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β-Cyclodextrin as a recyclable catalyst: aqueous phase one-pot four-component synthesis of polyfunctionalized pyrroles[†]

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An elegant, mild and straightforward methodology was explored for the first time towards the synthesis of polyfunctionalized pyrroles using β -cyclodextrin as a reusable supramolecular catalyst in aqueous medium. The present method provides various diversely substituted pyrroles from the commercially available synthons in good to excellent yields. The advantages of this novel protocol are use of environmentally benign reaction medium and recyclability of β -cyclodextrin over the existing methods.

Introduction

The pyrrole structural skeleton has gained prominence in heterocyclic chemistry,¹ due to the numerous applications associated with it as well as its presence as an important structural motif in a wide variety of natural, biological and pharmacologically potent molecules (Fig. 1)² such as porphyrins, bile pigments, coenzymes and alkaloids. Of these aforementioned class of compounds, polysubstituted pyrroles exhibit significant role as synthetic intermediates,3 pharmacophores,⁴ and functional materials.⁵ Traditional methods for the synthesis of polysubstituted pyrroles include Knorr reaction,6 Hantzsch reaction⁷ and Paal-Knorr condensation reaction.⁸ Even though many alternate methodologies have been described in the literature, the synthesis of functionalized pyrroles is challenging tasks to the researchers worldwide because of lack of selectivity and the problems associated with the polymerization.9 Rao and co-workers have developed a facile one-pot synthesis of polyarylpyrroles from 2-butene and but-2yne-1,4-diones under microwave irradiation.10 Bimal and co-

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Fig. 1 Biologically active molecules with pyrrole as core skeleton.

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pyrroles and N-bridgehead pyrroles *via* regioselective propargylation/amination/cycloisomerization.

Camp et al., reported a concise synthesis of highly substituted pyrroles via intermolecular addition of oximes to activated alkynes and subsequent thermal rearrangement of in situ generated O-vinyl oximes to form pyrroles via nucleophilic catalysis.21 Hashemi and co-workers22 described a mild method for the synthesis 2-alkyl-5-aryl-(1H)-pyrrole-4-ol in water at room temperature via three component condensation reaction between β-dicarbonyl compounds, arylglyoxals and ammonium acetate. Rodríguez et al.,23 synthesized tetrasubstituted pyrroles via coupled domino process through µv-assisted rearrangement of 1,3-oxazolidines to pyrroles. Liu and co-workers²⁴ described an efficient method for the synthesis of polysubstituted pyrroles *via* [4C + 1N] cyclization of 4-acetylenic ketones with primary amines using FeCl₃. Recently Maiti et al. developed a direct synthesis of polysubstituted pyrroles using FeCl₃ as a catalyst under refluxing conditions and very recently Dong et al. synthesized substituted pyrroles using iron-containing metalorganic frameworks (MOFs) as heterogeneous catalysts.²⁵ In view of these above mentioned reports were suffered with severe draw backs. Therefore, we need to explore and development of a mild, efficient and environmentally benign synthetic protocol involving a recyclable organic catalyst in water medium is highly desirable. Earlier our own research group has reported a one-pot three component strategy to access 1,2,3,5-substitued pyrroles catalysed by β-cyclodextrin in water.²⁶ In continuation of our efforts towards the synthesis of polysubstituted pyrroles, we report here in for the first time a facile one pot four component condensation protocol for the synthesis of 1,3,4,5substituted pyrroles in aqueous medium under the supramolecular catalysis using β -cyclodextrin.

Due to the significant development achieved in the field of aqueous organic synthesis and water being inexpensive nontoxic and environmentally benign reaction medium, researchers are viewing organic reactions from different perspective with new additions to the already existing synthetic strategies by the invention of useful additives to water to enhance the substrate solubility to carry forward the reaction.

Results and discussion

Cyclodextrins are cyclic oligosaccharides possessing hydrophobic cavities. They are torus-like macro rings consisting of six (α -CD), seven (β -CD), and eight (γ -CD) 1,4-linked α -D-glucopyranose units. Cyclodextrins and modified cyclodextrins have attracted much attention as aqueous based hosts for inclusion complex phenomenon with a wide variety of guest molecules. Inclusion complex formation occurs as a result of non-covalent bond interaction between hydrophobic cavity of CD and hydrophobic guest molecules. In continuation of our ongoing research program involving cyclodextrins,²⁷ as reusable organic supramolecular catalysts, for the synthesis of a library of hetero cyclic derivatives, the present one pot four component synthesis of polyfunctionalized pyrroles, mediated by cyclodextrins through host guest complexation phenomenon is reported, for the first time (Scheme 1).



Scheme 1 Synthesis of polyfunctionalized pyrroles mediated by $\beta\text{-}$ cyclodextrin.

In our initial study towards the development of the present method, benzaldehvde (1.0 mmol) was taken, in preheated aqueous solution of β -cyclodextrin (1.0 mmol), to which nitromethane (1.0 mL), aniline (1.5 mmol), and acetylacetone (1.0 mmol) were added successively at 70-80 °C and stirred for 8 h. Work up of the reaction medium resulted in polyfunctionalized pyrrole in excellent yield (90%) (Table 2, entry 1). Although, we optimized different kinds of supramolecular catalysts were carried out by this present methodology such as α -cyclodextrin, β -cyclodextrin, γ -cyclodextrin, 2-hydroxy propyl- β -cyclodextrin and methyl- β -cyclodextrin. Of these cyclodextrins (Table 1), β -CD and y-CD were found to be superior mediators and both gave moderate to excellent yield of the desired product. As β cyclodextrin was inexpensive and readily available when compared to γ -cyclodextrin. Therefore, β -cyclodextrin was selected as a better choice. On the other hand, we examined the progress of the four-component reaction in presence of sodium dodecyl sulphate (SDS), PEG-400 and water. When SDS was used as an additive the reaction resulted in corresponding polyfunctionalized pyrrole in only 20% yield whereas in case of PEG-400 or water alone as reaction medium, the reaction did not afford the desired product.

After having optimized the reaction conditions the scope of this reaction has been extended to study the reactivity of a variety of substituted aldehydes fixing aniline, acetylacetone and nitromethane as common reactants. It was observed that the substitution pattern on aldehyde component played crucial role in governing the product yield. Aldehyde with electron donating substituent increases the product yield (Table 2, entry 5) whereas electron withdrawing substituents decrease the product yield (Table 2, entry 14) due to electronic factors

Table 1 Optimization of different catalysts on this methodology^a $\operatorname{Yield}^{b}(\%)$ Entry Catalyst γ-Cyclodextrin 1 66 2 α-Cyclodextrin 10 3 β-Cyclodextrin 90 2-Hydroxy propyl-β-cyclodextrin 29 4 5 Methyl-\beta-cyclodextrin 30 Sodium dodecyl sulphate 6 207 PEG-400 n.r' Water n.r^c

^{*a*} All reactions were carried out using benzaldehyde (1.0 mmol), aniline (1.5 mmol), and acetylacetone (1.0 mmol) with nitromethane (1.0 mL). ^{*b*} Yield obtained after column chromatography. ^{*c*} n.r = no reaction.

Table 2 Synthesis of functionalized pyrroles with various aromatic aldehydes using $\beta\text{-cyclodextrin}$ in water^a



 a Reaction conditions: aldehyde (1.0 mmol), nitromethane (1.0 mL), amine (1.5 mmol), acetyl acetone (1.0 mmol) and β -CD (1.0 mmol) at 70–80 °C.

associated with the functionality. Sterically demanding aldehydes hamper the reaction and gave lesser yields (Table 2, entries 6, 11, 13, 15). Hetero-aromatic aldehydes such as furfuraldehyde (Table 2, entry 18), thiophene-2-carbaxaldehyde and propionaldehyde (Table 2, entry 17 & 19) reacted well to afford corresponding products in encouraging yields in case of heteroaromatic aldehydes and gave lower yield in case of aliphatic aldehyde.

We further examined the reaction with several substituted amines. In general all the reactions proceeded well with various substituted and unsubstituted amines and results were presented in Table 3. Here we also determined the electronic factors associated with substituents on amine component played a significant role in governing the product yield. It is Table 3 Synthesis of functionalized pyrroles with several aromatic amines using β -cyclodextrin in water^{*a*}



 a Reaction conditions: aldehyde (1.0 mmol), nitromethane (1.0 mL), amine (1.5 mmol), acetyl acetone (1.0 mmol) and β -CD (1.0 mmol) at 70–80 °C.

observed that aromatic amines with electron donating groups such as p-methoxy aniline (Table 3, entry 1), p-toluidine (Table 3, entry 2) reacted effectively and gave corresponding products in excellent yields, whereas electron withdrawing aromatic amines such as p-NO₂ aniline (Table 3, entry 7) gave lower product yield. Above all the optimized reaction conditions worked well with aliphatic amine (Table 3, entry 10). Further the present protocol was evaluated with different benzyl amines also and the investigation revealed that benzylamines reacted interestingly to afford corresponding pyrroles in moderate to excellent yields (Table 4). The reaction of unsubstituted benzylamine with benzaldehyde, acetylacetone and nitromethane yielded the corresponding N-benzylpyrrole in excellent yield (Table 4, entry 1). When experiments were conducted with simple benzyl amine as a common reactant with different substituted aldehydes (Table 4, entries 2, 3, 4, 5), it was observed that substitution pattern of aldehyde component has a clear influence on the overall product yield. In the case of reaction with five membered heteroaromatic aldehydes, the reaction proceeded satisfactorily to obtain corresponding products in moderate yields (Table 4, entries 6, 7). When we carried out the reaction with ethylacetoacetate an unsymmetrical 1,3-dicarbonylcompound, the reaction yielded only one product which was characterized and compared with reported literature.28

Table 4 Synthesis of functionalized pyrroles with various benzyl amines using β -cyclodextrin in water^{*a*}



 a Reaction conditions: aldehyde (1.0 mmol), nitromethane (1.0 mL), amine (1.5 mmol), acetyl acetone (1.0 mmol) and β -CD (1.0 mmol) at 70–80 °C.

All the products were characterized by ¹H & ¹³C NMR, IR and mass spectrometry. The catalytic efficiency of β -cyclodextrin was established by conducting the reaction in water alone without any additive, in which case product formation was not observed even after prolonged reaction times, highlighting the significant role of β -cyclodextrin as a promoter in carrying out the reaction forward. This was further established by the formation of β -CD–aldehyde inclusion complex when β -CD and aldehyde were warmed in water in 1 : 1 ratio. Comparative study of ¹H NMR spectra of both aldehyde and β -CD–aldehyde inclusion complex, recorded in DMSO-d₆ clearly indicated that there was an up field shift of H-3 (0.02 ppm) and H-5 (0.02 ppm) due to the



Fig. 2 Plausible mechanistic pathway.



Fig. 3 Recyclability of β -CD using benzaldehyde, nitromethane, aniline and acetyl acetone in water at 70–80 °C (Table 2, entry 1).

incorporation of guest molecule in to the hydrophobic cavity of β -cyclodextrin.²⁹ We conclude that the hydrophobic environment of β -CD facilitated the reaction by forming β -CD-aldehyde inclusion complex, which reacts with nitromethane to form nitrostyrene, which inturn reacts *via* Michael addition reaction with *in situ* generated β -ketoenamine (B), followed by oxidative aromatization affording the corresponding polyfunctionalized pyrroles as shown in the Fig. 2. After completion of the reaction, the reaction medium and reused further four-cycles with same substrates (Table 2, entry 1) as we observed that the desired product yield was slightly decreased after three to fourth cycle as shown in Fig. 3.

Conclusion

In conclusion, we have accomplished an efficient, environfriendly one-pot four-component condensation protocol for the synthesis of polyfunctionalized pyrroles using β -cyclodextrin as a promoter in aqueous medium. In addition, we have prepared many pyrrole motifs using different aromatic aldehydes, aromatic amines, and benzyl amines *via* a fourcomponent reaction in β -CD under aqueous medium. The present strategy was an inexpensive useful addition to synthetic organic chemistry, and utilizes the readily available starting materials to access a wide variety of highly substituted pyrroles with little effort.

Experimental section

General procedure for the synthesis of polyfunctionalized pyrrole derivatives

 β -Cyclodextrin (1.0 mmol, 1.135 g) was dissolved in water (15 mL) at 70 °C and to this clear solution, aldehyde (1.0 mmol), nitromethane (1.0 mL) followed by aromatic amine (1.5 mmol) and acetyl acetone (1.0 mmol) after which the reaction mixture was heated at 70–80 °C until completion of the reaction as indicated by TLC. The reaction mixture was cooled to the room temperature and β -CD was filtered, the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with water, saturated brine solution and dried over

anhydrous Na_2SO_4 . The combined organic layers were evaporated under reduced pressure and the resulting crude product was purified by column chromatography by using ethyl acetate and hexane (1:9) as eluent to give corresponding polyfunctionalized pyrrole.

1-(2-Methyl-1,4-diphenyl-1*H*-pyrrol-3-yl)ethanone (Table 2, entry 1). Light brown solid, mp 106–109 °C. IR (KBr) 3060, 2923, 1642, 1495, 1400, 1226 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS) δ = 7.30–7.34 (m, 3H), 7.37–7.50 (m, 7H), 6.67 (s, 1H), 2.41 (s, 3H), 2.07 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃, TMS) δ 12.8, 30.9, 114.5, 120.5, 122.4, 126.1, 126.3, 126.7, 128.0, 128.1, 128.8, 129.2, 135.2, 135.9, 138.6, 197.5 ppm; HRMS: *m/z* calcd for C₁₉H₁₇NONa 298.1207; found 298.1200.

1-(2-Methyl-1-phenyl-4-*p***-tolyl-1***H***-pyrrol-3-yl)ethanone (Table 2, entry 2). Brown oil. IR (KBr) 3022, 2924, 1644, 1495, 1410, 1224 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS) \delta = 7.41–7.50 (m, 3H), 7.32 (d,** *J* **= 7.7 Hz, 2H), 7.24–7.26 (m, 2H), 7.18 (d,** *J* **= 7.7 Hz, 2H), 6.63 (s, 1H), 2.38 (s, 6H), 2.07 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃, TMS) \delta 12.9, 29.7, 31.1, 110.8, 120.6, 122.4, 125.0, 126.2, 128.2, 128.4, 129.3, 130.4, 132.8, 134.5, 135.5, 138.6, 196.9 ppm; HRMS:** *m/z* **calcd for C₂₀H₂₀NO (M + 1) 290.1544; found 290.1548.**

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