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Journal of Photochemistry and Photobiology A: Chemistry 184 (2006) 34–43
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Selectivity in photolysis of benzyl acetate and benzyl hexanoate upon cyclodextrin complexation

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Received 6 October 2005; received in revised form 8 March 2006; accepted 16 March 2006
Available online 30 March 2006

Abstract

Irradiation of benzyl acetate (**1**) and benzyl hexanoate (**2**) in methanol yields products from both heterolytic and homolytic pathways. However, in presence of cyclodextrin, photolysis of **1** in aqueous solution and in solid state produces benzyl alcohol as the predominant product and this is attributed to the stabilization of benzylcarbonium ion by secondary hydroxyl groups present at the rim of the cyclodextrin cavity. However, photolysis of **2**, in presence of cyclodextrin, produces hexylbenzene as the predominant product via a homolytic pathway and the change in selectivity is explained by the coinclusion of spacer group inside the cyclodextrin cavity.

Keywords: Cyclodextrin; Photolysis; Benzyl esters; Homolytic and heterolytic mechanisms

1. Introduction

Photochemical cleavage of arylmethyl compounds with a leaving group ($ArCH_2$-LG) has attracted considerable interest both for mechanistic reasons and functional group protection chemistry [1]. For substituted benzyl acetates, most of the work is based on a mechanism originally proposed by Zimmerman and Sandel [2]. The competition between homolytic versus heterolytic cleavage for arylmethyl–heteroatom bond is responsible for radical derived and ion derived products.

Typical radical coupling, disproportionation and hydrogen abstraction products are obtained from the radical pair. In protic, nucleophilic solvents, the ion pair is trapped by the solvent to give substitution products (photosolvolysis). This competition between the two pathways is dependent on many factors such as the leaving group, the aromatic ring (benzene versus naphthalene, benzene versus substituted benzenes), the solvent and the multiplicity of the excited state (singlet or triplet). The ease of photoheterolysis follows the reverse of ground state reactivity (i.e. *meta*-substituted benzyl acetates give ion-derived products more than the *para*-isomer and this is termed as "*meta* effect") [3,4].

Pincock and co-workers [5,6] have extensively studied photolysis of a series of substituted benzyl acetates in methanol and propose a homolytic cleavage followed by ground state electron transfer as the dominant pathway for formation of ion pair intermediate and thus ion-derived products. Kojima and co-workers [7,8] have reported the photochemistry of α-methyl-substituted naphthylmethyl and benzyl alkanoate, and demonstrated that the steric hindrance around the ester bond has large influence on the yields of photoproducts. Mechanistic study of *ortho*-substituted benzyl acetates in methanol is reported and it is pointed out that the *ortho*-substituents as well as *meta*-substituents have an electron donating effect in the excited singlet state [9]. Decomposition of phenylacetic acid and its methyl ester on photolysis is reported [10]. 1-Naphthyl methyl esters on photolysis clearly show that the final product mixture need not be a direct measure of the initial excited state bond cleavage process since electron transfer may allow interconversion between radical pair and the ion pair [11]. Rate of decarboxylation have been estimated for the acyloxy radicals formed in the photolysis of substituted 1-naphthylmethyl alkaonate [12]. Acid controlled photoreaction of various aryl alkanoates are extensively studied, in which various pathways such as, competition of transesterification, fries rearrangement and/or transposition leading to different products are proposed [13]. Rate of decarboxylation have been estimated for the acyloxy radicals formed in the photolysis of substituted 1-naphtylmethyl alkaonate [14,15].

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doi:10.1016/j.jphotochem.2006.03.017

Cyclodextrins (CDs), having the ability to form host–guest complexes with different guest molecules of appropriate size, can be used as reaction vessels in many reactions, as their cavity can geometrically constrains the guest, stabilize intermediates and regulates the traffic of the incoming reagents or reactive intermediates towards certain accessible positions. These promising features of cyclodextrin as reaction media for photochemical transformations have been well recognized and exploited extensively [16–20]. The interesting mechanistic features of arylmethyl ester photolysis and its dependence on several factors such as ring substitution, solvent polarity, etc., have prompted us to carry out photolysis of benzyl acetate (**1**) and benzyl hexanoate (**2**) inside the cyclodextrin cavity and the salient features are discussed below.

2. Experimental

2.1. Materials

Cyclodextrins α, and γ (American Maize Products, Indiana), β (Aldrich) were used as received. All the solvents used in the reactions were distilled and purified prior to the use. Benzyl acetate (**1**) was synthesized from benzyl alcohol and glacial acetic acid by literature procedure [21]. Benzyl hexanoate (**2**) was synthesized from benzyl alcohol and hexanoyl chloride as given below.

A well-stirred solution of benzyl alcohol (0.02 mol) and 1 ml of pyridine in 50 ml of dry benzene was slowly added to the hexanoyl chloride (0.02 mol) in 30 ml of benzene at room temperature. The pyridinium hydrochloride salt was precipitated, and after all of the acid chloride was added, the solution was stirred for overnight. Then 50 ml of water was added and the two layers were separated. The benzene layer was washed twice with 10% aqueous HCl, once with 5% aqueous NaOH and finally with water. The organic layer was then dried with anhydrous sodium sulphate and rotaevoprated to yield the ester. The ester was purified by column chromatography using silica gel (50:50, pet ether/ethyl acetate as the eluent). It was characterized by its ^{1}H NMR and GC-MASS data [22].

2.2. Preparation and characterization of cyclodextrin complexes

1:1 CD complexes were prepared [23] by mixing an equimolar amount of the substrates (**1** and **2**) and the appropriate CD, stirring for 12 h, filtering and washing with small amount of ether to remove any uncomplexed substrate. This complex was dried in an air oven at 50 °C for 6 h. The host–guest ratio was calculated by adopting the following procedure. A known amount of the solid complex was dissolved in a minimum amount of distilled water and the guest was extracted with warm chloroform. The amount of the recovered guest was estimated gravimetrically after the removal of chloroform. The values are closer to unity indicating that a 1:1 complex is formed in all the cases.

A stock solution (1×10^{-2} M) of substrates **1** and **2** was prepared by dissolving a known mass in 2% acetonitrile–water mixture. 0.1 ml of this stock solution was transferred into 10 ml volumetric flask, the respective cyclodextrin (from a 0.01 M freshly prepared stock solution in water) was added, diluted to 10 ml with water and stirred for 6 h to ensure equilibrium upon complexation. Absorption spectra were recorded at room temperature using a JASCO 550 UV–vis spectrophotometer by monitoring the absorption maximum for substrates **1** and **2** at 254 and 263 nm, respectively. The existence of an inclusion complex inside the cyclodextrins was evidenced by the measurement of dissociation constants using a non-linear curve-fitting method [24] (Fig. 1) using the following equation:

$$\Delta OD = \frac{[\varepsilon_{SCD} - \varepsilon_{S_0}]K_1[CD][S_0]}{1 + K_1\,[CD]}$$

Where ΔOD is the change in absorbance of substrate in presence and absence of cyclodextrin; $[S]_0$ and [CD] the initial concentrations of substrate and cyclodextrin, respectively; ε_{SCD} and ε_{S_0} the molar extinction coefficient of the complex and substrate; and K_1 is the binding constant value of the 1:1 guest and host complexes. These equations are solved by non-linear regression analysis using PRISM (trial software).

α-, β- and γ-CD complexes of substrates **1** and **2** were also characterized by their ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, ^{1}H-^{1}H NOESY spectra recorded in D_2O at 25 °C on a Bruker 300 MHz instrument (using the pulse sequences and standard procedures offered by Bruker) [25]. In NMR

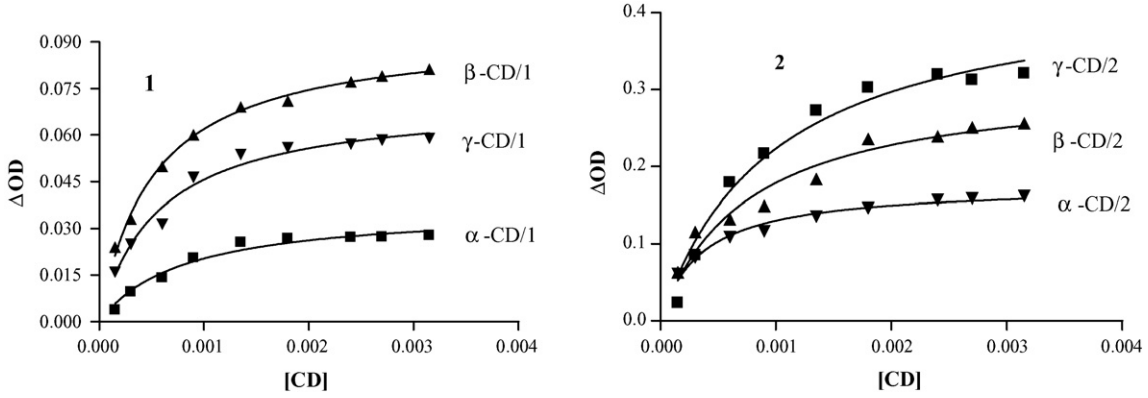


Fig. 1. Plots 1 and 2 are binding curve plot obtained from non-linear curve fitting method [sub] = 1×10^{-4} M, [CD] = 1×10^{-4} to 3.15×10^{-3} M.

Table 1
Results of photolysis of benzyl acetate (**1**) in various media

Medium	Conversion of **1** (%)	Percentage of photoproducts[a]			
		3	**4**	**5**	**6**
MeOH[b] (dried)	8.20	100	–	–	–
MeOH/H_2O (50%, v/v)[b]	53.2	33.2	20.6	30.9	15.3
Hexane[b]	Nil	–	–	–	–
Benzene[b]	Nil	–	–	–	–
α-CD/MeOH[b]	44.1	6.30	67.8	25.9	–
β-CD/MeOH[b]	27.8	6.90	75.0	18.1	–
γ-CD/MeOH[b]	32.3	8.00	60.3	31.7	–
α-CD/H_2O[c]	87.0	–	–	100	–
β-CD/H_2O[c]	67.6	–	–	98.4	1.60
γ-CD/H_2O[c]	78.3	–	–	94.8	5.20
α-CD/solid[d]	27.7	–	–	100	–
β-CD/solid[d]	31.9	–	–	100	–
γ-CD/solid[d]	50.4	–	–	100	–

Reaction mixtures are analyzed using a Shimadzu GC-17A, SE-30 (10%) capillary column with high purity nitrogen as the carrier gas and FID detector; error limit ±3%.
[a] Yield of photoproducts are normalized to 100; mass balance in most cases is ∼85–90%.
[b] Irradiated for 18 h.
[c] Irradiated for 4 h.
[d] Irradiated for 48 h.

measurements, 15–20 mg of the appropriate CD complex is dissolved ∼1 ml of D_2O (concentration $\sim 1 \times 10^{-2}$ M) and the spectrum is recorded. Mode of complexation of benzyl acetate and benzyl hexanoate is also evidenced from circular dichroic studies using a JASCO J-810 spectropolarimeter, furnished with a 150 W xenon lamp. The measurements were performed under nitrogen flux at 25 ± 1 °C and the samples contained in a quartz cuvette of pathlength of 0.1 cm. The acquisition parameters were: wavelength range 200–500 nm at steps of 1 nm, bandwidth 2 nm, time constant 0.5 s and sensitivity 2 mdeg./div. The instrument was calibrated by using a 0.06% aqueous solution of ammonium D-10-camphosulphonate, from JASCO.

2.3. General procedure for photolysis of substrates *1* and *2* in solution and as cyclodextrin complexes

For solution photolysis, 0.050 ml of **1** and **2** in 5 ml of respective solvents was irradiated (Tables 1 and 2) in N_2 atmosphere at

Table 2
Results of photolysis of benzyl hexanoate (**2**) in various media

Medium	Conversion of **2** (%)	Percentage of photoproducts[a]					
		3	**4**	**5**	**9**	**10**	**11**
MeOH (dried)[b]	39.1	21.3	11.9	34.7	4.50	13.6	14.0
MeOH/H_2O (50%, v/v)[b]	44.5	19.9	9.80	32.5	–	22.1	15.7
Hexane[b]	<1.30	–	–	Trace	–	Trace	–
Benzene[b]	<1.00	–	–	Trace	–	Trace	–
α-CD/MeOH[b]	100	–	–	–	52.9	47.1	–
β-CD/MeOH[b]	71.7	–	10.6	11.6	16.5	51.1	9.20
γ-CD/MeOH[b]	79.4	19.5	17.8	16.3	14.6	21.2	10.6
α-CD/H_2O[c]	62.8	–	–	43.4	–	56.6	–
β-CD/H_2O[c]	55.9	–	–	14.5	–	16.1	69.4
γ-CD/H_2O[c]	63.2	–	–	9.90	–	12.3	77.8
α-CD/solid[d]	38.1	–	–	4.50	–	59.4	36.1
β-CD/solid[d]	16.4	–	–	18.2	–	19.6	62.2
γ-CD/solid[d]	15.9	–	–	9.10	–	13.2	77.7

Reaction mixtures are analyzed using a Shimadzu GC-17A, SE-30 (10%) capillary column with high purity nitrogen as the carrier gas and FID detector; error limit ±3%.
[a] Yield of photoproducts are normalized to 100; mass balance in most cases is ∼85–90%.
[b] Irradiated for 18 h.
[c] Irradiated for 4 h.
[d] Irradiated for 48 h.

the appropriate wavelength (254 nm). Photolysis of cyclodextrin complexes of **1** and **2** was carried out as follows. Microcrystalline CD complexes of **1** and **2** (150 mg) were taken in Quartz tubes dissolved in 50 ml of distilled water and degassed with high purity N_2 gas for 30 min. The tubes were then placed in HEBER multilamp photoreactors fitted with (8 × 8 W) 254 nm lamps 4 h. As the solubility of CD is lesser in methanol, more dilute solutions (with lesser solute and more solvent) are taken and are photolyzed as above. During photolysis, the tubes were rotated periodically to ensure uniform irradiation. All the solid state photoreactions of CD complexes were carried out by placing the solid complexes in Quartz tubes, degassed with N_2 and then sealed. They were then photolyzed for 48 h with periodic rotation of the tubes after every 30 min.

After irradiation, the products were extracted from the cyclodextrin cavity with hot chloroform and the resultant reaction mixture was analyzed by gas chromatograph (Shimadzu GC-17A model, SE-30 (10%) capillary column with FID as detector and high purity nitrogen as the carrier gas). Products were identified by coinjecting with authentic samples and were also characterized by GC-MASS [22].

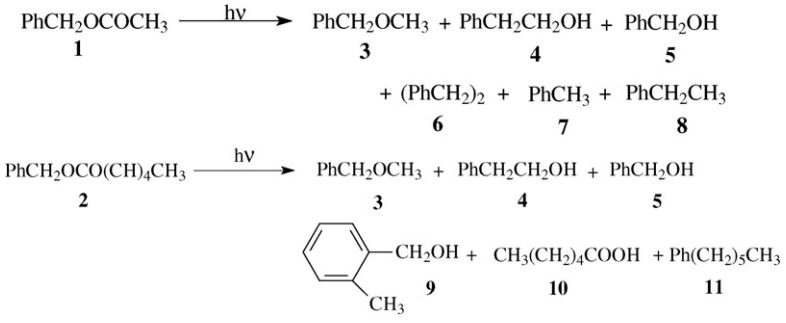
3. Results and discussion

Photolysis of benzyl acetate **1** is carried out in presence of polar as well as non-polar solvents. α-, β- and γ-CD complexes of **1** are also photolyzed in presence of MeOH and water as well as their solid complexes. The observed results are given in Table 1 and the structures of various products obtained in photolysis are given in Scheme 1. As the solubility of **1** in water is poor under the experimental conditions, photolysis is not carried out in aqueous solution. While products **3** and **5** are derived from benzylcarbonium ion by a heterolytic cleavage from the excited singlet state, products **4**, **6**–**8** are derived from radical intermediates by a homolytic cleavage. Acyloxy radicals becomes decarboxylated after diffusion from the solvent cage and the resultant methyl radical then abstracts a hydrogen atom from methanol (exothermic by ∼50 kJ/mol) [5] to form $^{\bullet}CH_2OH$. The benzylic radical either dimerizes to **6** or couples with $^{\bullet}CH_2OH$ radical to form **4**. It can also undergo in-cage coupling with $^{\bullet}CH_3$ radical to give **8** or can abstract a hydrogen to give **6**. It is also likely that formation of ionic intermediates can take place (in addition direct heterolytic cleavage from the excited singlet state), by single electron transfer between the radical pair formed in the homolytic pathway. These general mechanistic features are presented in Scheme 2.

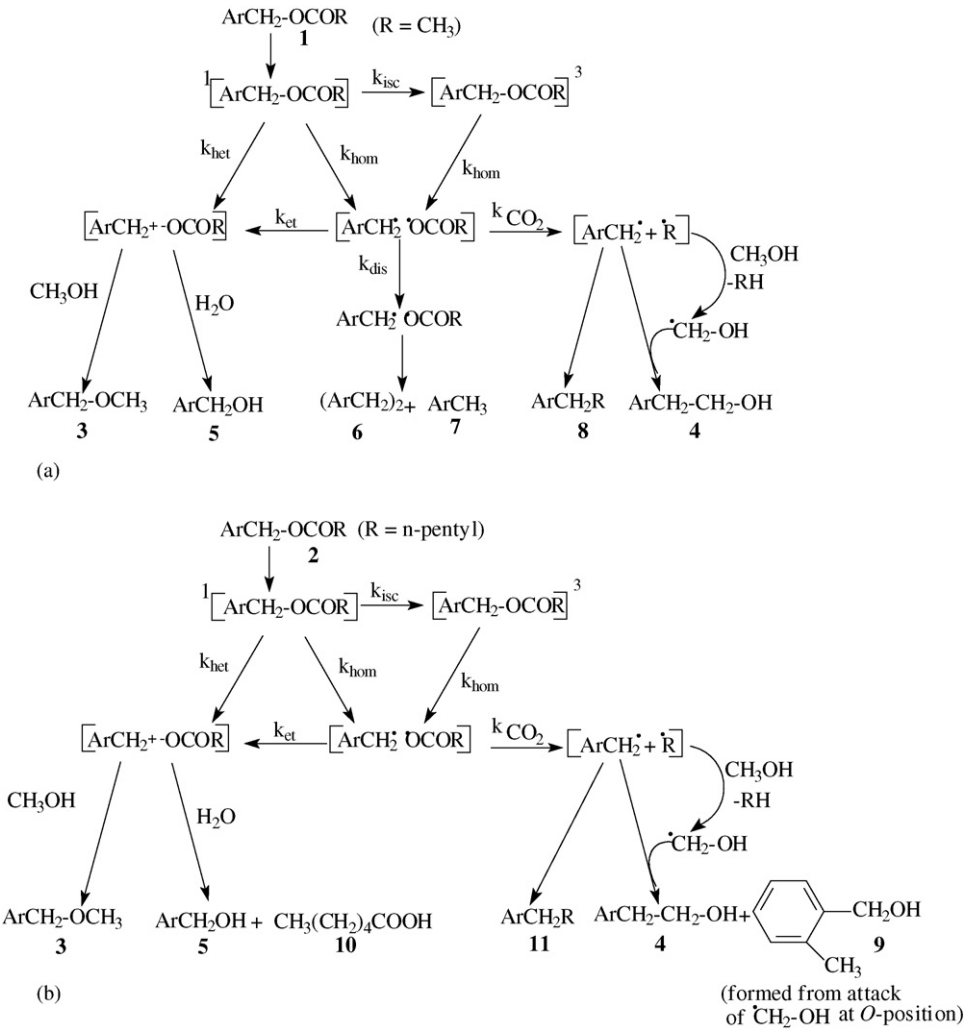
Analysis of Table 1 shows that photolysis of **1** in MeOH solvent (distilled commercial sample) results in the formation of benzyl methyl ether (**3**), 2-phenylethanol (**4**), benzyl alcohol (**5**) and bibenzyl (**6**). Hydrocarbons like toluene (**7**) and ethylbenzene (**8**) are not identified. However, when pure methanol (dried over Mg turnings and distilled over calcium chloride guard tube) is used, only **3** is obtained as the exclusive product. Photolysis in non-polar solvents, namely hexane and benzene results in no reaction. When the irradiation of **1** is carried out in presence of α-, β- and γ-CDs in methanol medium, formation of **3** is suppressed and alcohols **4** as well as **5** are formed in larger amounts (with the former produced more than the later). However, when the photolysis of **1** is performed in presence of cyclodextrin in aqueous medium, a remarkable product selectivity is observed in that benzyl alcohol is formed as the predominant product along with small amount of the coupled product **6**. The percentage conversion is also higher compared to the solution irradiation. Photolysis of solid CD complexes of **1** also shows remarkable selectivity to yield product **5** exclusively.

It is relevant to recall that in aqueous medium as well as in methanol, CD complexes of **1** and **2** may dissociate and are likely to exist in a dynamic equilibrium. However, as water is much more polar compared to the interior of the CD cavity, the aryl ring of benzyl esters has a stronger affinity for the later. Consequently, we believe, dissociation from the complex in water is likely to be very much weaker. This observation finds strong support from the high values of formation constants [24] for **1** and **2** with all the three cyclodextrins. The highest value for γ-CD/**2** complex provides additional support for the coinclusion of hexyl spacer also. With methanol as solvent, dissociation of the complex is likely to be significant. This is reflected in the relative yield of the various photoproducts, which is quite different in both the media.

This selective formation of **5** in presence of CD in aqueous medium and also in solid complexes is explained as given in Scheme 3. Inclusion of the aryl ring into the CD cavity, followed by photolysis gives predominantly the ion pair (formed by either a heterolytic cleavage or from the radical pair after

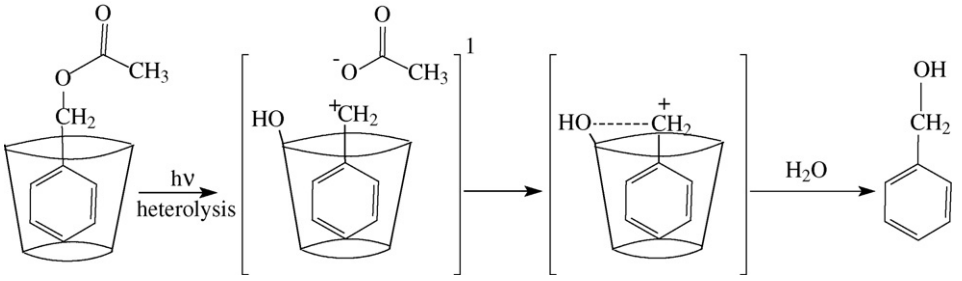


Scheme 1. Structures of the various products formed in photolysis of benzyl acetate (**1**) and benzyl hexanoate (**2**).



Scheme 2. Mechanisms of photolysis of benzyl acetate (a) and benzyl hexanoate (b).

electron transfer). This preferred formation of ionic intermediate may be due to stabilization of the benzylcarbonium ion by the secondary hydroxyl groups present in the wider rim of CD cavity and also by the polar solvent, namely water. At this stage, however, we cannot deduce any direct evidence for contact between the benzylcarbonium ion and the secondary hydroxyl group (which may be either a hydrogen bonding type stabilization or even a covalent linkage). In this context, it is relevant to note that in bromination of various aromatic unsymmetrical olefins [20], the bromohydrin is obtained as the major product in presence of α-CD compared to the solution reaction, which produces only the dibromide. To account for the formation of bromohydrin, stabilization of open carbocationic intermediate by cyclodextrin secondary hydroxyl group is proposed which provides the chemical evidence for the participation of hydroxyl group in stabilizing the carbocationic intermediate.



Scheme 3. Effect of CD complexation in photolysis of benzyl acetate (**1**).

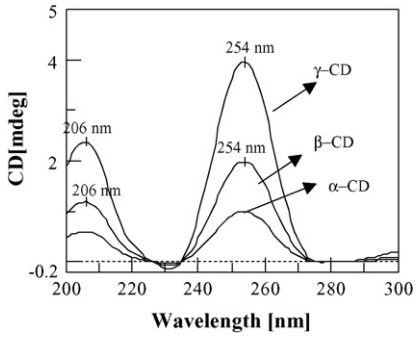


Fig. 2. ICD spectra of **1** (1.5×10^{-4} M) in presence of α-, β- and γ-cyclodextrins (7.5×10^{-3} M).

The mode of inclusion of benzyl acetate inside the cyclodextrin is evident from the ICD spectra of **1** in presence of α-, β- and γ-cyclodextrins as shown in Fig. 2. The positive ICD peak at 254 nm is attributed to the π–π* transition of phenyl group. In all the cyclodextrins, ICD peaks are positive as the electric transition dipole moment of the π–π* transition of **1** lies parallel to the symmetry axis of the cyclodextrin cavity (axial inclusion). The magnitude of ICD is higher in the case of γ-CD, as the hexyl group which acts as a spacer, ensures a tighter fit of **2** inside γ-CD cavity. It may also be attributed to the presence of **1** near the narrower rim of the cyclodextrin cavity. It is also confirmed from the ^{1}H-^{1}H NOESY spectra of 1 in presence of α-CD (Fig. 3) which shows cross peaks A (due to the interaction of H-3 proton of cyclodextrin the with *o*-proton of the phenyl ring) and B (due to the interaction of H-5 proton of CD with the *p*-proton of the phenyl group) and this justifies the mode of inclusion of 1 as shown in Scheme 3.

In the less polar methanol medium too, cyclodextrin complexation has specific effects. While the expected formation of **3** by heterolytic pathway is suppressed (compared to the corresponding reaction in the absence of CD), 2-phenylethanol (**4**) is formed more compared to **5**. This selectivity which is different from that is observed in aqueous medium may be rationalized by the cage effect exerted by the CD cavity which holds together the radical pair for a sufficient length of time. This promotes decarboxylation, followed by hydrogen abstraction by the $^{\bullet}CH_3$ radical from solvent to give a $^{\bullet}CH_2OH$ radical (exothermic) [5] which combines with the benzyl radical to give **4** as the major product. As the reaction is now carried out in a less polar methanol medium, radical pair formation by homolytic cleavage predominates now and this explains why the selectivity has changed in methanol solution with cyclodextrins. The formation of benzyl alcohol is also significant and this may be explained as follows. The radical pair, upon subsequent electron transfer may produce the ion pair inside the cyclodextrin cavity, which stabilizes the later through its secondary hydroxyl groups (Scheme 3).

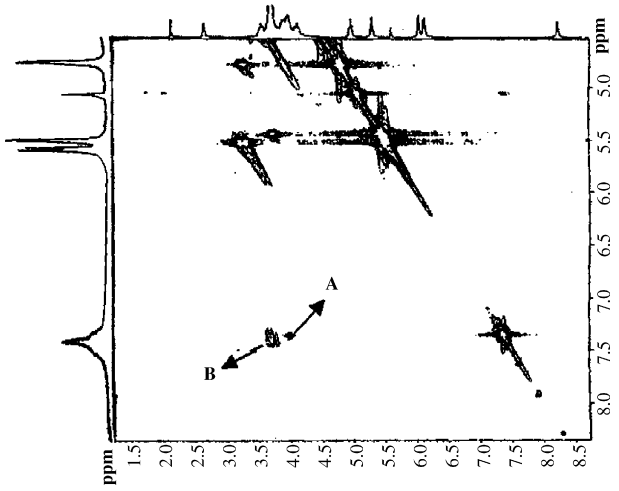
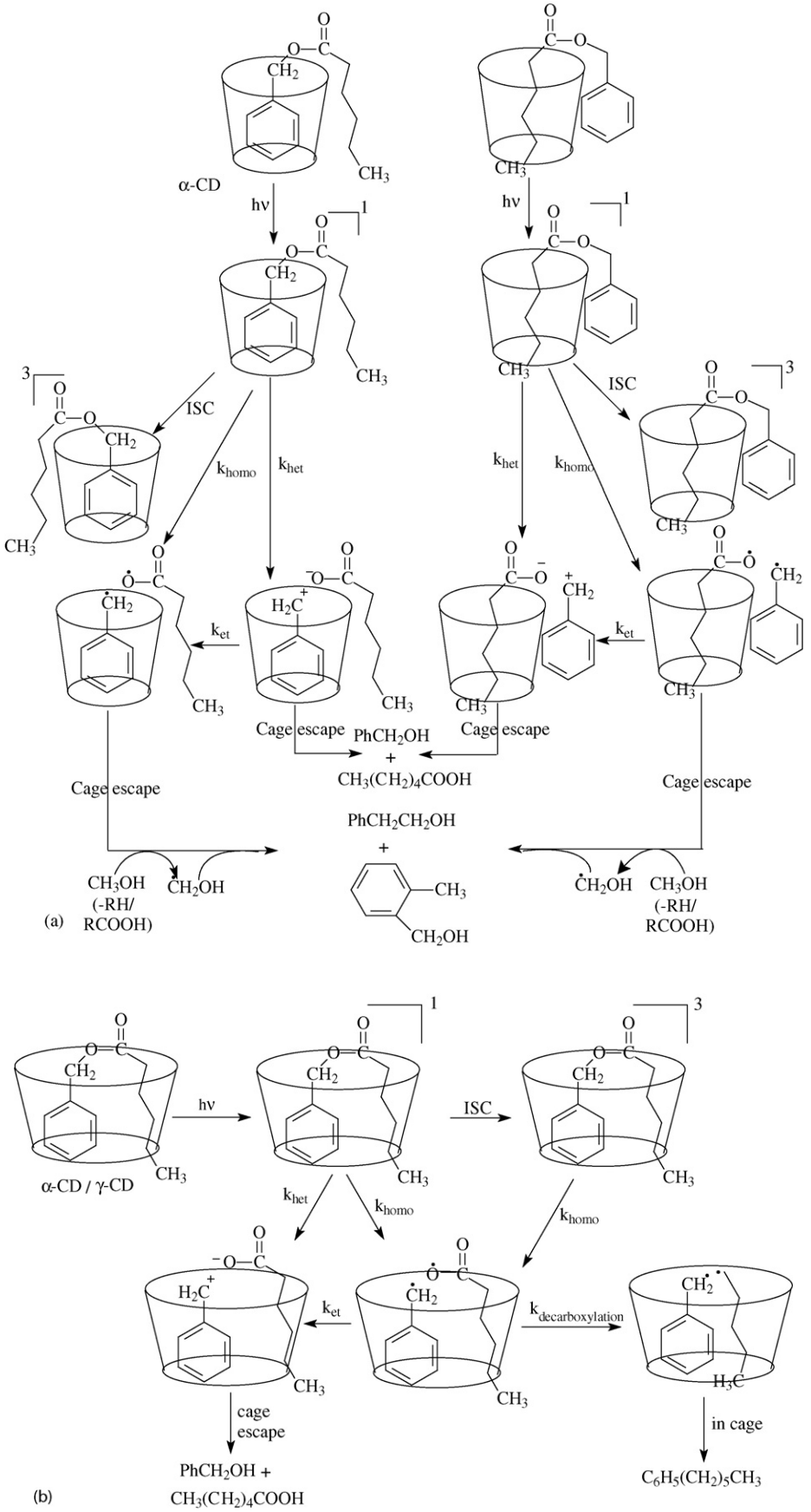


Fig. 3. ^{1}H-^{1}H NOESY spectra of **1**/α-CD in D_2O at 25 °C.

As for the presence of water molecules in the solid state reaction, it is likely that during work-up, where the complex is dissolved in water and extracted with hot chloroform, attack by water on the benzylcarbonium ion may have taken place leading to the formation of **5**.

To substantiate our observation that the more polar aqueous medium promotes a heterolytic pathway leading to the formation of benzyl alcohol (**5**), while in less polar methanol, formation of 2-phenylethanol (**4**) via radical mechanism is noticed, photolysis experiments are extended to benzyl hexanoate (**2**). This substrate has a long chain hexyl group which acts as a spacer to ensure a tight fit when the substrate is included into the cyclodextrin cavity. As this spacer hinders the interaction between benzylcarbonium ion and the secondary hydroxyl groups of cyclodextrin, more radical derived products are expected with this substrate **2**.

During solution photolysis of **2** in MeOH–H_2O mixture (Table 2), ionic as well as radical derived products are formed significantly. However in non-polar solvents, such as benzene and hexane, the conversion is less than 1% and benzyl alcohol **5** and hexanoic acid **10** are formed in trace. Photolysis of cyclodextrin complexes of **2** in methanol medium produces very interesting product selectivities and a radical mechanism is operating preferentially. Within the smaller cavity of α-CD, *ortho*-methylbenzyl alcohol (**9**) is the major product (along with hexanoic acid (**10**)) and as the size of the CD increases, formation of benzyl alcohol **4** increases and **9** decreases. With α-CD, either the phenyl group or the hexyl group (more probable) goes into the cavity (Scheme 4a). Consequently, the radical pair, formed from homolysis of **2**, interacts readily with the methanol solvent to generate $^{\bullet}CH_2OH$ radical. Attack of this radical at *ortho*-position leads to the formation of **9** and at the side chain leads to the formation of 2-phenylethanol (**4**). In photolysis of cyclodextrin complexes of **2** in aqueous medium and also in the solid phase, radical mechanism is still predominant and hexylbenzene is obtained as the major product. This is much more pronounced in β- and γ-cyclodextrins. The larger cavity size in β- and γ-CD accommodates both the phenyl ring and hexyl spacer into their cavities (Scheme 4b) [26]. This cage effect facilitates coupling of the radical pair (formed after decarboxylation) to yield hexylbenzene (**11**) predominantly. A small portion of ion pair may escape from the cage, yielding **5** and **10** in small quantities.



Scheme 4. Effect of cyclodextrin complexation in photolysis of benzyl hexanoate (**2**) (a) α-CD; (b) β- and γ-CDs.

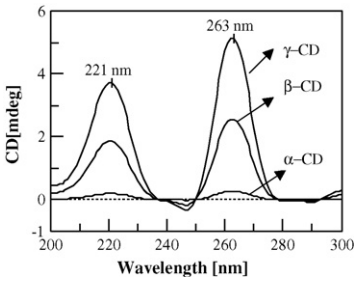


Fig. 4. ICD spectra of **2** (1.5×10^{-4} M) in presence of α-, β- and γ-cyclodextrins (7.5×10^{-3} M).

The mode of inclusion of **2** with its hexyl spacer group inside β- and γ-CDs is very clearly evidenced from the ICD and ^{1}H ^{1}H NOESY spectra. ICD spectra (Fig. 4) shows a peak at 262 nm which is due to the π–π* transition of phenyl group. In all the cyclodextrins, positive ICD bands are observed since the electric transition dipole moment of the π–π* transition of **2** lies parallel to the symmetry axis of the cyclodextrin cavity (axial inclusion). The magnitude of ICD is higher in the case of γ-CD as the spacer ensures a tighter fit inside the γ-cyclodextrin cavity. It is relevant to note that ICD of **2**/α-CD indicating that the hexyl group rather than benzyl group, may be preferentially included into the CD cavity. It is relevant to note that ICD of **2**/α-CD complex is much weaker than that of **1**/α-CD indicating that the hexyl group, rather than benzyl group, may be preferentially included into the CD cavity.

NOESY spectra for **2**/α-CD and **2**-γ-CD are given in Figs. 5 and 6, respectively. In Fig. 5, cross peaks A (due to interaction of H-3 proton of CD with *o*-proton of **2**) and (due to interaction of H-5 of CD with *p*-proton of **2**) are observed but there is no interaction with cyclodextrin inner proton with the hexyl protons of **2** as there is no corresponding cross peaks. Also, in the 2D NMR data for α-CD complex of **2** there is no cross peak obtained for the resonance of benzylic protons with the hexyl spacer group. However, difference in chemical shift (upfield) values are observed for H_d, H_c and H_b protons by 0.012, 0.03 and 0.08δ, respectively. The benzylic protons on the other hand are unaffected.

Whereas in the case of 2/γ-CD, cross peaks A–C (Fig. 6a) due to the interaction of H_d proton of hexyl group with H-3 of CD, interaction of H_b and H_c proton of hexyl group with H-5 proton of CD and interaction of Ha with H-6 of CD, respectively, are observed. Fig. 6b shows the interaction of aromatic group of **2** with cyclodextrin protons, which show two cross peaks D and E corresponding to the interaction of H-5 proton of CD with the *ortho*-proton of phenyl and H-6 proton of CD with the *para*-proton of aromatic ring.

This can be considered as a strong evidence for the inclusion of the hexyl spacer group inside the γ-cyclodextrin cavity and the

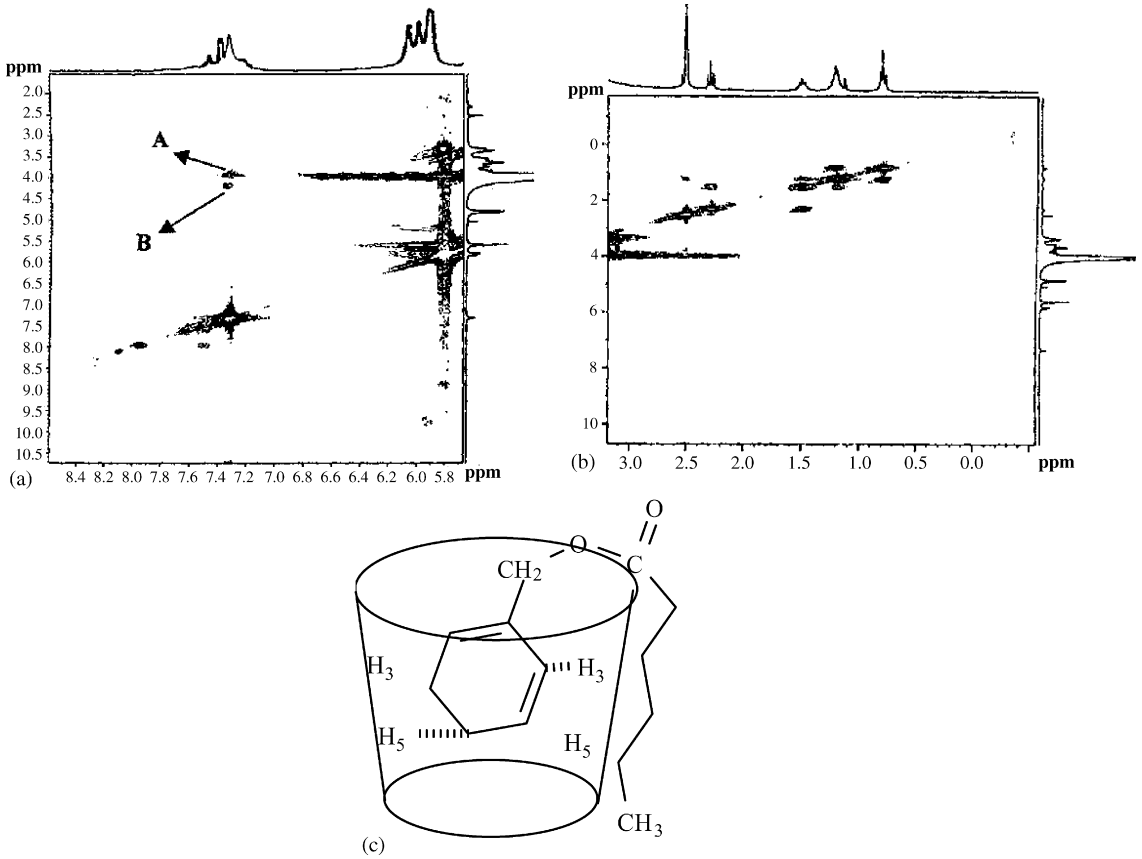


Fig. 5. (a and b) ^{1}H-^{1}H NOESY spectra of **2**/α-CD in D_2O at 25 °C. (c) Schematic representation of mode of inclusion of **2** inside the α-CD.

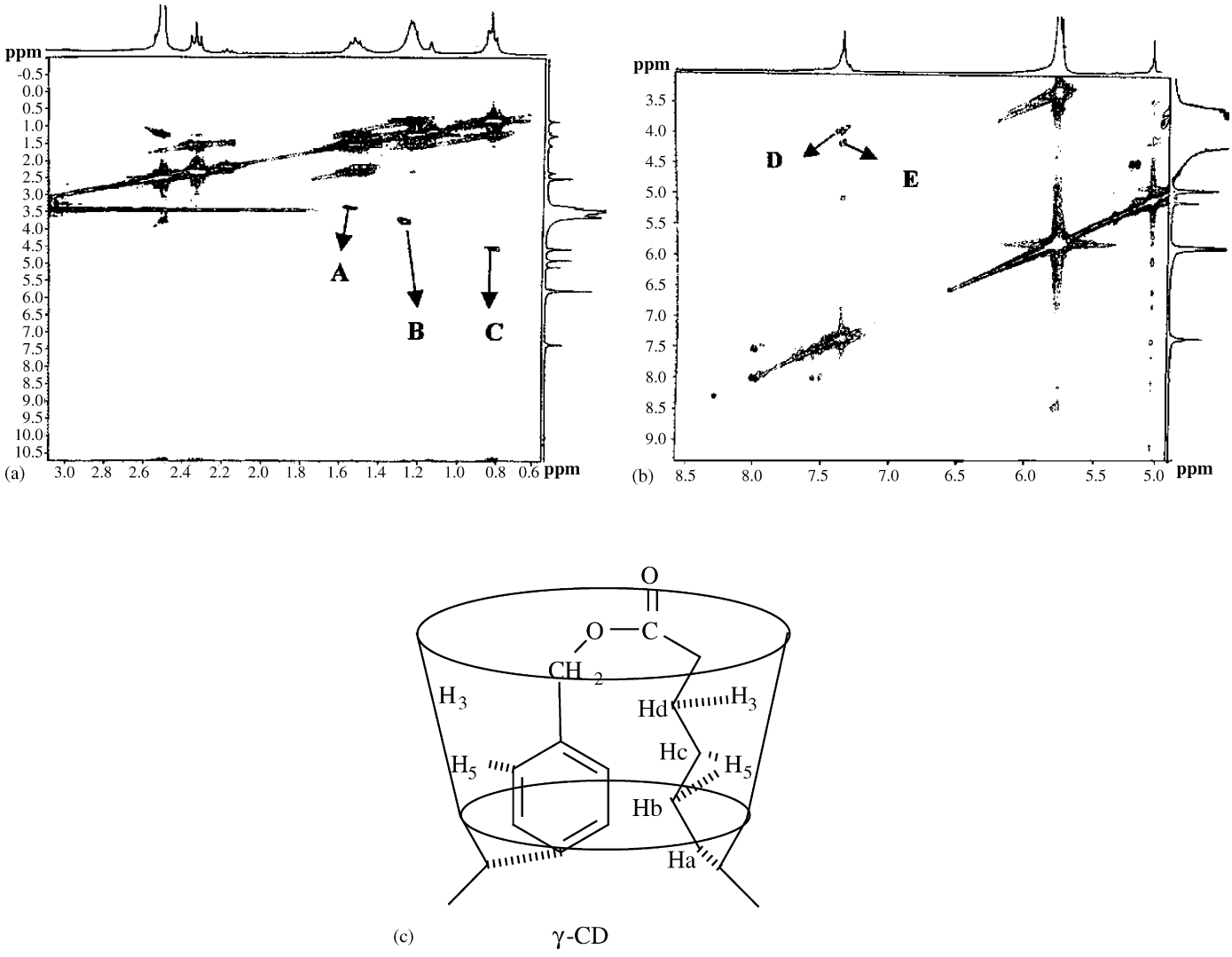


Fig. 6. (a and b) ^{1}H-^{1}H NOESY spectra of **2**/γ-CD in D_2O at 25 °C. (c) Schematic representation of mode of inclusion of **2** inside the γ-CD.

observed information from the NOESY is given as a schematic representation in Fig. 6c.

4. Conclusions

Thus, the results of the present study indicate clearly that photolysis of benzyl acetate (**1**) mediated by cyclodextrin (both in aqueous media and also as solid cyclodextrin complexes) results in the formation of benzyl alcohol (**5**) as the predominant product by the way of a heterolytic mechanism. This effect of cyclodextrin in suppressing the radical pathway and shifting the mechanism towards a heterolytic pathway is explained as due to stabilization of benzylcarbonium ion by the secondary hydroxyl groups of cyclodextrin. Photolysis is also selective in the less polar methanol medium yielding 2-phenylethanol as the major product, mainly by way of a radical route. However, in photolysis of benzyl hexanoate (**2**) with its longer alkyl chain, the homolytic pathway is predominant and hexylbenzene (**11**) is obtained as the major product. Coinclusion of the spacer group into the CD cavity (particularly with β- and γ-CD) is attributed to this selectivity.

Acknowledgement

Financial assistance from Council of Scientific and Industrial Research (CSIR), New Delhi, is gratefully acknowledged.

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[22] (a) ^{1}H NMR data δH (300 MHz; CDCl3) and GC-Mass data for benzyl hexanoate (**2**): 0.89 (3H, t), 1.34 (4H, m), 1.52 (2H, m), 2.34 (2H, t), 5.01 (2H,s), 7.35–7.45 (5H m); *m*/*z* (EI): 206, 188, 176, 114, 107, 91 (base peak). (b) GC-Mass data (*m*/*z* (EI)) for the photoproducts: benzyl methyl ether (**3**): 121, 120, 91 (base peak); 2-phenylethanol (**4**): 122, 91, 65; benzyl alcohol (**5**): 108, 79, 51; bibenzyl (**6**): 182, 91; 2-methylbenzyl alcohol (**9**): 122, 107, 104, 91, 77; hexanoic acid (**10**): 116, 96, 86, 72; hexylbenzene (**11**): 162, 132, 104, 92, 77. All the photoproducts reported also identified by coinjection with authentic samples.
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To calculate the binding constant values, a non-linear curve fitting method (using prism software) is adopted. The formation constant values for benzyl acetate calculated by this approach in α-, β- and γ-CDs are 1251 ± 20.9, 1329 ± 28.3 and 1771 ± 39.5, respectively; for benzyl hexanoate in α-, β- and γ-CDs are 1018 ± 27.7, 1962 ± 11.3 and 2826 ± 39.5, respectively. Binding isotherm curves for **1** and **2** with α-, β- and γ-CDs are given below (Fig. 1, Plots 1 and 2).

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^{1}H NMR chemical shifts exhibit an upfield shift for H-3 and H-5 protons of CD in all CD-ester complexes. Chemical shifts for cyclodextrin protons were assigned based on the software [Advanced Chemistry, Development: Toronto; http://ww2.acdlabs.com/ilab/]. For example, the chemical shifts (in Hz) for uncomplexed α-CD are H1-1392, H2-1167, H3-1071, H4-1104, H5-1191, H6-1254 and for α-CD-benzyl acetate (**1**) complex the corresponding values are H1-1386, H2-1155, H3-1116, H4-1101, H5-1176, H6-1296, for α-CD-benzyl hexanoate (**2**) complex the corresponding values are H1-1404, H2-1176, H3-1086, H4-1107, H5-1203, H6-1236, Such change in chemical shift values are known to be strong the consequence of diamagnetic anisotropic effect of the aromatic ring residing inside the cavity and are considered to be evidence for the formation of inclusion complex in aqueous CD solution.

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