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REVIEW ARTICLE

Recent advance of cyclodextrins as nanoreactors in various organic reactions: a brief overview

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Abstract Cyclodextrins have been widely used in organic syntheses, which can bind substrates and catalyze chemical reactions with high selectivity as well as transfer hydrophobic molecules into environmental friendly medium by supramolecular interaction through reversible formation of host–guest complexes. Herein we provide an overview of the recent developments of native and modified cyclodextrins as catalyst in several reactions. These reactions are classified into twelve types involving oxidation, reduction, addition, Tsuji-Trost reaction, cyclization, protection, bromination, coupling, oxygen–sulfur exchange, ring-opening, hydrolysis and photochemical reaction.

Keywords Cyclodextrins · Catalyst · Organic reaction · Environmental friendly · Selective catalysis · Nanoreactor

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides usually composed of six (α-), seven (β-) or eight (γ-cyclodextrin) D-glucopyranose units connected by α-1,4-glycosidic linkages, which have the ability to encapsulate a wide range of guest substrates into their cavity, both in the solid state and in solution [1–3]. During the past decades, CDs have been widely used in organic synthesis, which can bind substrates and catalyze chemical reactions with high selectivity as well as transfer hydrophobic molecules into water by supramolecular interaction through reversible formation of host–guest complexes [4, 5]. This property suggests that CDs, particular the β-cyclodextrins, are attractive host molecules, which can influence the microenvironment of guest molecules and change traditional reaction conditions to improve the yield of production [6–8]. It is unsurprising therefore that many types of organic reactions using CDs as catalyst have been reported in the literature [9].

This report aims to provide an overview of the recent development of applications of CDs in several organic reactions involving oxidation, reduction, addition, Tsuji-Trost reaction, cyclization, protection, bromination, coupling, oxygen–sulfur exchange, ring-opening, hydrolysis and photochemical reaction. To our best knowledge, no comprehensive review of these classes of reactions has been published in recent years, even though some papers that review the catalytic effect of CD were reported [10, 11].

General study: different reactions using CDs as nanoreactors

Oxidation reaction mediated by native or modified β-cyclodextrin

Native β-cyclodextrin promoted oxidation reaction

CDs have been extensively used as catalyst in the green oxidation reactions under mild condition. In 2003, Surendra et al. employed β-cyclodextrin as catalyst for the chemoselective oxidative of different kinds of alcohols to aldehydes and ketones, respectively, and also diols to α-aldehydes or α-ketones [12]. These reactions were carried out by dissolving alcohols with *o*-iodoxybenzoic acid (IBX) in water/acetone (86:14) in the presence of a

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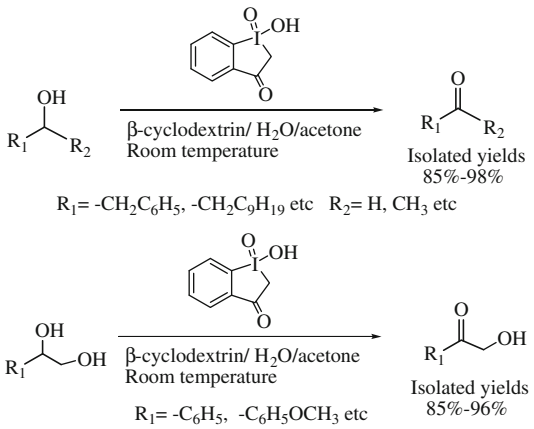
catalytic amount of β-cyclodextrin (Scheme 1). The authors found that all the alcohols investigated gave good yields ranging from 85 to 98%. No overoxidation was observed in the case of the corresponding carbonyl compounds.

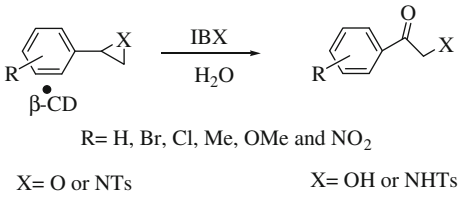
Subsequently, Surendra et al. reported the highly selective oxidation cleavage of epoxide/aziridine in the presence of IBX and β-cyclodextrin using water as solvent [13]. When water solvent was employed in the presence of β-cyclodextrin, the yields of the desired compounds were up to 92% (Scheme 2). However, the yields were decreased to be 30–40% in the absence of β-cyclodextrin in different organic solvents. The authors found that these reactions did not take place in the absence of β-cyclodextrin in water. This was ascribed to the insolubility of IBX in water. These results suggested that CD not only forms a CD–IBX complex via H-bond but also activates the epoxide/aziridine.

Similarly, Reddy et al. showed the preparation of α-tosylamino ketones from arylaziridines in the presence of β-cyclodextrin but using NBS instead of IBX (Scheme 3). The experimental results suggested that these reactions could not take place in the absence of β-cyclodextrin because of the absence of CD complex. The authors observed that only α-position of the aziridine ring was exposed to attack due to the inclusion of methylene β-position carbon of the aziridine as well as the methyl and tertiary carbons of the *p*-toluenesulfonyl group in the hydrophobic activity of the CD [14].

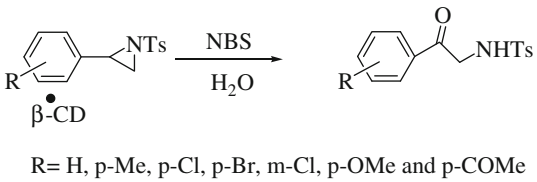
A new metal-free and CD catalytic approach to the oxidation of benzylic and allylic alcohols to aldehydes was investigated by Ji et al. using water as an only solvent in a homogeneous system [15]. High yields (>99%) were achieved by employing a catalytic amount of CD and NaOCl, which were essential for the improvement of yield. With the aim to increase the yield, the authors investigated the effects of the different reaction conditions involving the



Scheme 1 Chemoselective oxidative of different kinds of alcohols to aldehydes and ketones



Scheme 2 Selective oxidation cleavage of epoxide/aziridine



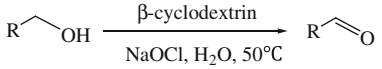
Scheme 3 Synthesis of α-tosylamino ketones from arylaziridines

amount of β-cyclodextrin and NaOCl, and reaction temperature on the catalyzed reaction. The authors found that the best experimental conditions to prepare the desired compounds required the reaction of 1 mmol of β-cyclodextrin and 5 mL of NaOCl (10%) at 50 °C (Scheme 4).

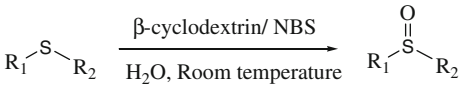
Surendra et al. reported NBS as an effective oxidant for sulfoxidation catalyzed by β-cyclodextrin [16]. The reaction was carried out using β-cyclodextrin (1 mmol) as catalyst in the presence of NBS (1 mmol) in water/acetone mixed solvents (Scheme 5). Under optimized conditions, several sulfides were cleanly oxidized to sulfoxides in excellent yields (88–96%) depending on the reaction time (6–8 h).

Direct synthesis of carbonyl compounds from THP ethers was reported by Narender et al. using β-cyclodextrin as catalyst and IBX as oxidizing agent in water (Scheme 6). The authors found that the yields of the desired compounds were decreased when a nitro group was present on the aromatic ring. This was assigned to the decrease in the nucleophilicity of the alcoholic oxygen. The authors also found that no reaction took place when glycerol was employed as solvent and in the absence of CD. CD promoted reactions by supramolecular interaction through H-bonding as seen in enzymes [17].

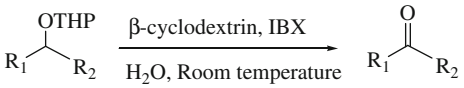
Recently, Reddy et al. employed β-cyclodextrin as catalyst in the oxidation of oxiranes to α-hydroxymethylaryketones [18]. Under mild conditions, α-hydroxymethylaryketones could be easily prepared from oxiranes within 24 h in the presence of β-cyclodextrin in acetone (Scheme 7). Good to high yields (67–96%) were obtained and no overoxidation was observed. However, the reaction did not take place in the



Scheme 4 Synthetic route of aldehydes from benzylic and allylic alcohols



Scheme 5 Oxidation of sulfides to sulfoxides



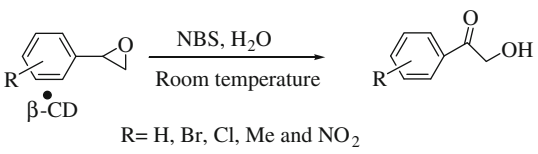
Scheme 6 Preparation of carbonyl compounds from THP ethers

absence of *β*-cyclodextrin. This indicated that the effect of *β*-cyclodextrin on the reaction should be a result of the formation of CD hypobromite and the activation of the epoxide.

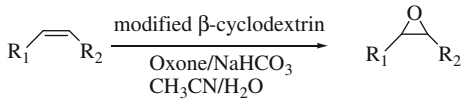
Modified β-cyclodextrin promoted oxidation reaction

In 2003, Chan et al. prepared a further novel *β*-cyclodextrin derivative endowed with a reactive ketone moiety and reported its ability as catalyst for stereoselective epoxidation of alkenes [19]. Treatment of several alkenes with Oxone in CH_3CN/H_2O mixed solvents in the presence of $NaHCO_3$ and modified *β*-cyclodextrin resulted in the corresponding epoxides in good yields (Scheme 8). Depending on the different substituents of various alkenes, the conversions to epoxides varied from 9 to 100% via flash column chromatography. Enantioselective epoxidation of styrenes were also investigated using the same catalyst. Up to 40% ee was obtained for 4-chlorostyrene at 0 °C in aqueous acetonitrile solution. However, no enantioselectivity was observed when using water as solvent. Being similar to this report, Rousseau et al. synthesized four CD ketones for epoxidation of alkenes in 2005 [20]. The employing of these catalysts in the presence of Oxone resulted in the epoxidation of mono-, di and trisubstituted alkenes in the yields of 17–100% and an entiomeric excess of up to 45%.

In 2006, Marinescu and Bols [21] used the bridged ketocyclodextrins as catalyst to oxidize a series of benzylic alcohols to aldehydes in good yields and high selectivity using hydrogen peroxide as oxidant in aqueous solution (Scheme 9). The authors found that the reaction rate was



Scheme 7 Oxidation of oxiranes to α-hydroxymethylaryketones



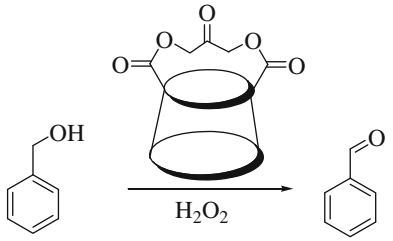
Scheme 8 Stereoselective epoxidation of alkenes

increased significantly in the presence of the bridged ketocyclodextrins when compare to using 1,3-diacetoxyacetone as catalyst. This could be assigned to the formation of hydrogen bonding between the proton of the benzylic alcohol and the keto hydroxyl group.

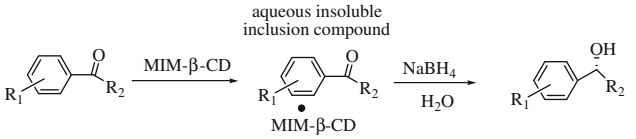
Reduction reaction mediated by modified *β*-cyclodextrin

CDs with chiral cavities can induce unsymmetrical reduction reactions. In the year of 2006, Tang et al. reported a novel chiral ionic liquid of mono-6-(1-methyl-3-imidazolium)-6-deoxy-*β*-cyclodextrin tosylate, synthesized from *β*-cyclodextrin, which was successfully applied for the enantioselectivity asymmetric reduction of various ketones [22]. The reduction route of substituted acetophenones was depicted in Scheme 10. The reduction of acetophenones involved the reaction of mono-6-(1-methyl-3-imidazolium)-6-deoxy-*β*-cyclodextrin tosylate (MIM-*β*-CDOTs) with an equimolar amount of ketone in the presence of Na_2CO_3 in acetonitrile/water mixed solvents affording the corresponding CD complex, which was converted into the desired alcohol in good yield by reacting with $NaBH_4$. Although the enantioselectivity was enhanced by MIM-*β*-CDOTs in comparison with *β*-cyclodextrin, the authors found that the absolute configurations of the desired alcohols obtained using MIM-*β*-CDOTs were the same as those using *β*-cyclodextrin. This may be ascribed to the inclusion of the guest ketones.

In the same year, Ravichandran reported the stereoselective hydrogenation of (2S, 5R)-(−)-menthone in the presence of *β*-cyclodextrin or its derivatives [23]. This reaction was carried out by reacting (2S, 5R)-(−)-menthone with Raney nickel suspension using *β*-cyclodextrin as



Scheme 9 Oxidation of benzylic alcohols to aldehydes



Scheme 10 Enantioselectivity aysmmetric reduction of various ketones

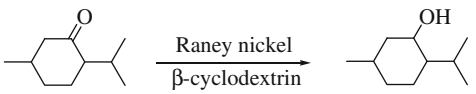
catalyst (Scheme 11). The authors found that the hydrogenation reaction led to a lower yield (10.1%) of alcohols in the absence of alkali. However, the yields of the desired compounds were increased in the presence of *β*-cyclodextrin (56.7%). Unfortunately, the yield was decreased to 17.75% in the presence of *β*-cyclodextrin-polymer. Surprisingly, the highest yield of alcohol was obtained upon addition of CTAB. With the aim to increase the yield, a small amount of alkali was added in this reaction. In this method, good yield (>90%) of alcohols was obtained in the presence of CTAB, *β*-cyclodextrin and its derivatives.

Two amino alcohol linked *β*-cyclodextrin **1** and **2** were prepared in good yields as crystalline compounds by reacting mono (*O*-6-tosyl)-*β*-cyclodextrin with an excess of the amino alcohol, which were converted into the corresponding Ru complexes of the amino alcohol *β*-cyclodextrins **3** and **4** as catalyst for the enantioselective reduction of aromatic and aliphatic ketones (Scheme 12). When the *β*-cyclodextrin derivative **3** was used as catalyst, the R configuration alcohol products were obtained with *ee* values of up to 47%. When the *β*-cyclodextrin derivative **4** was used as catalyst, the S configuration alcohol products were obtained with *ee* values of up to 97% and in good to excellent yields (77–97%) [24].

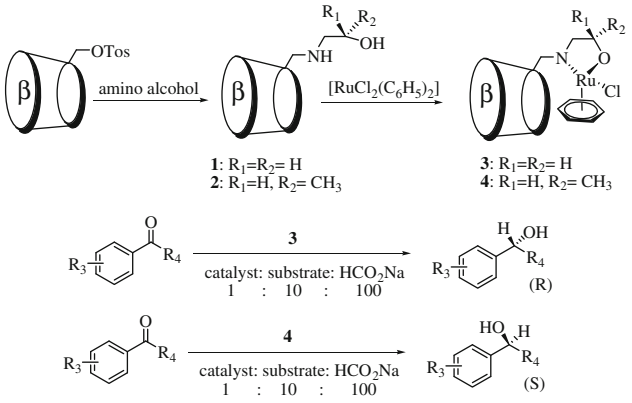
Addition reaction mediated by native or modified *β*-cyclodextrin

Native β-cyclodextrin promoted addition reaction

In the year of 2005, an environmentally benign and highly efficient Strecker reaction between trimethylsilyl cyanide and imines was reported by Surendra et al. [25]. The reaction was carried out under biomimetic conditions in the presence of *β*-cyclodextrin in water affording the desired α-aminonitriles in excellent yields within 1–2 h (Scheme 13). The catalyzed mechanism could be explained as follows: the electrophilicity of the imine carbon was increased due to formation of H-bonding between CD



Scheme 11 Stereoselective hydrogenation of (2S, 5R)-(−)-menthone

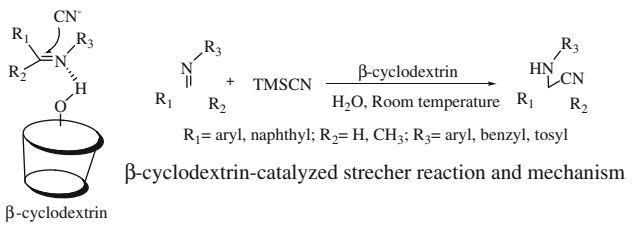


Scheme 12 Enantioselective reduction of aromatic and aliphatic ketones

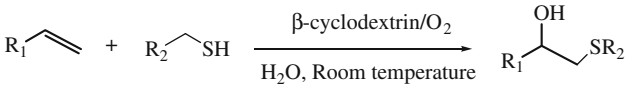
hydroxyl and the nitrogen of the imine, thus activating the α-imine for attack by the cyanide ion (Scheme 13).

In the year of 2006, Surendra et al. reported the synthesis of *β*-hydroxysulfides via the addition reaction of alkenes with various thiols using water as solvent in the presence of *β*-cyclodextrin [26]. This reaction could take place efficiently at room temperature in the absence of any acid or base catalyst, which was the first practically feasible anti-Markovnikov addition reaction of various thiols with alkenes (Scheme 14). No byproduct was observed in this reaction. The remarkable catalytic activity of *β*-cyclodextrin in the anti-Markovnikov addition could be established by the fact that no reaction took place without CD. When DCM, MeOH, THF and MeOH, etc. were used as solvent, only thioether was obtained. The authors also found that when the reaction was carried out under argon atmosphere, only the addition product thioether was observed. These results indicated that aerial oxygen was involved in the formation of the desired *β*-hydroxysulfides. In the same year, Surendra et al. described the aza-Michael addition of various amines to α, *β*-unsaturated alkenes under biomimetic conditions catalyzed by *β*-cyclodextrin in water at room temperature (Scheme 15). The authors found that these reactions also took place in the presence of α-cyclodextrin, but *β*-cyclodextrin was chosen due to its inexpensive and easily accessible [27].

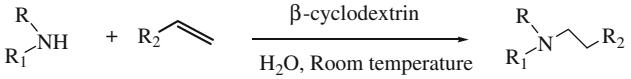
A novel and highly efficient *β*-cyclodextrin catalyzed reaction of aldehydes with allyltributyltin was reported by



Scheme 13 Strecker reaction between trimethylsilyl cyanide and imines



Scheme 14 Anti-Markovnikov addition reaction of various thiols with alkenes



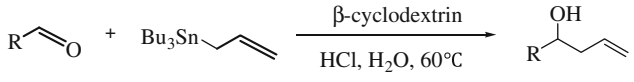
Scheme 15 Aza-Michael addition of various amines to unsaturated alkenes

Krishnaveni et al. [28]. The procedure involved the reaction of aldehydes with allyltributyltin in the presence of *β*-cyclodextrin and HCl in water affording the corresponding homoallylic alcohol in good yields (Scheme 16). This reaction took place efficiently at 60 °C in the absence of Lewis acid or transition metal catalyst within 2.0–3.5 h.

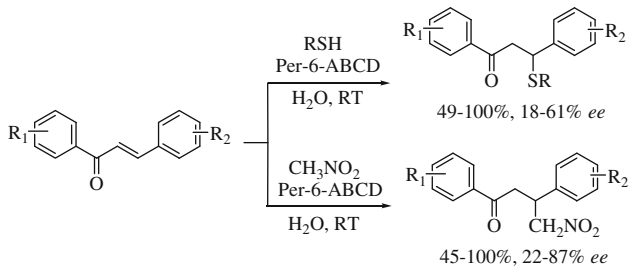
Modified β-cyclodextrin promoted addition reaction

In the year of 2008, Pitchumsni and Suresh used per-6-amino-*β*-cyclodextrin (Per-6-ABCD) as catalyst for the asymmetric Michael addition of nitromethane and thiols to trans-chalcones [29]. Treatment of substituted chalcones bearing electron-donating and electron-withdrawing groups with nitromethane or thiols resulted in the corresponding Michael adducts in good yields and with better enantiomeric excess (Scheme 17). This indicated that the electronic factors only displayed a negligible effect on this Michael reaction. The authors found that this catalyst could be recovered and reused without loss of its catalytic activity. In case of the reaction of non-substituted chalcone with nitromethane, this catalyst retained its catalytic activity even after three consecutive reactions in the yield of 100% of the desired compound. However, the *ee* was decreased to 58.0% from 68.5% in the third run. In this method, per-6-amino-*β*-cyclodextrin not only acted as a chiral acceptor by enhancing the enantiomeric excess but also as a base to catalyze this Michael addition reaction.

Modified *β*-cyclodextrin is an efficient catalyst for the asymmetric direct aldol reaction due to its character to provide both reactive sites and chiral receptor and to form inclusion complexes with organic compounds. In the year of 2005, Shen et al. reported several direct intermolecular aldol reactions catalyzed by *β*-cyclodextrin-immobilized (4S)-phenoxy-(S)-proline [30]. Treatment of (4S)-phenoxy-(S)-proline with *β*-cyclodextrin in ethanol/water mixed solvents resulted in the immobilized catalyst *β*-cyclodextrin-immobilized (4S)-phenoxy-(S)-proline. This catalyst could effectively promote these aldol reactions between acetone



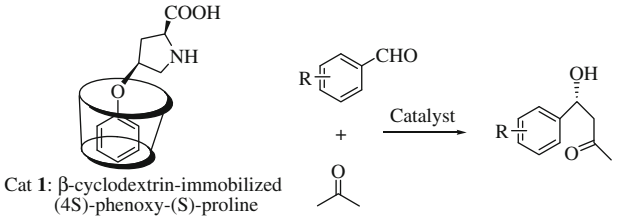
Scheme 16 Preparation of homoallylic alcohol from aldehydes and allyltributyltin



Scheme 17 Asymmetric Michael addition of nitromethane and thiols to trans-chalcones

and the corresponding aldehydes (Scheme 18). The catalytic activity of this catalyst was investigated using the reaction of acetone and *o*-nitrobenzaldehyde as the model. When using 10% of the *β*-cyclodextrin-immobilized (4S)-phenoxy-(S)-proline as catalyst, the desired chiral compound was obtained in the yield of 90.2% with 83.4% *ee*. When using 10% of the free (4S)-phenoxy-(S)-proline as catalyst, the *ee* value was decreased to be 77.9% with the yield of 89.9%. Surprisingly, the authors found that the reaction rate was obviously increased in the presence of 30% of the *β*-cyclodextrin-immobilized (4S)-phenoxy-(S)-proline when compare to the presence of 10% of the immobilized catalyst. This difference was assigned to the changed microenvironment around the catalytic center due to the interaction between (4S)-phenoxy-(S)-proline and the chiral *β*-cyclodextrin. Similarly, Huang et al. reported an asymmetric catalytic system inwater in the presence of *β*-cyclodextrin but using L-proline, trans-4-(*tert*-butoxy)-L-proline, α, α-diphenyl-L-prolinol, trans-4-(4-*tert*-butylphenoxy)-L-proline and cis-4-(4-*tert*-butylphenoxy)-L-proline instead of (4S)-phenoxy-(S)-proline, respectively [31].

In the year of 2010, Hu et al. developed an asymmetric supramolecular catalyst by combing the *β*-cyclodextrin with a chiral primary amine catalyst [32]. This catalyst was obtained by reacting mono-(*O*-6-tosyl)-*β*-cyclodextrin with (1S, 2S)-cyclohexane-1,2-diamine in DMF at 80 °C under an argon atmosphere. The catalytic ability of this catalyst in asymmetric aldol reactions was investigated using the reaction of *p*-nitrobenzaldehyde with acetone as a model reaction. Under optimized reaction conditions (pH = 4.60–4.80), good and excellent enantioselectivity was obtained and no apparent retro-aldol and dehydration compounds were observed. Catalytic mechanism was depicted in Fig. 1. This process involved three steps: (a) assembly of acetone and *p*-nitrobenzaldehyde via the



R	Catalyst(mol%)	Time(h)	Yield(%)	Ee(%)
O-NO_2	cat **1**(10)	16	90.2	83.4
O-NO_2	Free cat **1**(10)	16	89.9	77.9
m-NO_2	cat **1**(10)	16	85.7	72.1
p-NO_2	cat **1**(10)	16	81.8	73.5
O-Cl	cat **1**(10)	16	89.1	71.5
m-Cl	cat **1**(10)	72	76.5	71.3

Scheme 18 Aldol reactions between acetone and the corresponding aldehydes

hydrophobic interaction and noncovalent interaction; (b) product-generating C–C bond formation through enamine addition to *p*-nitrobenzaldehyde; (c) product release from the *β*-cyclodextrin cavity and regeneration of catalyst.

Tsuji-Trost reaction mediated by modified *β*-cyclodextrin

In the year of 2001, Bricout et al. reported the substrate-selective catalytic reactions in a biphasic system in the presence of per (2,6-di-*O*-methyl)-*β*-cyclodextrin (DMCyD) (Scheme 19) [33]. The authors found that high selectivity was observed using DMCyD as mass transfer promoter. However, no selectivity was observed using acetonitrile instead of DMCyD. For example, the deprotection of a 50:50

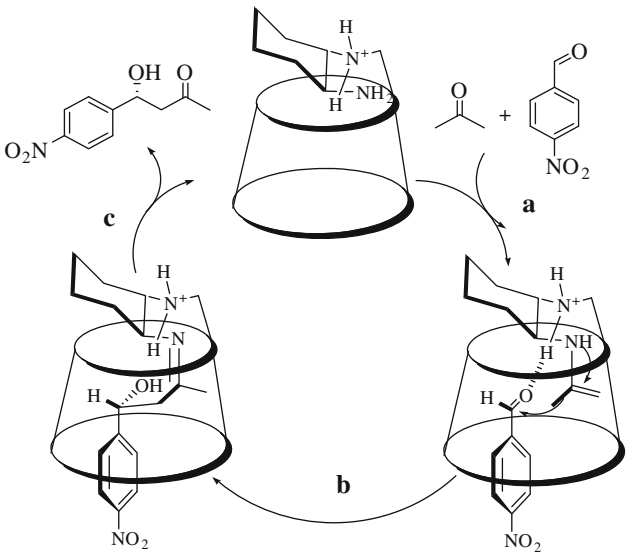


Fig. 1 Catalytic mechanism between *p*-nitrobenzaldehyde and acetone

mixture of *N*-dodecyl-*O*-allyl urethane and *N*,*N*-dihexyl-*O*-allyl urethane in the presence of DMCyD led to a 97:3 ratio of dodecylamine and *N*,*N*-dihexylamine.

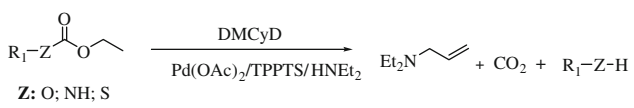
Subsequently, the same study group investigated the Tsuji-Trost reaction of allylundecylcarbonate with the different amounts of palladium and randomly methylated *β*-cyclodextrin (RAME-*β*-CD) as catalyst (Scheme 20) [34, 35]. The authors studied the effect of the palladium concentration on the reaction rate. The experimental results indicated that the reaction took place very slowly whatever the amount of palladium catalyst in the absence of RAME-*β*-CD. This was ascribed to the limited mass transfer without RAME-*β*-CD. The authors found that the ration of tris (3-sodium-sulfonatophenyl) phosphine (TPPTS)/RAME-*β*-CD should be accurately controlled, if not, the RAME-*β*-CD could be poisoned by the ligand and the substrate transfer could be diminished.

Cyclization reaction mediated by native or modified *β*-cyclodextrin

Native β-cyclodextrin promoted cyclization reaction

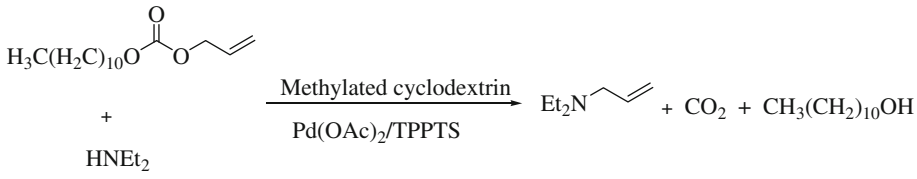
The thiazole ring system is an important and useful structural motif found in many biologically active molecules. Although various approaches involving solid supported synthesis and solution phase preparation have been reported for the preparation of thiazoles, most of them suffer from high reaction temperatures, long reaction time, hazardous solvents, low yields and the requirement for cleavage of the solid support using acids. In order to develop a simple and practical procedure for the preparation of thiazoles and aminothiazoles, Narender et al. described the aqueous phase synthesis of thiazole ring system by reacting phenacyl bromides with thioamide/thiourea in the presence of *β*-cyclodextrin [36]. This process involved the preparation of inclusion complex obtained from *β*-cyclodextrin and a phenacyl bromide using water as solvent, which was converted into the desired thiazole or aminothiazole via the addition of thioamide or thiourea within 1.0–2.5 h (Scheme 21). The authors found that the reaction also occurred without *β*-cyclodextrin, but the yields were decreased to 20% with a long reaction time (12 h).

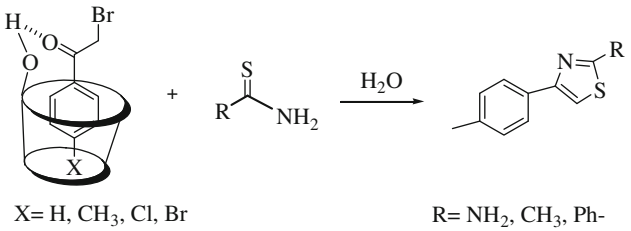
Furan-2(5H)-ones have attracted considerable attentions in the area of organic chemistry due to their biological activity and presence in many natural products. In the year



Scheme 19 Substrate-selective catalytic reactions in a biphasic system

Scheme 20 Tsuji-Trost reaction mediated by modified cyclodextrin





Scheme 21 Synthesis of thiazole ring system in the aqueous phase

of 2009, Murthy and coworkers reported that *β*-cyclodextrin, a recyclable supramolecular catalyst, can catalyze the preparation of 3,4,5-substituted furan-2(5H)-ones derivatives [37]. They reacted diethylacetylenedicarboxylate, benzaldehyde and aniline in water in the presence of *β*-cyclodextrin to afford the corresponding 3,4,5-substituted furan-2(5H)-one in good yield (Scheme 22). This procedure has been used to prepare other similar 3,4,5-substituted furan-2(5H)-one derivatives in good yields with good amount of catalyst recovery. Depending on the substituents in the substrate, the yields varied from 78% to 88% within 12–16 h. If the substrate bearing electron donating group, the desired compound was obtained in good yield (88%). Substrate containing electron withdrawing group (such as para-fluoro) resulted in a low yield of the corresponding furan-2(5H)-one derivatives due to the electronic factors.

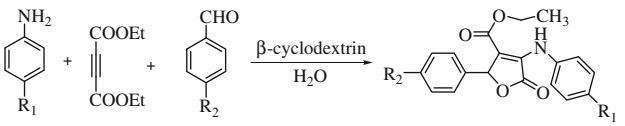
Modified β-cyclodextrin promoted cyclization reaction

Subsequently, the same authors investigated the preparation of various dihydropyrano [2,3-c] pyrazole derivatives using per-6-amino-*β*-cyclodextrin (per-6-ABCD) as supramolecular host [38]. As shown in Scheme 23, the reactions were carried out with hydrazine, malononitrile, ethyl acetoacetate and 4-nitrobenzaldehyde. The authors studied the effect of different reaction conditions on the yield of the desired compound. They found that no product was obtained in aqueous medium using *β*-cyclodextrin as catalyst. When using DMSO and DMF as solvent, 58.2–61.6% yields were obtained. However, when using methylamine, triethylamine, diethylamine and piperidine as catalyst in the absence of solvent, the yields were increased to 68.1%. Surprisingly, when per-6-amino-*β*-cyclodextrin was employed as catalyst in the same reaction conditions, 98–100% yields were obtained within 1 min. This catalyst could be reused at least six times without any change in the catalytic efficiency. These results suggest that per-6-amino-*β*-cyclodextrin was an efficient catalyst as an excellent supramolecular host.

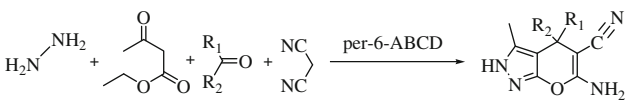
More recently, Lopez et al. reported the synthesis and catalytic properties of new cup-shaped α-cyclodextrin derivatives [39]. All these catalysts were obtained from the known 6^A, 6^D-di-*O*-(prop-2-methylidene-1,3-dienyl)-hexadeca-*O*-benzyl-α-cyclodextrin. Treatment of 2-hydroxyaniline with H_2O_2 in the presence of cup-shaped α-cyclodextrin resulted in 2-aminophenoxazin-2-one in good yield. Depending on the different substituents in α-cyclodextrin, the relative reaction rate affected by catalyst containing one aldehyde substituent could be increased significantly when compared to the other analogues (Scheme 24).

Protection reaction mediated by native *β*-cyclodextrin

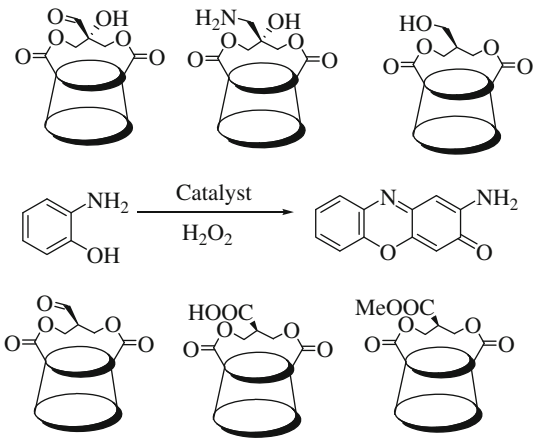
The selective protection of amines with the benzyloxycarbonyl (Cbz) group in the presence of catalytic amounts of *β*-cyclodextrin in aqueous phase has been investigated by Kumar et al. [40] (Scheme 25). The corresponding carbamates were obtained in excellent yields (89–98%). First, *β*-cyclodextrin was dissolved in water and then reacted with amine to give the corresponding complex. Second, Cbz-Cl selectively attacked the amine resulting in the desired *N*-benzyloxycarbonyl derivatives. These results prompted them to investigate the Cbz protection of amino acids. The authors found that although this reaction also occurred in water using *β*-cyclodextrin as catalyst, it gave the desired compounds in very low yields within long reaction times. With the aim to improve the yield, they



Scheme 22 Synthesis of 3,4,5-substituted furan-2(5H)-ones derivatives



Scheme 23 Preparation of various dihydropyrano [2,3-c] pyrazole derivatives

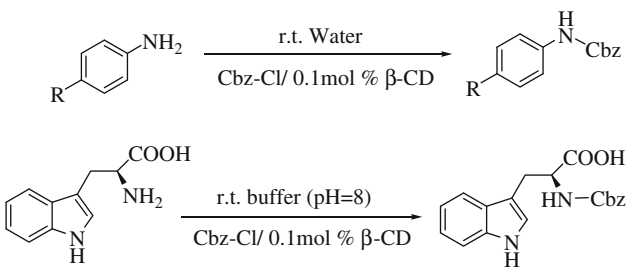


Scheme 24 Modified β-cyclodextrin promoted cyclization reaction

studied the effect of various pH values on the reaction. Fortunately, this reaction was finished in 7–15 min in yields of 84–97% at pH 8 using a mild carbonate buffer in the presence of β-cyclodextrin.

Bromination reaction mediated by native β-cyclodextrin

Suresh et al. investigated the regioselective monobromination of substituted phenols involving 2-chlorophenol, 4-chlorophenol, 3-chlorophenol and 3-nitrophenol in the presence of β-cyclodextrin [41]. First, the bromination of 3-nitrophenol was carried out using methanol as solvent in the presence of amounts of Br_2/CCl_4 (Scheme 26). It was found that polybrominated products and tribromide were formed more significantly. This was ascribed to the presence of the activating hydroxyl group. Then, the bromination was studied in the presence of β-cyclodextrin with the aim to increase the yield of monobromination products. Interestingly, a significant selectivity toward monobromination products was observed using β-cyclodextrin as catalyst. Bromination of 3-nitrophenol was also investigated in polar solvent water. Unfortunately, no bromination products were observed even after 24 h. However, a stable product hypobromide was observed by NMR and GC



Scheme 25 Selective protection of amines with benzyloxycarbonyl group

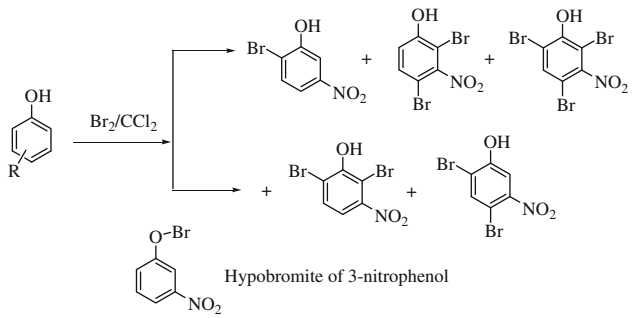
(Scheme 19). Similar results were also observed for the bromination of 2-chlorophenol, 4-chlorophenol and 3-chlorophenol. In these works, it was also demonstrated that the electronic effects, which are usually dominant in phenol bromination, played a less significant role when phenols were include inside the β-cyclodextrin cavity.

Coupling reaction mediated by native or modified β-cyclodextrin

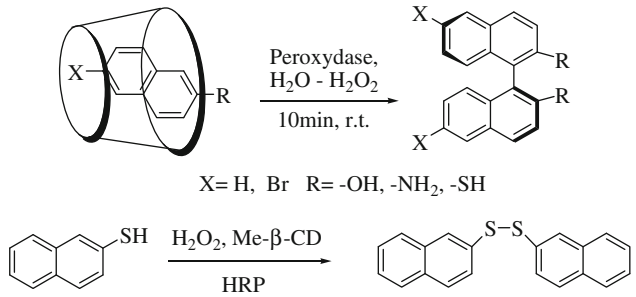
Modified β-cyclodextrin promoted coupling reaction

The coupling of naphthol and naphthylamine in the presence of a suitable CD has been reported by Trotta et al. in 2002 [42]. It was found that, in the presence of suitable methyl-β-cyclodextrin, the solubility of these compounds was enhanced greatly compare to the absence of CD. For example, the solubility of 2-naphthol was increased up to 50-fold in pure water. Under optimized conditions, the desired binaphthyl derivatives were obtained by reacting these naphthyl compounds with H_2O_2-horseradish peroxidase system using methyl-β-cyclodextrin as catalyst at room temperature in few minutes (Scheme 27). Indeed, these reactions could not take place in the absence of methyl-β-cyclodextrin or in the presence of unmodified β-cyclodextrin. This indicated that methyl-β-cyclodextrin not only acted as solubilising agents but also as catalyst. Interestingly, treatment of thiol-2-naphthol with the same reaction system, no oxidative coupling was observed. The final product was the corresponding disulfide compound. This was attributed to the delocalisation of the unpaired electron in the aromatic ring and the immediately pairing of thiol radicals.

In the same year, Strimbu et al. investigated the Suzuki cross-coupling reaction using β-cyclodextrin-capped Pd nanoparticles as catalyst (Scheme 28) [43]. It was demonstrated that the reaction in acetonitrile/water mixed solvents was more rapid than in aqueous media or organic solvents. This was assigned to the different solubility of β-CD-capped Pd nanoparticles and the reactants and products in water or organic solvents. Under optimized



Scheme 26 Bromination reaction mediated by native β-cyclodextrin

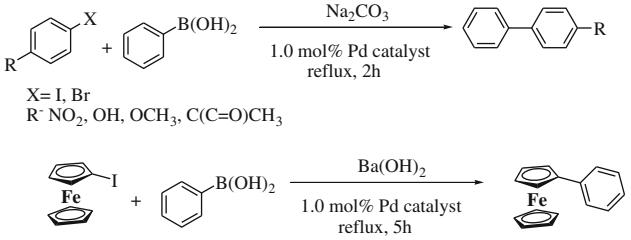


Scheme 27 Coupling reaction of naphthol and naphthylamine in the presence of modified *β*-cyclodextrin

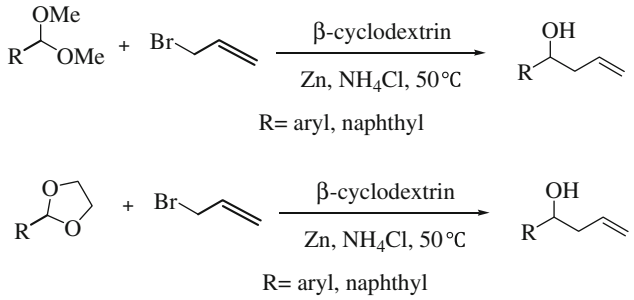
conditions, the desired compounds were obtained in good to excellent yields (77–98%). In order to take advantage of the binding ability of CD receptors, iodoferrocene was prepared for the research of its coupling reaction with phenylboronic acid. This reaction was carried out by reacting iodoferrocene with a 5-fold excess phenylboronic acid in EtOH/water mixed solvents in the presence of $Ba(OH)_2$ as the base using *β*-CD-capped Pd nanoparticles as the catalyst. The phenylferrocene product was obtained in an isolated yield of 70%. The authors found that the same reaction in the presence of 3 equiv ferrocene under otherwise identical conditions afforded phenylferrocene in considerably lower yield of 35%. The binding ability of iodoferrocene with the *β*-CD cavities was verified by this experiment result.

Native β-cyclodextrin promoted coupling reaction

Allylation of carbonyl compounds is an important carbon–carbon bond forming reaction in organic chemistry for the preparation of homoallylic alcohols, which can be easily converted into many important building blocks for the construction of natural products. With the aim to develop an environmentally benign process for carbon–carbon bond formation, Surendra et al. employed *β*-cyclodextrin as catalyst for the zinc-mediated allylation reaction using water as solvent [44]. The authors found that these reactions could be effectively carried out at 50 °C and did not take place without *β*-cyclodextrin (Scheme 29). These reaction also proceed in the presence of aliphatic acetals



Scheme 28 Modified cyclodextrin promoted Suzuki cross-coupling reaction



Scheme 29 Native *β*-cyclodextrin promoted coupling reaction

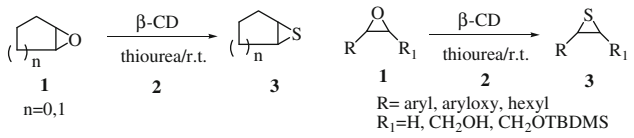
and dioxolanes, however, the yields (15–20%) were much lower when compared to the presence of *β*-cyclodextrin (80–86%).

Oxygen–sulfur exchange reaction mediated by native *β*-cyclodextrin

The preparation of thiiranes from oxirane with thiourea using *β*-cyclodextrin as catalyst has been reported by Surendra et al. in 2004 [45]. Treatment of *β*-cyclodextrin with the epoxide **1** in water resulted in the corresponding *β*-cyclodextrin complex (Scheme 30), which was converted into the desired thiiranes **3** by reacting with thiourea **2** in good to excellent yields (80–96%). These reactions occurred at room temperature and no byproduct or rearrangement was observed. The yields of these reactions were much higher when compared to the conventional methods. These reactions could not take place without *β*-cyclodextrin suggesting that CD not only formed the *β*-cyclodextrin complex but also activated the epoxide. The inclusion of *β*-cyclodextrin and epoxide was verified by the upfield shift of H-3 (0.03 ppm) and H-5 (0.057 ppm) of CD. Thus, it could be concluded that the reaction took place via supramolecular catalysis.

Ring opening reaction mediated by native *β*-cyclodextrin

N-Activated aziridines and oxiranes are important precursors for the preparation of many biological active molecules. In fact, remarkable studies have been made in recent years in the area of the ring opening of aziridines and oxiranes due to their high reactivity and ease of preparation.



Scheme 30 Oxygen-sulfur exchange reaction mediated by native *β*-cyclodextrin

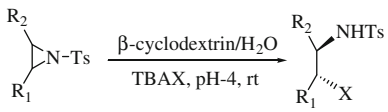
In the year of 2004, Narender et al. carried out a study on the regioselective ring opening of aziridines to haloamines using β-cyclodextrin as catalyst in water (Scheme 31) [46]. Treatment of β-cyclodextrin with aziridine **1** resulted in the corresponding complex, which was converted into the desired haloamines **2** in good yields by the addition of the tetrabutylammonium halide (TBAX). The authors investigated the effect of TBAX on the rate of haloamine formation. They found that the reaction rate decreased in the order n-$Bu_4NI > n$-$Bu_4NBr > n$-Bu_4NCl. This could be ascribed to the decrease in softness of the halide ion. Another comparative study was also carried out by reacting styrene aziridine with TBAX in the absence and presence of β-cyclodextrin under neutral and acidic conditions (pH = 4.0). Higher yields were obtained in the presence of β-cyclodextrin at pH 4.0 due to the facile abstraction of proton by the intermediate anion from the acidic solvent. Being similar to Bartender's work, Reddy et al. investigated the regioselective ring-opening of aziridines in the presence of β-cyclodextrin but using KSCN instead of TBAX as nucleophile (Scheme 32) [47].

Ring opening of oxiranes with phenoxides using β-cyclodextrin as catalyst in water was reported by Surendra et al. in 2003 [48]. The synthesis of β-hydroxyl ethers involved the reaction of β-cyclodextrin with various epoxides in water affording the corresponding β-cyclodextrin complex. Treatment of this complex with various phenoxides at 60 °C resulted in the desired β-hydroxyl ethers in good to impressive yields (77–96%) (Scheme 33). These reactions also occurred smoothly at room temperature, but the reaction times were much longer (18–24 h) when compared to at 60 °C. Being similar to this report, the same study group investigated the ring opening of the similar or same oxiranes in the presence of β-cyclodextrin complex but using benzeneselenol, thiophenoxide and NaCN as nucleophile, respectively [49–51].

Hydrolysis reaction mediated by native or modified β-cyclodextrin

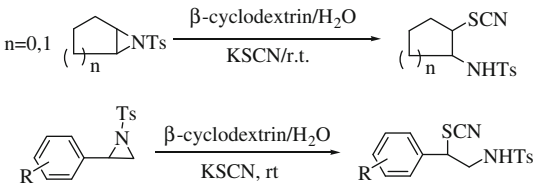
Modified β-cyclodextrin promoted hydrolysis reaction

Ortega-Caballero et al. employed the cyclodextrin cyanohydrin as catalyst for the hydrolysis of various glycosides [52]. Treatment of β-cyclodextrin dialdehyde with KCN in



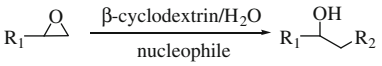
R_1= Phenyl, Alkyl; R_2= H; X= Br and I

Scheme 31 Regioselective ring opening of aziridines to haloamines



R= H, *p*-Cl, *p*-Br, *p*-OMe and *p*-COMe

Scheme 32 Regioselective ring-opening between aziridines and KSCN



R_1=aryloxy, aryl, hexyl; R_2=OC_6H_5, OC_6H_4-4Cl, OC_6H_4-4OCH_3
nucleophile= ArONa, PhSeH, ArSNa or NaCN

Scheme 33 Ring opening of oxiranes with phenoxides

ether/MeOH/H_2O mixed solvents resulted in the important intermediate, which was converted into the desired cyclodextrin cyanohydrin by hydrogenolysis of the benzyl protection groups. The catalytic hydrolysis reaction was carried out in the presence of 0.42 mM of cyclodextrin diacid at 59 °C (pH = 7.4). Various glycosides involving 4-nitrophenyl-β-D-glucoside, 4-nitrophenyl-α-D-glucoside, 4-nitrophenyl-α-D-mannoside, 4-nitrophenyl-α-D-galactoside and 2-nitrophenyl-β-D-glucoside were hydrolyzed to the corresponding substrates. Proposed mechanism for the catalysis was depicted in Fig. 2. During this process, the cyanohydrin hydroxyl group in cyclodextrin diacid delivers a proton to the exocyclic oxygen facilitating hydrolysis. Being similar to this study, Ortega-Caballero et al. investigated the catalytic ability of (6^AR, 6^DR)-6^A, 6^D-Di-*C*-cyano-β-cyclodextrin, 6^A, 6^D-Di-*C*-cyano-α-cyclodextrin and 6-*C*-cyano-β-cyclodextrin for the hydrolysis of aryl glycoside [53]. These catalysts could promote the hydrolysis of aryl glycosides with rate increased to 10^4. Subsequently, Bjerre et al. reported the hydrolysis of toxic natural glucosides catalyzed by (6^AR, 6^DR)-6^A, 6^D-Di-*C*-cyano-β-cyclodextrin

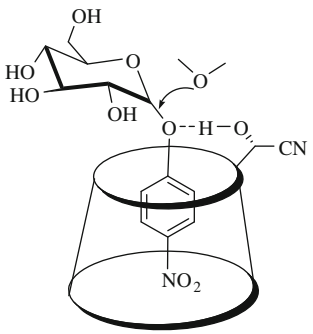


Fig. 2 Proposed mechanism for the hydrolysis reaction

[54]. Similar catalytic results were also observed when compared to the previous report [52, 53].

In the year of 2005, Rousseau et al. developed a CD-based artificial enzyme that would be able to mimic the reaction of a glycosidase [55]. β-cyclodextrin-6^A, 6^D-diacids, α-cyclodextrin-6^A, 6^D-diacids and β-cyclodextrin-6^A, 6^D-di-*O*-sulfate were found to be artificial glycosidase with K_{cat}/K_{uncat} of 80–1,000 for the hydrolysis of aryl glycosides. These catalysts could form complexes with the corresponding substrates with K_M of 2–10 mM, thus activating the nitrophenoxy units towards being substituted by phosphate (Scheme 34).

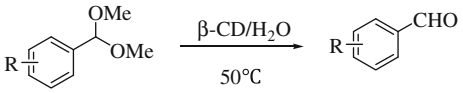
Native β-cyclodextrin promoted hydrolysis reaction

The hydrolysis of aromatic acetals under biomimetic conditions using water as solvent in the presence of β-cyclodextrin at 50 °C has been reported by Krishnaveni et al. [56] (Scheme 35). According to this procedure, the yields of the deprotection compounds aldehydes were impressive between 80 and 90%. This reaction could occur in the presence of only catalytic amount of β-CD, i.e., 0.1 mol/1 mol acetals; however, it did not take place without β-CD. Although these reactions also occurred with acetals of aliphatic aldehydes, the yields were less than satisfactory.

Photochemical reaction mediated by γ-cyclodextrin

Native γ-cyclodextrin promoted photocyclodimerization reaction

On recent years photocyclodimerization reactions using CD catalytic host have attracted considerable attention due to its chiral cavity that efficiently transfer the host's chiral information to the several organic guests. The CD could accelerate the photocyclodimerization reactions of various substrates upon inclusion in its cavity. Early work in this area of photocyclodimerization reaction follows Tamaki's initial work when, in 1984, Tamaki et al. carried out a study on the photocyclodimerization of 2-anthracenecarboxylate with 1- and 2-anthracenesulfonates in the presence of γ-cyclodextrin, which resulted in the chiral products [57, 58]. About nineteen years later, Nakamura and Inoue investigated the photocyclodimerization behavior of 2-anthracenecarboxylate in the presence of native γ-cyclodextrin. They found that 1:2 complexes were formed between γ-cyclodextrin and 2-anthracenecarboxylate, which resulted in four cyclodimers **1**–**4** upon illumination



R= acetyl, allyloxy, OMe, OTBDMS, OAc, allyloxy, methylenedioxy

Scheme 35 Native β-cyclodextrin promoted hydrolysis reaction

at 366 nm (Scheme 36) [59]. The head-to-tail compounds **1** and **2** were obtained as the major products in the yields of 85–90%. But the yields of head-to-head dimers **3** and **4** were much lower when compared to compounds **1** and **2**. The 41% *ee* value of compounds **2** at 0 °C was higher than at 25 °C (32%). The *ee* value of compound **3**, however, never exceeded 5%.

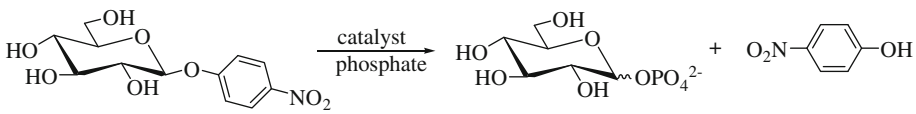
Modified γ-cyclodextrin promoted photocyclodimerization reaction

Recently, Ikeda et al. [60] also studied the same complexation and photocyclodimerization reaction but only using 6-mono- and 6^A, 6^X-dipyridino-γ-cyclodextrins instead of native γ-cyclodextrin, which resulted in an improved *ee* for compound **3** (1–13%) and a lower *ee* for compound **2** (10–30%). In the same year, Nakamura and Inoue also demonstrated the same reaction using the 6^A-(2-(dimethylamino) ethylamino)-6^A-deoxy-γ-cyclodextrin as a templating chiral host [61]. They found that the yields of compounds **1** and **2** decreased with the lowering temperature. The yields of **3** and **4**, however, increased with the lowering temperature. Surprisingly, the yield and *ee* value of compound **3** increased with the reducing solvent polarity and/or temperature. This may be ascribed to the stabilization of the diastereomeric precursor complex resulting in a significant enhancement of the diastereodifferentiation. Following Nakamura's early work, further studies of photocyclodimerization of 2-anthracenecarboxylate by Ke et al. [62] and Yang et al. [63] described efforts to investigate catalytic enantiodifferentiating photocyclodimerization reaction in the presence of different modified γ-cyclodextrins. They found that the modified γ-cyclodextrins not only accelerated the photoreaction but also controlled the selectivity of substrate 2-anthracenecarboxylate.

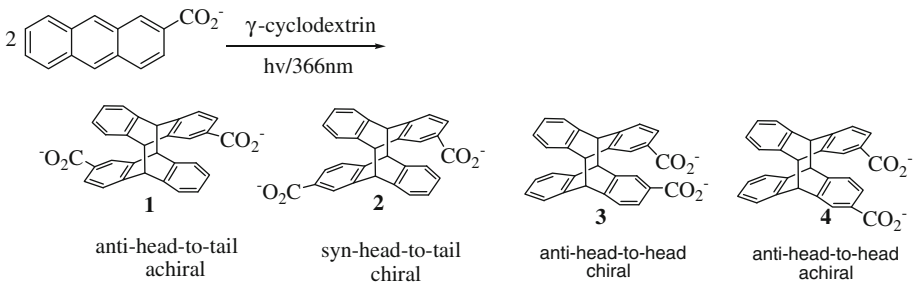
Native γ-cyclodextrin promoted photo-Fries reaction

CD-mediated selectivity photo-Fries reaction of 1-naphthyl phenyl acylates upon irradiation was investigated by

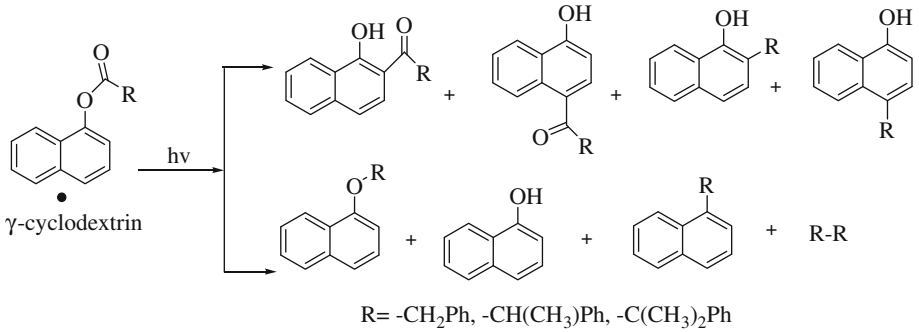
Scheme 34 Modified β-cyclodextrin promoted hydrolysis reaction



Scheme 36 Native γ-cyclodextrin promoted mediated photocyclodimerization reaction



Scheme 37 Native γ-cyclodextrin promoted mediated photo-Fries reaction



Koodanjeri et al. in 2003 [64]. This procedure involved the reaction of 1-naphthyl phenyl acylates with γ-cyclodextrin in ether/water mixed solvents, affording the solid CD-reactant complexes followed by washing with diethyl ether to remove uncomplexed guest molecules. Then, treatment of the latter complexes upon irradiation in hexane resulted in a mixture of compounds (Scheme 37). In fact, the *ortho* rearranged product was topochemically favored in the presence of γ-cyclodextrin. This was assigned to the rapid rate of the recombination of the phenylacyl and naphthoxy radicals within a γ-cyclodextrin cavity.

Conclusions

The application of native and chemically modified CDs in several organic reactions reported to date has been reviewed. They could be used as scaffold and templates with the aim to build molecular reaction vessels at the molecular level. Indeed, a wide range of catalytic reactions involving oxidation, reduction, addition, Tsuji-Trost reaction, cyclization, protection, bromination, coupling, oxygen–sulfur exchange, ring-opening, hydrolysis and photochemical reaction have been reported in the presence of CDs. Most of these reactions take place efficiently in water due to their ability to form inclusion complexes with a wide range of substrates in this environmentally friendly medium. Thus, it is critically important to further explore novel modified CDs to promote several reactions using environmentally friendly mediums as solvents [65, 66]. This is beginning to take shape as a promising field of research.

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