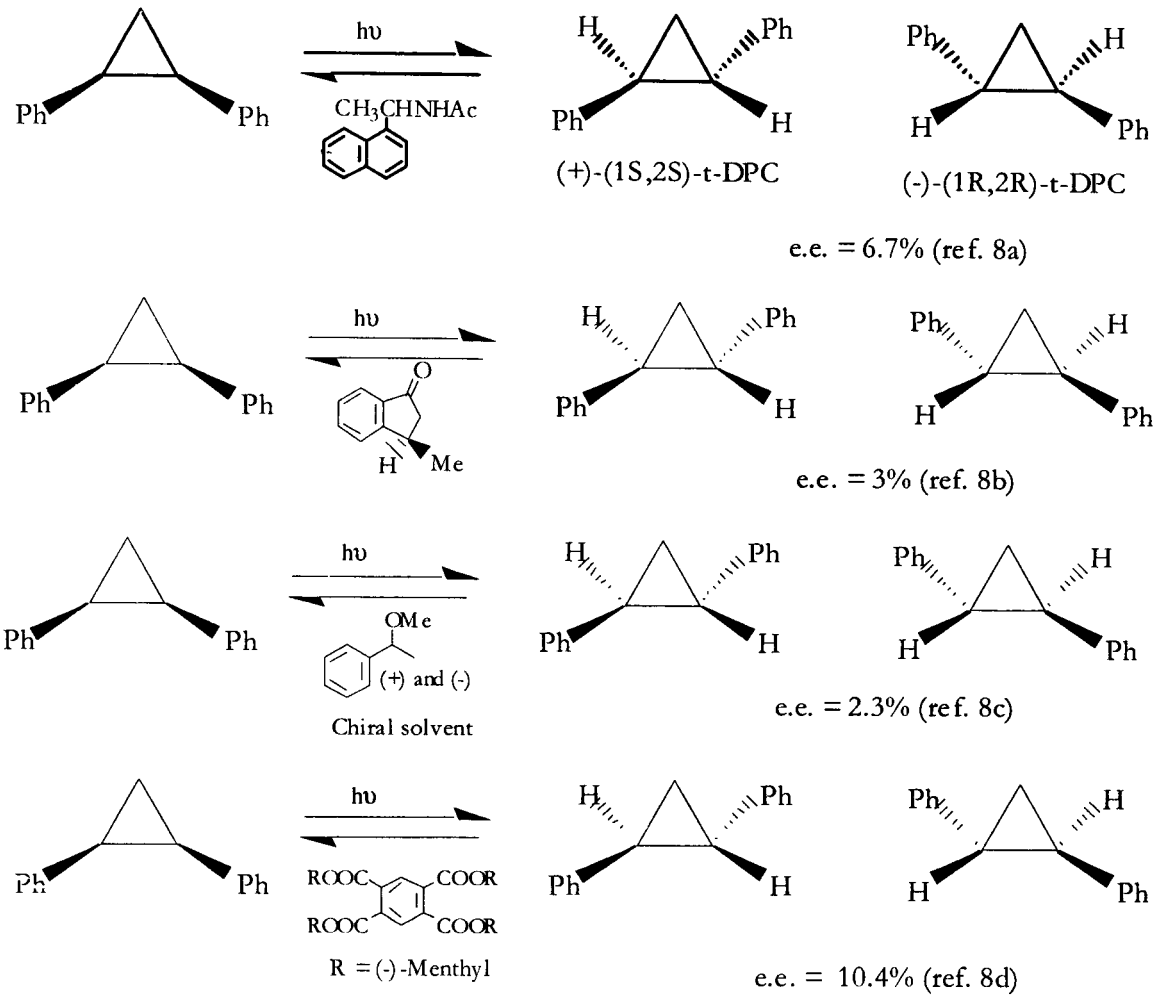
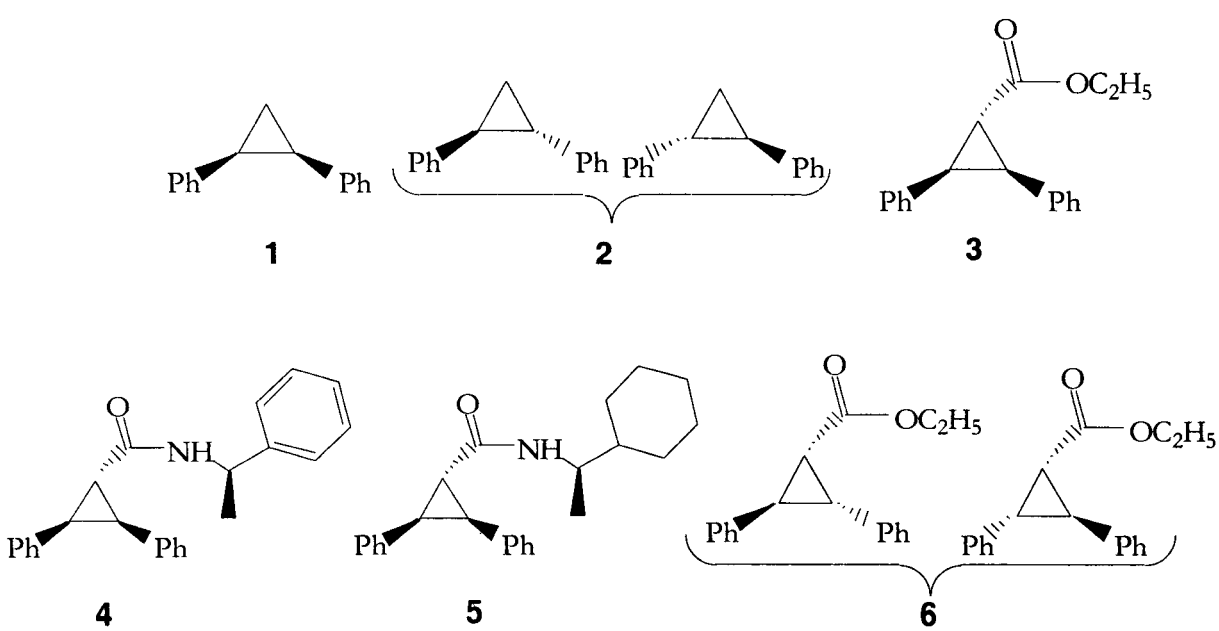


Scheme 1



Scheme 2

saturated aqueous solution of cyclodextrin and stirring overnight precipitated a white solid which was filtered and washed several times with diethyl ether to remove the uncomplexed guest. The precipitate was then dried under reduced pressure (10^{-2} torr) at 50°C for 12 hours. The molar ratio of the diphenylcyclopropane and its derivatives and the CD was calculated by estimating the amount of guest extracted from a known amount mechanical mixture of CD and the guest (Fig. 2).

The room temperature ^{13}C CP MAS NMR spectra of β CD and compounds **3**, **4** and **5** complexed with β CD are presented in Fig. 3. The spectrum of β CD is similar to those previously reported[9]. The different carbon resonances are assigned to C-1 (97-104ppm), C-4 (79-86 ppm), C-2,3,5 (70-77 ppm) and C-6 (55-67 ppm). The most important feature of

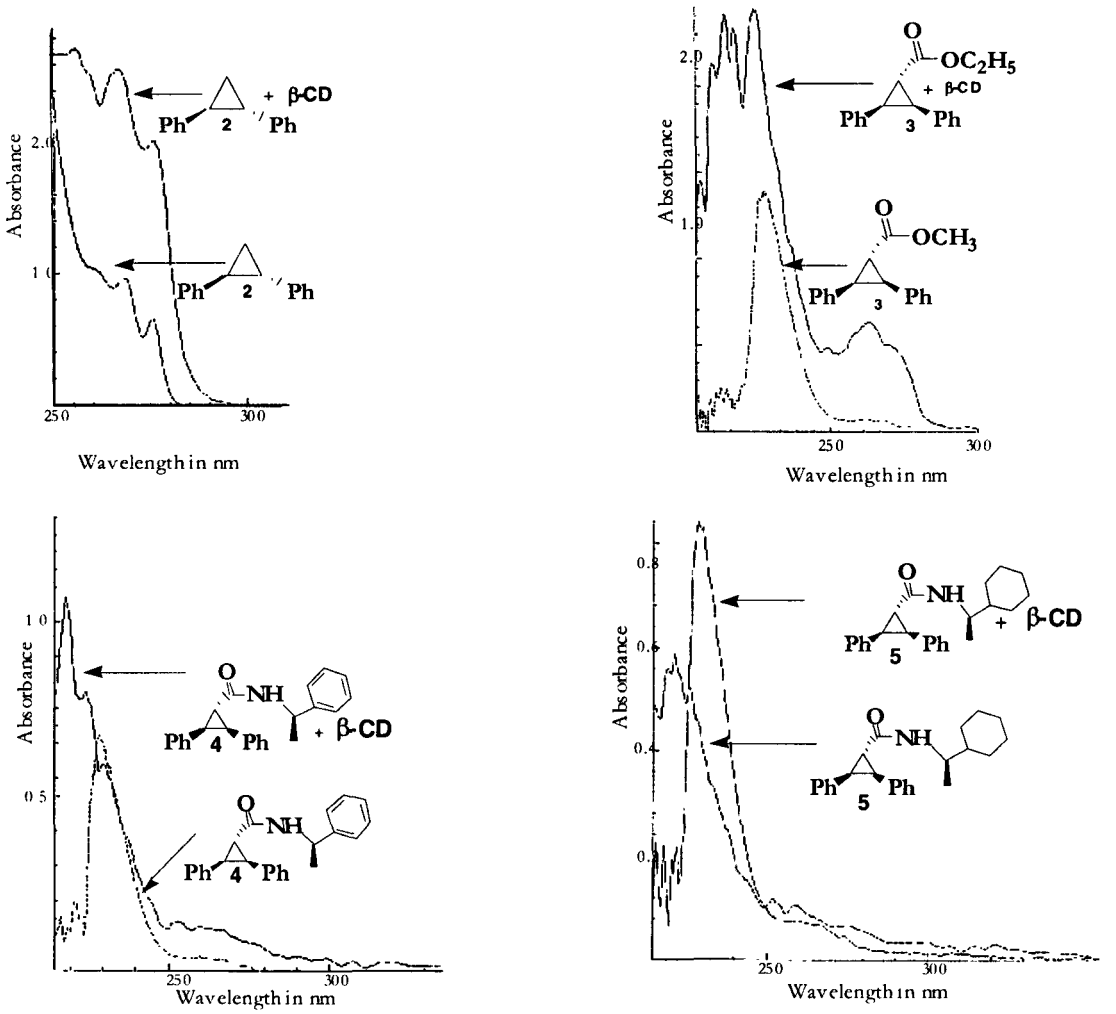


Fig.1 UV Absorption and Diffuse reflectance spectra

of the complex. Compounds **1** and **3** form a 1:1 complexes while compounds **4** and **5** form 10:1 complexes with the host β CD respectively.

The complexes were characterized by their UV, X-ray powder diffraction and solid state NMR. The UV absorption spectrum of the CD complex and the solution spectrum are identical (Fig. 1).

The X-ray powder pattern of the precipitated white solid complex differed from that of pure CD suggesting the precipitate to be a true complex and not a the spectrum is the existence of several resonances for each carbon of β CD. Such an observation is mainly correlated with different torsion angles about the C-1 and C-4 linkages between two D-glucopyranose units and different torsion angles describing orientation and hydroxyl group[9]. In addition to the carbon signals, the spectrum also indicate the presence of spinning sidebands denoted by asterisks. Fig. 3 also presents the ^{13}C CP MAS NMR spectra of compounds **3**, **4** and **5** with β CD as complexes. It is very clear from

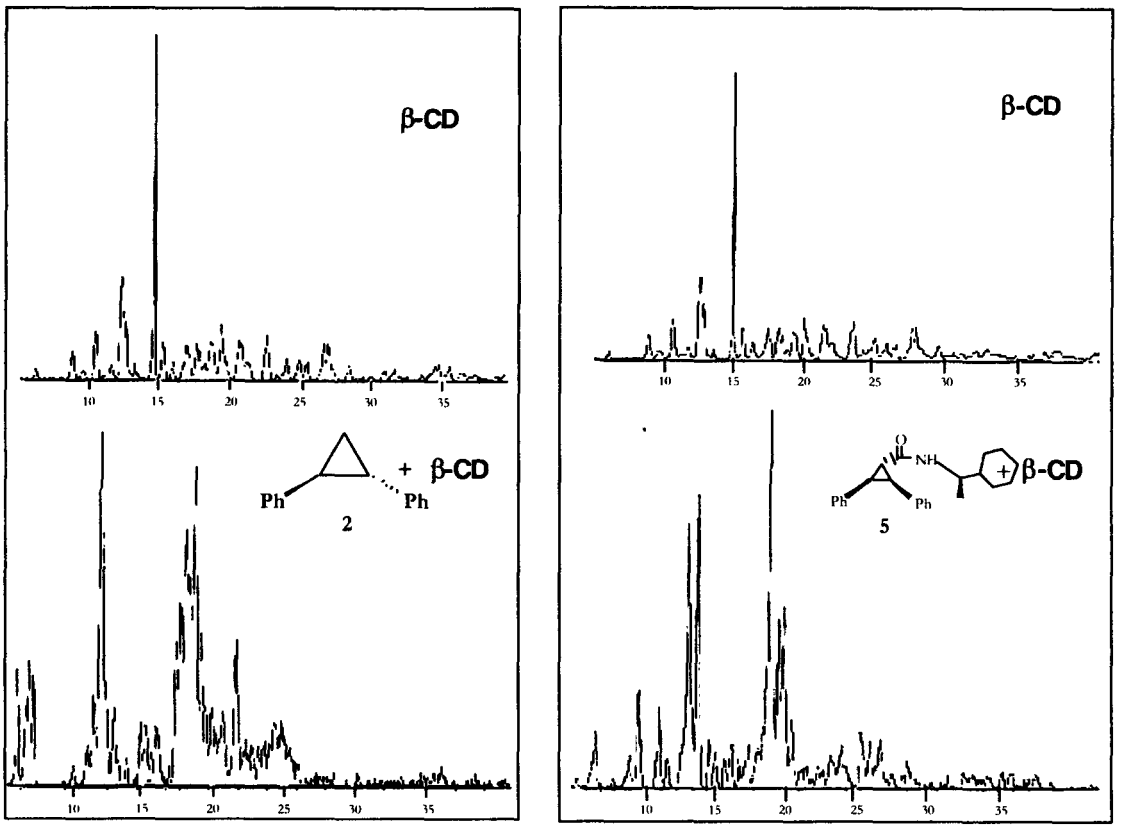


Fig. 2 X-Ray powder photographs of β CD and its complex with *trans*- diphenyl cyclopropane (**2**) and 1-cyclohexylethylamide of *trans, trans* -2,3-diphenylcyclopropane-1-carboxylic acid (**5**).

these spectra that β CD carbon resonances of the complexes are less well resolved compared to the free β CD. However the extent of loss in resolution varies with the guest molecule. For example complexation of compounds **3** and **4** with β CD affects resolution of all the carbons of the β CD, while the complexation of compound **5** mainly affects the resolution of C-4 carbon of β CD. Similar observation has been reported earlier when various guest molecules complexed with β CD[9]. Such an observation is correlated with small changes in carbon chemical shifts due to bond distortion and/or modification in magnetic environment due to the presence of guest molecules. It may be noted that when a physical mixture (in the same ratio as the complex) was made of β CD and compounds **3**, **4** and **5**, such a loss in spectral resolution of ^{13}C CP MAS NMR spectra was not observed (not reported). Thus the solid state NMR study supports the existance of strong interaction and complexation between β CD host and various guest molecules. In addition to the carbon resonances of β CD, ^{13}C CP MAS NMR spectrum of the complex of compound **3** also indicate the presence of carbon resonances of the guest molecules. Prominent among them are the resonance of carbonyl carbon of the ester group (170.0 ppm). Resonances due to aliphatic (14-33 ppm) and aromatic (126-135 ppm) carbons however are too close to the spinning sidebands to be identified specifically. ^{13}C CP MAS NMR of the complexes of **4** and **5** with β CD however did not give any resonances for guest molecules. Point to be noted here is that complexation ratio of **4** and **5** with CD is much higher than compound **3** with CD.

Photochemistry

Irradiation of complexes was carried out both as solids and aqueous solutions. For solid irradiation of CD complexes of **1**, the complex was made into a fine powder (usually about 100mg) and mixed with a preweighed amount of triplet sensitizer, 4′ methoxy acetophenone, (varied from 10-40mg) using a mortar and pestle. This mixture of the complex and sensitizer was then placed between two quartz plates and sealed around the edges with tape. The quartz plate was hung using copper wire into the Rayonet reactor well

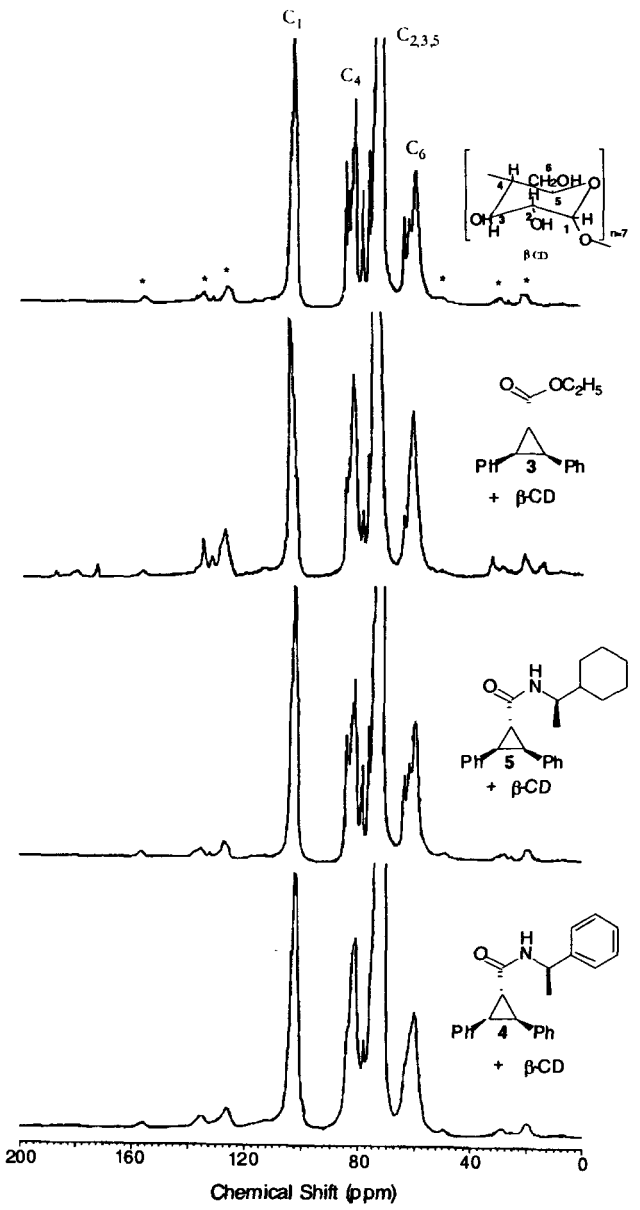
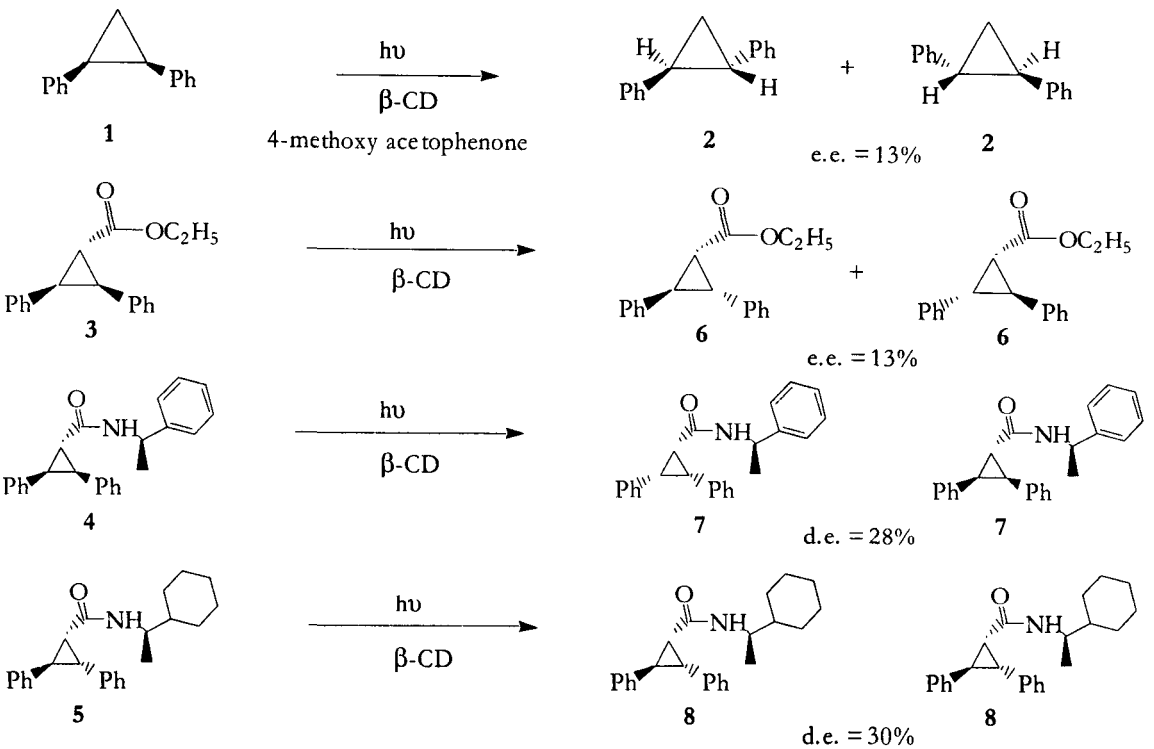


Fig. 3 Room temperature ^{13}C CP MAS NMR spectra with 1.5ms contact time of just β CB, complex of *trans, trans*-2,3-diphenyl cyclopropane-1-ethylester (**3**), 1-cyclohexyl ethyl amide of *trans, trans*-2,3,-diphenylcyclopropane-1-carboxylic acid (**5**), 1-phenyl ethyl amide of *trans, trans*-2,3-diphenylcyclopropane-1-carboxylic acid (**4**) and β CD. Asterisks denote spinning sidebands.

containing bulbs of 350nm wavelength. After irradiation was complete the complex was dissolved in deionized water and extracted with dichloromethane. Product analysis was carried out using a chiral HPLC column (Chiralcel OJ). For solution irradiations the complex was dissolved in distilled water (enough water to obtain a clear solution) and then irradiated. Following irradiation, the products were extracted with dichloromethane and analyzed as above. While moderate e.e. (13%) has been obtained in the solid state, solution irradiations gave lower e.e. value (1.5%). Irradiation of solid CD complexes of **3** was carried out between quartz plates using a 250nm Rayonet reactor in a similar manner used for compound 1 (no sensitizer required) and followed by extraction and analysis. Product analysis for compound **3** was carried out using a chiral GC column (Supelco β Dex 350 custom made capillary column # C5055-01A). Enantioselectivity of compound **3** inside β CD is moderate, 13% (6% in γ-CD). The complexes of **4** and **5** with β CD were dried under reduced pressure (10^{-3} Torr) at 65°C for 10 to 12 hours. The samples were irradiated inside a Rayonet reactor fitted with 300nm bulbs for 8 hrs in quartz tubes while being rotated. Products were extracted using acetonitrile and analyzed using achiral GC column (SPB-5). Higher diastereoselectivity was observed for compounds **4** (28% in β-CD and 8% in γ-CD) and **5** (30% in β-CD and 8% in γ-CD) when compared to the ester **3**. Results of photolysis of **1**, **3**, **4**, **5** are summarized in Scheme 3.

Importance of Water: Moisture Free Irradiation

It is important to note that unless the irradiation of the compounds **4** and **5** were carried out under moisture free conditions the reactions were messy with several products formed. It is possible that due to the presence of polar amide groups in these compounds they may show an affinity for water even inside the cyclodextrin cavity. That cyclodextrin contains water in its cavities was observed by conducting a TGA analysis of β CD alone and the complex of β CD–4 (Fig. 4). β CD alone contains about 13% water by weight and the complex β CD–4 contains about 10% water by weight. Similar observation has been reported recently for another amide salbutamol, complexed with β CD[10]. On carrying out the irradiation of **4** and **5** under moisture free conditions (drying under reduced pressure with heat and irradiating in the drying tube itself without exposure to the atmosphere) and extracting with acetonitrile, the reaction was not only clean but moderate selectivity was also observed in the product diastereomers (Scheme 3). These two factors clearly indicate that presence of water interferes with the photochemistry of the compounds inside cyclodextrins.



Scheme 3

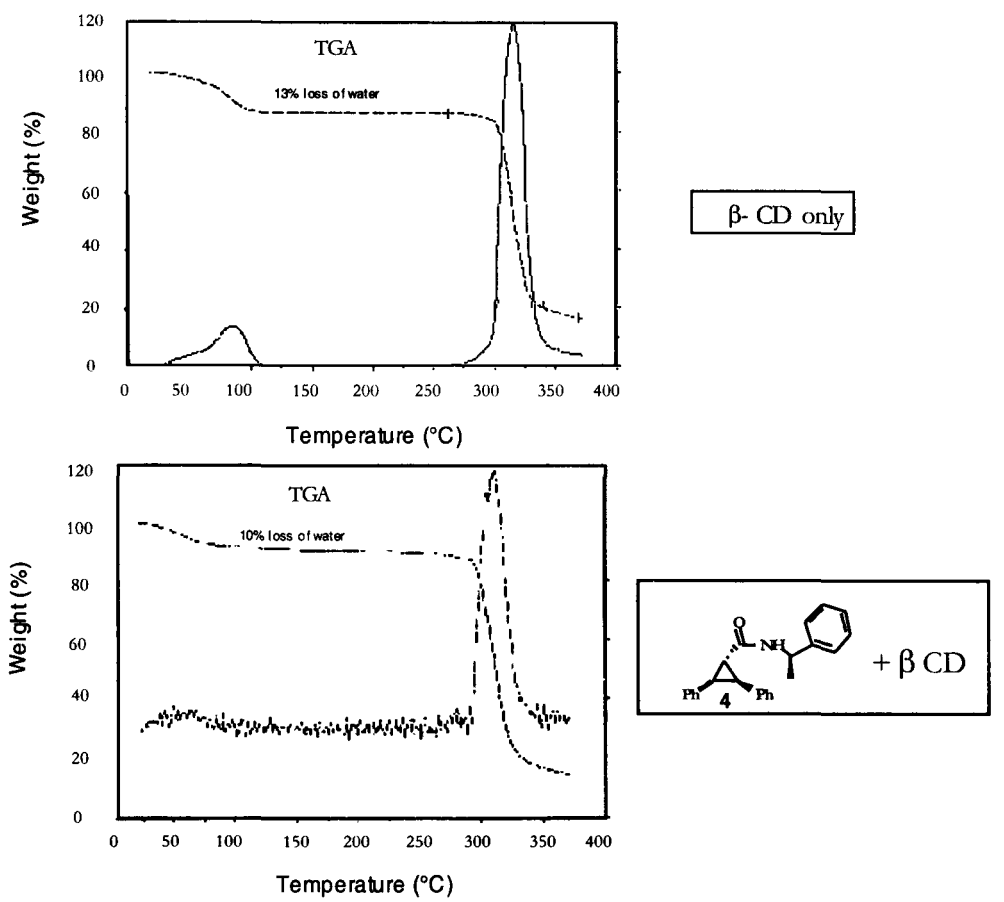
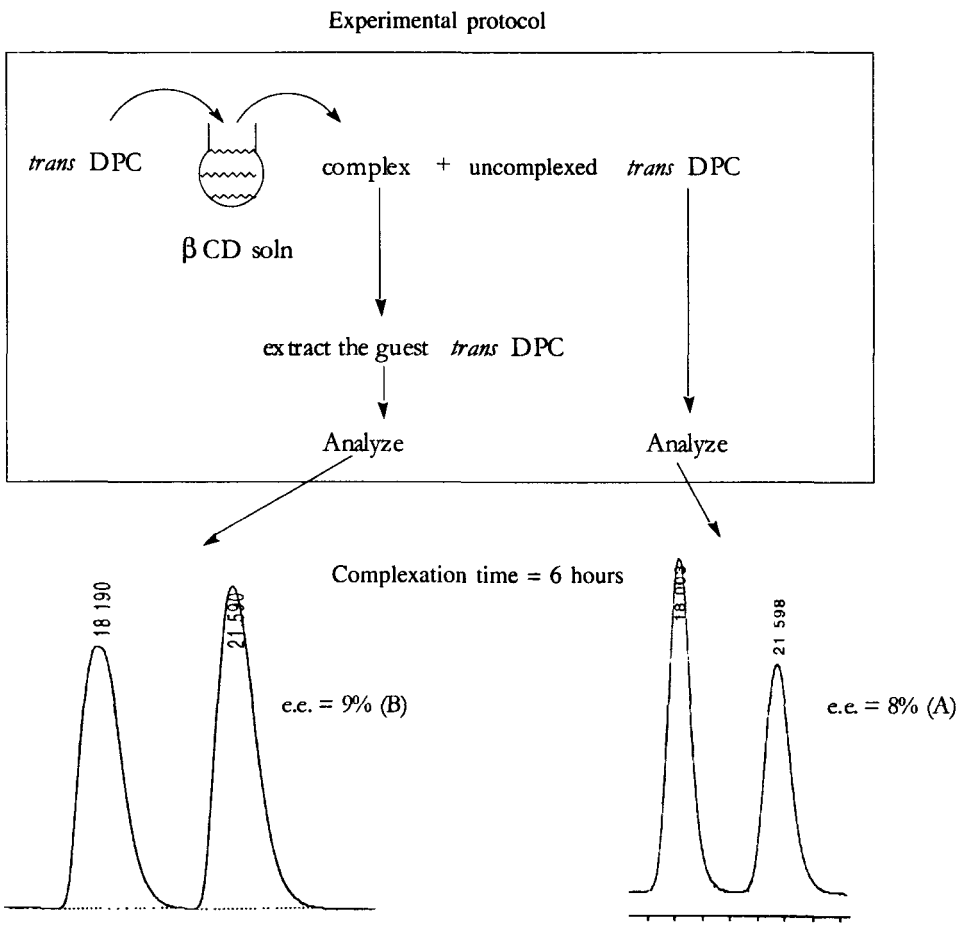


Fig. 4 TGA analysis of β CD and its complex with 1-phenylethylamide of *trans,trans*-2,3-diphenylcyclopropane-1-carboxylic acid (**4**)

Optical Resolution of *Trans*-isomers with CD: Is there any Preference for Inclusion of One of the Two Optical Isomers of *Trans*-DPC?

β-Cyclodextrin has a slight preference to include one enantiomer of *trans* DPC (2) over the other. This was established by obtaining the e.e. of the *trans* DPC before complexation to CD (e.e. = 0%) and after extraction from β-cyclodextrin (e.e. = 9 %; Scheme 4). Interestingly this preference is time dependent. When complexation is allowed for a shorter period of time selectivity is seen and lost when complexation is allowed for a longer interval of times viz. 6 and 12 hours and this selectivity decreases to almost zero when the complex was allowed to equilibrate in aqueous solution for 48 hours (Scheme 4). Encouraged by the complexation behaviour of **2**, similar time dependent complexation study was carried out with the photoproducts of compound **3**, **4** and **5** (i.e., the trans isomers **6**, **7** and **8**). β-CD showed a preference for one enantiomer of *cis, trans*-2,3-diphenyl cyclopropyl-1-ethyl ester 6 (6 hrs: 9%; 24 hrs: 2%). However, time dependent selective loading with compounds **7** and **8** did not exhibit much selectivity.



HPLC trace of enantiomers of *trans*-DPC that complexed with β CD

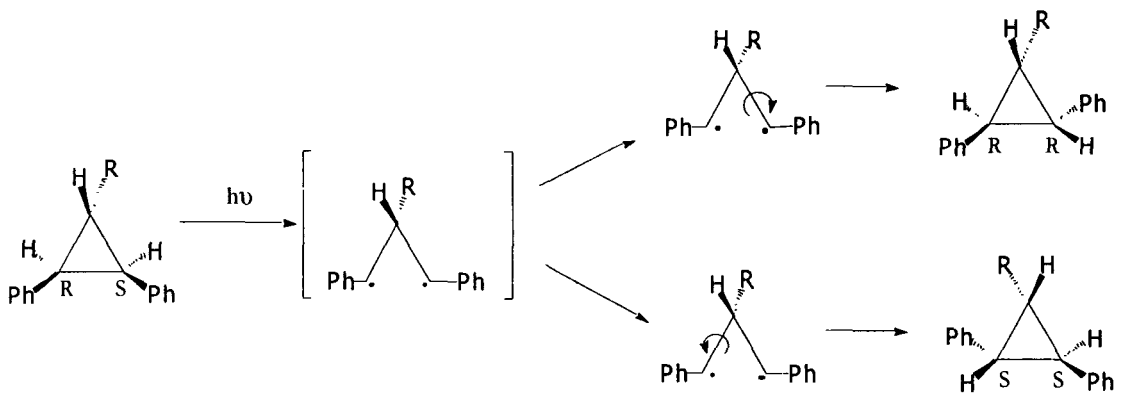
HPLC trace of enantiomers of *trans*-DPC that did not complex with β CD (remained in solution)

Scheme 4

time (3 hrs: 9%; 24 hrs: 0.5%). Time dependent study was carried out by loading enantiomers of *trans* DPC into β cyclodextrin. Four such identical complexations were set up. The guest was allowed to complex for 6, 12, 24 and 48 hours followed by extraction and analysis. It was found that there was selectivity for one enantiomer over the other at shorter complexation

A Model

All five compounds studied as complexes of β-CD have shown that the chiral cavity of CD's does play a role during the geometric isomerization of diphenylcyclopropane derivatives. Upon excitation the carbon-carbon bond substituted with *cis*-diphenyl groups undergo cleavage either in the excited singlet



Scheme 5

or triplet state. As illustrated in Scheme 5 rotation of either C_1—C_2 or C_1—C_3 can occur to yield the *trans* isomer.

Under normal conditions the rotation of either bond will occur with equal efficiency to yield a racemic mixture (e.e. or d.e will be zero). Clearly, when the *meso* diphenylcyclopropane derivatives are present within the cavities of cyclodextrin the rotation efficiencies are unequal to some degree. The chiral cavity offers different extents of steric hindrance for the two modes of rotation. An interesting and important point to note is that in the case of **1** as well as **3** the optical isomer that is favoured during photoisomerization is the same one that is preferentially included when the corresponding trans isomers (**2** and **6**) were equilibrated with β-CD in aqueous solution. This observation suggests that CD is able to influence the photoisomerization of **1** and **4** even at a very early stage. Further work is needed to understand this process.

Summary

In this report it has been shown that cyclodextrins due to their inherently chiral nature can bring about moderate enantio and diastereoselectivity in host-guest type of photoreactions. Photoisomerization of diphenylcyclopropane and its derivatives have been used as a useful probe for this purpose. Interestingly, the optical isomer that is favoured by β-CD during the photoisomerization of diphenylcyclopropane and its derivatives is the same one that is selectively included when a racemic mixture is equlibrated with β-CD. The low cost and readily availability of cyclodextrins during the last few years as well as accumulation of knowledge concerning the role of cyclodextrins in thermal reactions and their complexation behaviour in solution are expected to help photochemists to exploit them as chiral medium.

Experimental

Synthesis of Cis and Trans Diphenyl Cyclopropane (1 and 2)[11]

A mixture of 30g of *trans*-chalcone (97% Aldrich) and 50ml of 85% hydrazine hydrate was heated to reflux under nitrogen atmosphere for 3 hours. The reaction mixture was allowed to cool for 10 minutes and then diluted with 200ml of deionized water to give a yellowish hard polymer like substance. Next the aqueous layer was decanted and to the flask was added 5g of potassium hydroxide pellets along with 100ml diethylene glycol. The flask was fitted with an air condenser and the reaction refluxed for 4 hours. The reaction mixture was allowed to cool for 10 minutes and poured into 400ml of water to give a milky suspension. This was extracted with ether (3x200ml). The extracts were each washed with water (2x200ml), combined and dried using anhydrous magnesium sulfate. The solvent was removed in vacuo to give a dark brown oil. Purification was carried out by vacuum fractional distillation to obtain *cis* and *trans*-1,2-diphenyl cyclopropane in 98% and 97% purity respectively.

Spectral data for **1** (colourless liquid): ^{1}H-NMR ($CDCl_3$, 400MHz)[8d]: δ 1.37(m, 1H), 1.47(m, 1H), 2.49(m, 2H), 6.91-7.11(m, 10H). Mass Spectral data: m/e (relative intensity) 194 (M^+, 100), 179 (55), 165 (18), 152 (8), 139 (2), 128 (3), 115 (100), 103 (27), 91 (45), 77 (22), 65 (20.5), 51 (21), 39 (21).

Spectral data for **2** (colourless liquid): ^{1}H-NMR ($CDCl_3$, 400MHz)[8d]: δ 1.45(m, 2H), 2.17(m, 2H), 7.11-7.31(m, 10H). Mass Spectral data: m/e (relative intensity): 194 (M^+, 100), 179 (55), 165 (18), 152 (8), 139 (2), 128 (3), 115 (100), 103 (27), 91 (45), 77 (22), 65 (20.5), 51 (21), 39 (21).

Synthesis of Trans, Trans-2, 3-Diphenyl Cyclopropane-1-Ethylester (3)[12]

To a dry 250ml 3-necked round bottom flask 5g of *cis*-stilbene (Aldrich) was added followed by the addition of 0.45g of anhydrous copper sulfate and 21ml of benzene (solvent). Two water-cooled condensers were attached to the centre and side neck of the flask. To the third neck was attached a thermometer to monitor the reaction temperature. The flask was heated to 75°C (till benzene starts to reflux). Next 6.4g of ethyldiazoacetate (Aldrich) was allowed to slowly drip into the reaction flask over 5 hours and 20 minutes. The heat to the reaction flask was then turned off and the flask exposed to the atmosphere overnight. The reaction mixture was then filtered (after heating it again) to remove copper sulfate. The filtrate was distilled to remove benzene. What remained behind in the distilling pot was the crude product and starting *cis*-stilbene. The product crystallizes out as a solid. It was further purified by recrystallization from ethanol.

Spectral data for **3** (white solid): ^{1}H-NMR ($CDCl_3$, 400MHz): δ1.32-1.37 (t, 3H, J=7.2Hz), 2.54-2.58 (t, 1H, J=5.2Hz), 3.06-3.09 (d, 2H, J=5.2Hz), 4.22-4.29 (q, 2H, J=7.2Hz) 6.94-6.98 (m, 4H), 7.12-7.17 (m, 6H). Mass Spectral data: m/e (relative intensity): 266 (M^+, 2.5), 237 (2), 221 (4), 193 (53), 178 (19), 165 (12), 139 (1), 115 (100), 103 (4.5), 91 (26), 65 (10), 51 (6), 39 (4).

Synthesis of Racemic Cis, Trans- 2, 3-Diphenyl Cyclopropane-1-Ethylester (6)[12]

The procedure carried out was the same as that for the synthesis of *trans*, *trans*- 2, 3-diphenyl cyclopropane-1-ethylester except that *trans*-stilbene was used as the reactant instead of *cis*-stilbene.

Spectral data for **6** (colourless liquid): ^{1}H-NMR ($CDCl_3$, 400MHz): δ 1.32-1.37 (t, 3H, J=7.2Hz), 2.33-2.39 (dd, 1H, J=5.2Hz), 2.94-3.02 (dd, 1H, J=5.2Hz, 2.0Hz), 3.13-3.20 (dd, 1H, J=5.2Hz, 2.0Hz), 4.22-4.29 (q, 2H, J=7.2Hz) 6.94-6.98 (m, 4H), 7.12-7.17 (m, 6H). Mass Spectral data: m/e (relative intensity): 266 (M^+, 4), 237 (5), 221 (8), 193 (100), 178 (22), 165 (10), 152 (3), 131 (3), 115 (73), 103 (1), 91 (20), 65 (6), 51 (4), 39 (2.4).

Synthesis of Amides of Trans, Trans-2, 3-Diphenyl Cyclopropane-1-Carboxylic Acid (R) (4 and 5)[13]

The *trans*, *trans*-2,3-diphenylcyclopropyl-1-ethyl ester was hydrolyzed to its acid by adding 6g of sodium hydroxide in 45ml of ethanol (Aldrich) to the reaction mixture prepared for the synthesis of the ester. The reaction mixture was allowed to reflux for about 4 hours during which time the solution turned dark in color. The ethanol/benzene solvent mixture was distilled off. To the residue was added 50ml of deionized water and distilled further to remove any residual solvent mixture of ethanol/benzene. Next 200ml of boiling water was added to the residue in the distillation pot and filtered hot through a Buchner funnel. The residue was repeatedly washed with hot water till residue looked greenish black in colour indicating that only copper sulfate residue was left behind. The filtrate was then extracted with either petroleum ether or diethyl ether (3x100ml) to recover unreacted *cis*- stilbene. The water layer was then treated with 10% HCl solution to precipitate out the acid. The precipitate was allowed to settle and then filtered through a Buchner funnel. The residue was washed with water till the filtrate was no longer acidic. The brown precipitate was allowed to air dry on the funnel. Purification was done by recrystallization with methanol.

Spectral data for the acid (white solid): ^{1}H-NMR ($CDCl_3$, 400MHz): δ 2.54-2.60 (t, 1H, J=5.2Hz), 3.14-3.17 (d, 2H, J=5.2Hz), 6.95-7.00 (m, 4H), 7.1-7.2 (m, 6H). Mass Spectral data: m/e (relative intensity): 238 (M^+ 8), 220 (7), 219 (4), 192 (99), 178 (37), 165 (19), 152 (7), 131 (7), 116 (17), 115 (100), 91 (30) 77 (12), 65 (12), 51 (9), 40 (22).

Next 200mg (1eq) of the *trans trans*, 2,3-diphenylcyclopropane-1-carboxylic acid was dissolved in 50ml of dichloromethane to which (1.1eq) of the chiral amine (R(+)-1-phenylethyl amine for compound **4** and R(-)-1-cyclohexylethyl amine for compound **5** was added to this mixture 260mg (1.5eq) of DCC (N,N'-dicyclohexylcarbodiimide) and 10.3mg (0.1eq) of DMAP (4-(dimethylamino)pyridine) were added next and stirred for 3 hours at room temperature. The crude product obtained was purified by flash column chromatography using silica gel and 20% ethylacetate-petroleum ether as the eluant[10]. For the amides of *cis*, *trans*-2,3-diphenyl-1-cyclopropane-1-carboxylic acid, the chiral amine was coupled with *cis*, *trans*-2,3-diphenyl cyclopropane-1-carboxylic acid.

Spectral data for **4** (white solid): ^{1}H-NMR ($CDCl_3$, 400MHz): δ 1.55-1.60 (d, 3H, J=8.0Hz), 2.2-2.24 (t, 1H, J=5.6Hz), 3.07-3.10 (d, 2H, J=5.6Hz), 5.19-5.28 (m, 1H), 6.02-6.07 (bd, 1H), 6.88-6.98 (m, 4H), 7.08-7.18 (m, 5H), 7.26-7.42 (m, 6H). Mass Spectral data:

m/e (relative intensity): 341 (M^+ 2), 207 (4), 193 (100), 165 (6), 152 (3), 115 (84), 105 (68), 77 (19), 65 (11), 44 (7).

Spectral data for **5** (white solid): ^{1}H-NMR ($CDCl_3$, 400MHz): δ 0.95-1.06 (m, 1H), 1.1-1.14 (d, 3H, J=6.8Hz), 1.18-1.4 (m, 5H), 1.62-1.82(m, 5H), 2.17-2.22 (t, 1H, J=5.6Hz), 2.94-3.02 (m, 2H), 3.85-3.92 (m, 1H), 5.52-5.54 (bd, 1H), 6.84-7.2 (m, 10H). Mass Spectral data: m/e (relative intensity): 347 (M^+ 2), 270 (2), 264 (3), 238 (6), 221 (14), 194 (100), 178 (13), 143 (5), 115 (50), 111 (93), 91 (10), 69 (53), 41 (11).

Complexation of Diphenylcyclopropane and its Derivatives with Cyclodextrin

A typical procedure adopted for complexation of compounds 1-5 with β-CD is described below. To a saturated solution of cyclodextrin (0.17 gm of β-CD in 10 ml water) equimolar amount of the guest (compounds **1-3**) was added as a diethylether solution and left to stir for 24 to 48 hours. Adding equimolar amount of cyclodextrin to compounds 4 and 5 did not lead to sufficient precipitation. Almost 10 times more amount of cyclodextrin was added to obtain good precipitation. Also compounds **4** and **5** had to be predissolved in a minimum amount of dichloromethane before making it into a diethylether solution because they are poorly soluble in just diethylether. The precipitate was filtered and the residue washed several times with diethyl ether to remove any uncomplexed guest. The complex was dried overnight in a vacuum oven (10^{-2} torr) maintaining a temperature of 50°C. The complexes of compounds **1** and **3** were directly used for irradiation. Complexes of compounds **4** and **5** were further dried under vacuum (10^{-3} Torr) with heating (at 65°C) before irradiation.

Characterization of Diphenylcyclopropanes and its Derivatives as Solid Cyclodextrin Complexes

Diffuse reflectance spectra of the solid host-guest complexes were recorded using Shimadzu UV-2101PC spectrometer. X-ray powder photographs of the host CD and the host-guest complex were recorded on a Scintag XDS 2000 diffractometer. The solid state CP MAS NMR spectra were obtained using Bruker DSX-300 NMR spectrometer operating at resonance frequency 75.14 MHz. The frequency sweep width (SWH) was 30 KHz for all the measurements. The contact time and repetition times were 1.5 ms and 4 s respectively. For all the samples at least 12000 scans were averaged for each spectrum. The spinning frequency was 4.0 KHz. The liquid phase NMR spectra were obtained using a Varian Unity Inova 400 spectrometer. The ^{13}C chemical shift was referenced with respect to TMS and all the experiments were carried out at room temperature.

Determination of the Host-Guest Ratio

A preweighed amount of the dry complex (100mg of complex for compounds **1** and **3**) 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 weight of this compound when subtracted from the initial weight of the dry complex gave the amount of cyclodextrin present. The molar ratio of the host cyclodextrin and the guest gave the complexation ratio. Since compound **4** and **5** could not be extracted from their CD complexes in a similar manner, acetonitrile was used to extract the guest by stirring a known amount of the complex (100mg) in the solvent for 48 hours. The slurry was filtered and washed several times with acetonitrile. The filtrate was collected and then evaporated to dryness leaving behind the guest, which was weighed. This represented the amount of guest that complexed, which when subtracted from the weight of the complex gave the amount of cyclodextrin present. Again the molar ratio of the host cyclodextrin and the guest gave the complexation ratio.

For **1**: Weight of complex = 501.3mg, weight of extracted guest = 86.4mg (4.45×10^{-4} moles) therefore weight of β CD = 414.9mg (3.65×10^{-4}moles). Host:Guest = 0.8:1

For **3**: Weight of complex = 112mg, weight of extracted guest = 19.8mg (7.85×10^{-5} moles) therefore weight of β CD = 95.1mg (8.37×10^{-5}moles). Host:Guest = 1.06:1.

For **4**: Weight of complex = 2.982g, weight of extracted guest = 87mg (2.55×10^{-4} moles) therefore weight of β CD = 2.895g (2.55×10^{-3}moles). Host:Guest = 10:1

For **5**: Weight of complex = 1.696g, weight of extracted guest = 44.5mg (1.28×10^{-4}moles) therefore weight of β CD = 1.651g (1.45×10^{-3}moles). Host:Guest = 11:1 Weight of the extracted guest were verified by using a calibration compound.

Irradiation of diphenylcyclopropanes and its

derivatives as solid cyclodextrin complexes. The complexes were irradiated as solids and as aqueous solutions (for compounds **1** and **2**). For solid irradiation, a weighed amount of the dried complex (100mg) was finely crushed and placed between two quartz plates. In the case of compound **1** sensitizer was required (20mg). This was mixed with the complex by crushing both in a mortar pestle. This finely ground mixture was placed between two quartz plates. The sample was then subjected to UV irradiation (Rayonet reactor using light ranging from 250nm for compound **3**, 300nm for compounds **4** and **5**, 350nm for compound 1) for the required amount of time (ranging from 3 hours to 8 hours). Following irradiation, the complex was dissolved in water (500ml) and extracted at least three times with dichloromethane except for compounds **4** and **5**. The dichloromethane extracts were then dried using magnesium sulfate followed by evaporation of the solvent to get the products. Compounds **4** and **5** were extracted directly by adding acetonitrile to the irradiated complex and allowing it to stir overnight as exposure to moisture led to difficulty in analysis. The solvent was then filtered and the filtrate evaporated to get the products. The products of compounds **1** and **2** were analyzed by HPLC (Chiracel OJ wavelength used = 254nm, solvent mixture used = hexane:isopropyl alcohol 97:3, flow rate = 0.7ml/min), compound **3** by chiral GC (Supelco β-dex 320/1701 custom made, conditions for the analysis = 140°C isotherm for 40 minutes). Achiral GC (Supelco SPB-5, conditions for the analysis = 215°C isotherm for 45 minutes) was used for the analysis of product diastereomers of compound **4** and **5**. For solution irradiation (done for compound **1**) a weighed amount (~60 mg) of dried complex was dissolved in distilled water (100 ml) along with the sensitizer (10mg), purged with nitrogen gas and then subjected to irradiation for 3 hours. Extraction and analysis procedures were the same as with solid irradiation.

Acknowledgement

The authors are thankful to the National Science Foundation for support of the research (CHE-9904187) and for funding the procurement of Bruker DSX-300 solid state NMR through an equipment grant to the Department.

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