Multicomponent Approach Towards the Synthesis of Substituted Pyrroles under Supramolecular Catalysis Using β-Cyclodextrin as a Catalyst in Water Under Neutral Conditions

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Synthesis of substituted pyrroles in H_2O by using β-cyclodextrin as a supramolecular catalyst is described. This reaction has several advantages over existing methods and provides substituted pyrroles in good-to-excellent yields (79–89%). The supramolecular catalysis of the reaction was studied using ^{1}H-NMR spectroscopy. β-Cyclodextrin can be recovered and reused several times without loss of activity.

Introduction. – Multicomponent reactions (MCRs) are excellent strategies, being employed in the synthesis of many natural products. These MCRs are generally defined as reactions where more than two starting materials react to form a product, incorporating more or less all the atoms of the starting materials. Unlike the usual stepwise formation of individual bonds in a target molecule, in MCRs the formation of several bonds occurs in one single step. MCRs are convergent, in analogy to the convergent synthesis and in contrast to a divergent multistep synthesis. These reactions are classified into various ways based on the number of components involved in the reaction or their intrinsic variability [1]. The MCRs offer a wide range of advantages such as a single-step procedure, avoiding complicated purification processes and saving both solvents and reagents. The MCRs have attracted considerable interest owing to their exceptional synthetic efficiency. Recently, there has been tremendous development in three- and four-component reactions [2].

The pyrrole ring is widely distributed in many natural and biologically important molecules such as porphyrins, coenzymes, and alkaloids [3]. There has been an enhanced interest in the synthesis of pyrrole and its oligomers due to their potential application as conducting materials [4]. Although there are numerous routes reported for the synthesis of pyrroles [3d][5], most of them involve multistep synthetic operations, which lower the overall yields and reduce the use of expensive transition metal catalysts [6] in combination with organic solvents. Recently, a few one-step procedures [7] have been reported for the synthesis of pyrroles. However, these reports are far from satisfactory with regard to the reaction parameters such as costly transition metal catalysts, longer reaction times, and halogenated solvents, which are a threat to the environment. In view of these shortcomings, there is a need to develop a mild and ecofriendly synthetic methodology for the synthesis of pyrroles by replacing organic solvents, most of which are toxic, flammable, or carcinogenic by H_2O, and by using a

recyclable catalyst as a part of green chemistry approach. H_2O is a naturally occurring, cheap, and non-toxic ecofriendly solvent. In continuation of our efforts towards β-cyclodextrin-mediated biomimetic approaches [8], we report herein for the first time the versatile synthesis of substituted pyrroles from readily available building blocks in aqueous medium under supramolecular catalysis.

Cyclodextrins (CDs) and substituted cyclodextrins are cyclic oligosaccharides possessing hydrophobic cavities, which bind substrates selectively and catalyze chemical reactions with high selectivity. They catalyze reactions by supramolecular catalysis involving reversible formation of host–guest complexes by non-covalent bonding as seen in enzymes. These attractive features of CDs prompted us to carry out the synthesis of pyrrole derivatives (*Table 1*) from phenacyl bromide (=2-bromo-1-phenylethanone; **1**), pentane-2,4-dione (**2**), and amines in H_2O in presence of β-CD, as this is the most useful synthetic methodology involving MCRs in H_2O medium.

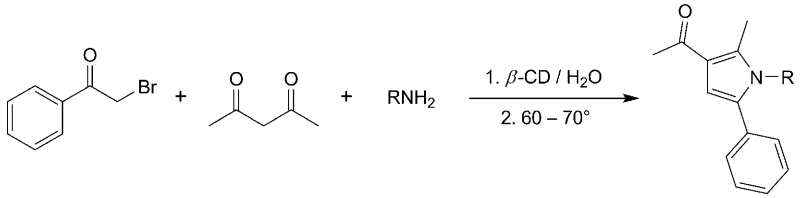
Results and Discussions. – In general, the reactions were carried out by *in situ* formation of the β-CD complex of phenacyl bromide (**1**) in H_2O at 50°, followed by the addition of pentane-2,4-dione (**2**) and amine **3**, stirring at 60–70°, giving the substituted pyrroles **4** as products in excellent yields (*Table 1*), as confirmed by ^{1}H- and ^{13}C-NMR, ESI-MS, and elemental analysis. However, the generality of the three-component reaction was checked by a model reaction done in *PEG-400* under catalyst-free conditions without using any base at 120°, and the reaction was sluggish. When 0.1 equiv. of bases like Cs_2CO_3, K_2CO_3, and Na_2CO_3 were used, product formation was observed in low yields.

It was found that aromatic amines with electron-donating groups in *p*-position gave excellent yields as shown in *Table 1* (*Entries 2* and *4*), whereas electron-withdrawing groups in *p*-position gave relatively lower yields. In case of aliphatic amines, the yields were lower, as shown in *Table 1* (*Entries 11* and *12*). This may be due to the electronic factors of substituents.

In this synthesis, the role of β-cyclodextrin appears to be to activate phenacyl bromide through H-bonding interactions, thereby promoting the reaction with pentane-2,4-dione and completing the reaction sequence with an amine. In the absence of β-CD, a reaction did not take place. β-CD can be recovered and reused. A plausible β-CD/phenacyl bromide complex was suggested by us as shown in *Fig. 1*, which was further supported by the isolation and characterization studies on β-CD/phenacyl bromide inclusion complex. ^{1}H-NMR of the inclusion complex indicated the upfield shift of H–C(3) and H–C(5) of β-CD, as shown in *Fig. 2* and *Table 2*. The inclusion complex was prepared by taking β-cyclodextrin and phenacyl bromide in equal amounts.

Conclusions. – We have demonstrated for the first time that substituted pyrroles can be synthesized with readily available starting materials by using β-cyclodextrin as a catalyst, in H_2O as the reaction medium. This novel environmentally friendly methodology following the green-chemistry approach may find a wide range of applications.

Table 1. *Synthesis of Substituted Pyrroles by β-Cyclodextrin as a Catalyst*



1 **2** **3** **4**

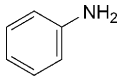
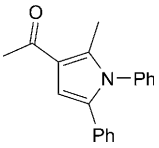
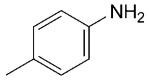
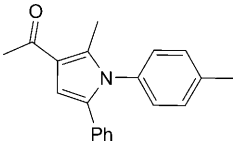
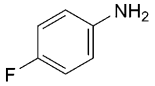
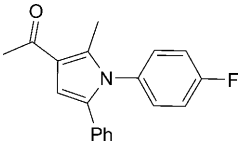
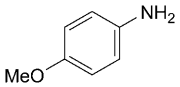
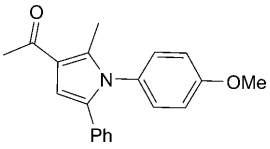
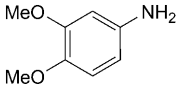
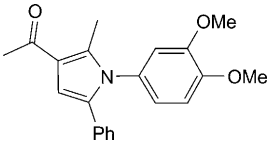
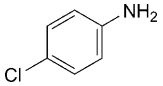
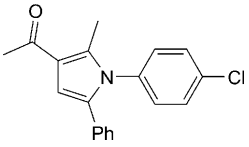
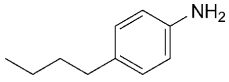
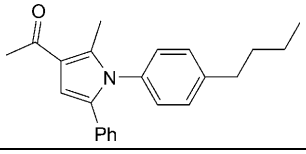
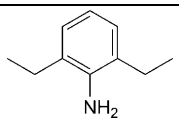
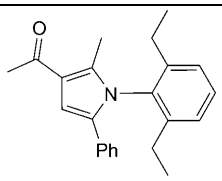
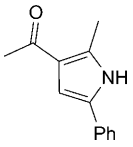
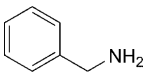
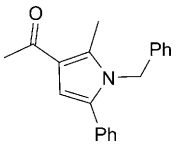
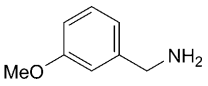
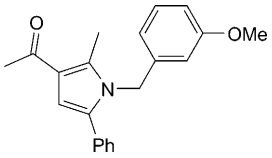
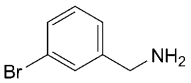
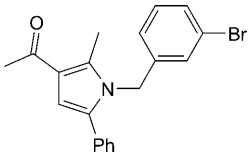
Entry	Amine **3**	Product **4**	Reaction time [h]	Yield [%][a])
1			8	86
2			7.5	88
3			8.5	84
4			7	89
5			8.5	87
6			7.5	83
7			8	85

Table 1 (cont.)

Entry	Amine **3**	Product **4**	Reaction time [h]	Yield [%][a])
8			8	85
9	NH_4OAc[b])		7.5	80
10			8.5	79
11			8.5	78
12			8.5	80

[a]) Yields after isolation after CC. [b]) 5 equiv. of NH_4OAc.

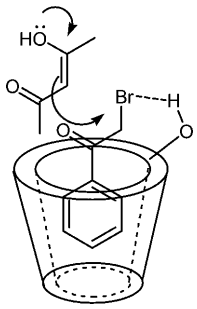


Fig. 1. *A plausible β-CD–phenacyl bromide complex for the mechanistic pathway of the reaction in the β-cyclodextrin cavity*

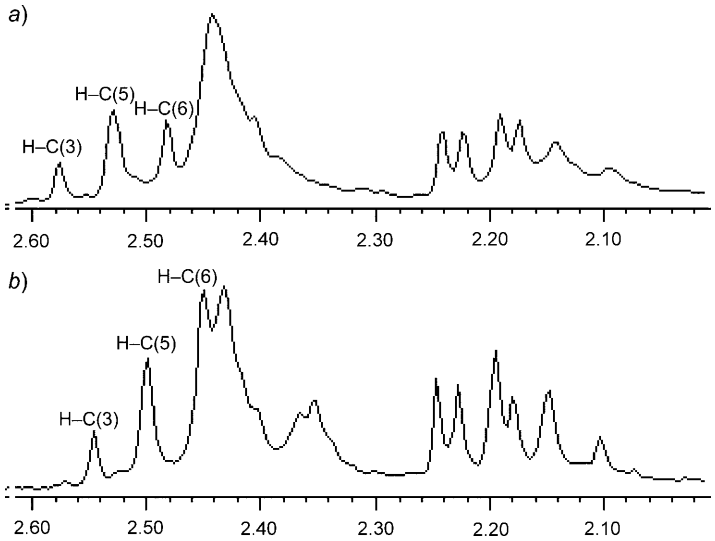


Fig. 2. *^{1}H-NMR Spectra of* a) *β-CD and* b) *β-CD/phenacyl bromide inclusion complex*

Table 2. *^{1}H-NMR Chemical Shifts of H–C(3) and H–C(5) in Native β-CD and β-CD–Phenacyl Bromide Inclusion Complex*[a])

H-atoms	β-CD	β-CD–phenacyl bromide complex	Δδ
H–C(3)	514.14	509.05	5.09
H–C(5)	499.31	489.78	9.53

[a]) Chemical shifts are expressed in Hz.

We thank *CSIR*, New Delhi, India, for fellowships to *S. N. M.* and *B. M.*, and *UGC* for a fellowship to *V. K. A.*

Experimental Part

General. All reactions were carried out without any special precautions in an atmosphere of air. Chemicals were purchased from *Fluka* and *S. D. Fine Chemicals* and used for the syntheses. TLC: precoated silica gel plates (*60 F_{254}*, 0.2 mm layer; *E. Merck*). M.p.: *Fischer–Johns* melting-point apparatus; uncorrected. ^{1}H-NMR Spectra: *Varian 200* or *Bruker 300* spectrometers; in $CDCl_3$; δ in ppm, *J* in Hz. MS: *VG Autospec*; in *m/z*.

General Procedure for the Synthesis of Substituted Pyrroles Using β-Cyclodextrin as a Catalyst. β-Cyclodextrin (1 mmol) was dissolved in H_2O (20 ml). To this clear soln., phenacyl bromide (**1**; 1.0 mmol) was added and stirred for 10 min, and then pentane-2,4-dione (**2**; 3.0 mmol) followed by amine **3** (1.0 mmol) were added, after which the mixture was heated at 60–70° until completion of the reaction, as indicated by TLC. The mixture was extracted with AcOEt (3 × 10 ml). The org. layers were washed with H_2O and sat. brine soln., and dried (Na_2SO_4). The combined org. layers were evaporated under reduced pressure, and the resulting crude product was purified by column chromatography (CC) with AcOEt/hexane 3:7 as eluent. The aq. layer was cooled to 5° to recover β-CD by filtration.

*Preparation of the β-CD–*Phenacyl Bromide Inclusion Complex. β-CD (1 mmol) was dissolved in H_2O (15 ml) by warming at 60° to get clear soln., and then phenacyl bromide (**1**; 1 mmol) was added, and the mixture was allowed to stirr for 30 min at 60° and then cooled to r.t. Then it was further cooled over night in a refrigerator. The obtained solid was filtered, dried, and analyzed by ^{1}H-NMR spectroscopy. The characterization data for all the isolated compounds are given below.

*1-(2-Methyl-1,5-diphenyl-1*H*-pyrrol-3-yl)ethanone* (**4a**; *Table 1*, *Entry 1*). Light yellow oil. IR: 2923, 1654, 1501, 1405, 1223. ^{1}H-NMR (300 MHz): 7.51–7.31 (*m*, 10 H); 6.67 (*s*, 1 H); 2.41 (*s*, 3 H); 2.08 (*s*, 3 H).^{13}C-NMR (75 MHz): 12.5; 31.1; 120.5; 126.2; 126.8; 128.0; 128.2; 129.3; 135.2; 135.9; 138.7; 197.6. ESI-MS: 298 ($[M+Na]^+$). Anal. calc. for $C_{19}H_{17}NO$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.90, H 6.15, N 5.11.

*1-[2-Methyl-1-(4-methylphenyl)-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4b**; *Table 1*, *Entry 2*). Light yellow oil. IR: 2922, 1654, 1517, 1407, 1223. ^{1}H-NMR (300 MHz): 7.29–7.24 (*m*, 5 H); 7.16 (*q*, *J* = 9.82, 4 H); 6.53 (*s*, 1 H); 2.37 (*s*, 3 H); 2.32 (*s*, 3 H); 1.97 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.7; 21.0; 30.8; 95.9; 120.3; 125.8; 126.5; 128.0; 129.1; 129.6; 135.1; 136.1; 137.7; 196.6. ESI-MS: 290 ($[M+1]^+$). Anal. calc. for $C_{20}H_{19}NO$ (289.37): C 83.01, H 6.62, N 4.84; found: C 83.07, H 6.65, N 4.87.

*1-[1-(4-Fluorophenyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4c**; *Table 1*, *Entry 3*). Yellow oil. IR: 2923, 1653, 1508, 1407, 1217, 759. ^{1}H-NMR (300 MHz): 7.38–7.34 (*m*, 5 H); 7.33 (*d*, *J* = 4.9, 2 H); 7.30 (*d*, *J* = 4.9, 2 H); 6.63 (*s*, 1 H); 2.38 (*s*, 3 H); 2.07 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.7; 31.0; 116.1; 116.4; 122.5; 126.3; 127.9; 128.0; 128.3; 129.2; 134.7; 135.3; 135.8; 160.4; 197.6. ESI-MS: 316 ($[M+Na]^+$). Anal. calc. for $C_{19}H_{16}FNO$ (293.33): C 77.80, H 5.50, N 4.77; found: C 77.82, H 5.48, N 4.79.

*1-[1-(4-Methoxyphenyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4d**; *Table 1*, *Entry 4*). Oil. IR: 2924, 1652, 1511, 1249. ^{1}H-NMR (300 MHz): 7.37 (*d*, *J* = 4.7, 2 H); 7.33–7.22 (*m*, 3 H); 7.23 (*d*, *J* = 8.8, 2 H); 6.97 (*d*, *J* = 8.8, 2 H); 6.62 (*s*, 1 H); 3.85 (*s*, 3 H); 2.38 (*s*, 3 H); 2.07 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.7; 31.0; 55.4; 96.0; 114.3; 120.7; 122.1; 126.0; 127.3; 128.1; 129.2; 131.5; 135.5; 136.0; 159.2; 197.3. EI-MS: 328 ($[M+Na]^+$). Anal. calc. for $C_{20}H_{19}NO_2$ (305.37): C 78.66, H 6.27, N 4.59; found: C 78.65, H 6.32, N 4.60.

*1-[1-(3,4-Dimethoxyphenyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4e**; *Table 1*, *Entry 5*). Yellow oil. IR: 2928, 1658, 1511, 1415, 1225. ^{1}H-NMR (300 MHz): 7.62–7.21 (*m*, 8 H); 6.63 (*s*, 1 H); 3.78 (*s*, 6 H); 2.37 (*s*, 3 H); 2.02 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.5; 31.2; 55.8; 101.0; 114.3; 120.7; 126.6; 127.6; 128.5; 129.0; 131.5; 133.8; 135.5; 139.7; 159.1; 197.5. ESI-MS: 336 ($[M+H]^+$). Anal. calc. for $C_{21}H_{21}NO_3$ (335.40): C 75.20, H 6.31, N 4.18; found: C 75.24, H 6.33, N 4.17.

*1-[1-(4-Chlorophenyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4f**; *Table 1*, *Entry 6*). Light brown oil. IR: 2924, 1651, 1510, 1401, 1219. ^{1}H-NMR (300 MHz): 7.36–7.32 (*m*, 5 H); 7.31 (*d*, *J* = 4.7, 2 H); 7.32 (*d*, *J* = 4.8, 2 H); 6.65 (*s*, 1 H); 2.36 (*s*, 3 H); 2.04 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.6; 31.2; 116.0; 116.5; 122.1; 126.3; 127.8; 128.3; 128.6; 129.2; 133.7; 135.3; 135.6; 161.4; 197.9. ESI-MS: 311 ($[M+H]^+$). Anal. calc. for $C_{19}H_{16}ClNO$ (309.79): C 73.66, H 5.21, N 4.52; found: C 73.68, H 5.26, N 4.49.

*1-[1-(4-Butylphenyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4g**; *Table 1*, *Entry 7*). Brown oil. IR: 2926, 1655, 1514, 1246. ^{1}H-NMR (300 MHz): 7.96 (*dd*, *J* = 6.7, 2 H); 7.64–7.40 (*m*, 7 H); 6.69 (*s*, 1 H); 2.48 (*s*, *t*, *J* = 6.0, 5 H); 2.24 (*s*, 3 H); 1.55–1.41 (*m*, 2 H); 1.33–1.23 (*m*, 2 H); 0.91 (*t*, *J* = 7.5, 3 H). ^{13}C-NMR (300 MHz): 12.5; 17.8; 25.4; 30.9; 33.8; 36.2; 108.2; 120.9; 126.8; 127.3; 128.5; 129.1; 132.5; 133.5; 136.6; 198.3. ESI-MS: 332 ($[M+H]^+$). Anal. calc. for $C_{23}H_{25}NO$ (331.45): C 83.34, H 7.60, N 4.23; found: C 83.36, H 7.63, N 4.21.

*1-[1-(2,6-Diethylphenyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4h**; *Table 1*, *Entry 8*). Oil. IR: 2925, 1651, 1520, 1407, 1223. ^{1}H-NMR (300 MHz): 7.35–6.87 (*m*, 8 H); 6.67 (*s*, 1 H); 2.57–2.31 (*m*, 7 H); 2.13 (*s*, 3 H); 1.20–1.09 (*m*, 3 H); 0.99 (*t*, *J* = 7.5, 3 H).^{13}C-NMR (300 MHz): 12.8; 19.8; 27.6; 31.3; 114.3; 120.7; 123.1; 126.0; 126.6; 127.7; 128.1; 129.2; 131.5; 135.2; 136.2; 158.6; 197.8. ESI-MS: 332 ($[M+H]^+$). Anal. calc. for $C_{23}H_{25}NO$ (331.45): C 83.34, H 7.60, N 4.23; found: C 83.36, H 7.63, N 4.21.

*1-(2-Methyl-5-phenyl-1*H*-pyrrol-3-yl)ethanone* (**4i**; *Table 1*, *Entry 9*). Light yellow oil. IR: 3291, 2926, 1655, 1514, 1246. ^{1}H-NMR (300 MHz): 7.50–7.26 (*m*, 5 H); 6.65 (*s*, 1 H); 5.23 (br. *s*, 1 H); 2.44 (*s*, 3 H); 2.05 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.2; 31.3; 118.4; 120.5; 127.2; 129.3; 133.2; 135.9; 138.7; 197.8. ESI-MS: 222 ($[M+Na]^+$). Anal. calc. for $C_{13}H_{13}NO$ (199.25): C 78.36, H 6.58, N 7.03; found: C 78.37, H 6.61, N 7.06.

*1-(1-Benzyl-2-methyl-5-phenyl-1*H*-pyrrol-3-yl)ethanone* (**4j**; *Table 1*, *Entry 10*). Yellow oil. IR: 2923, 1654, 1511, 1244. ^{1}H-NMR (300 MHz): 7.43 – 7.12 (*m*, 10 H); 6.69 (*s*, 1 H); 5.23 (*s*, 2 H); 2.38 (*s*, 3 H); 2.14 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.9; 31.2; 61.3; 118.2; 126.4; 128.7; 132.4; 136.3; 138.7; 149.3; 198.9. ESI-MS: 290 ($[M + H]^+$). Anal. calc. for $C_{20}H_{19}NO$ (289.37): C 83.01, H 6.62, N 4.84; found: C 83.04, H 6.66, N 4.80.

*1-[1-(3-Methoxybenzyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4k**; *Table 1*, *Entry 11*). Brown oil. IR: 2923, 1651, 1514, 1241. ^{1}H-NMR (300 MHz): 7.48 (*d*, $J = 6.8$, 2 H); 7.34 – 7.09 (*m*, 7 H); 6.67 (*s*, 1 H); 5.21 (*s*, 2 H); 3.78 (*s*, 3 H); 2.36 (*s*, 3 H); 2.12 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.7; 31.1; 56.2; 61.1; 118.2; 120.2; 124.6; 126.4; 128.7; 134.3; 136.4; 145.3; 163.5; 198.6. ESI-MS: 320 ($[M + H]^+$). Anal. calc. for $C_{21}H_{21}NO_2$ (319.40): C 78.97, H 6.63, N 4.39; found: C 78.94, H 6.62, N 4.40.

*1-[1-(3-Bromobenzyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl]ethanone* (**4l**; *Table 1*, *Entry 12*). Yellow oil. IR: 2922, 1658, 1516, 1238. ^{1}H-NMR (300 MHz): 7.46 – 7.11 (*m*, 9 H); 6.67 (*s*, 1 H); 5.24 (*s*, 2 H); 2.37 (*s*, 3 H); 2.11 (*s*, 3 H). ^{13}C-NMR (300 MHz): 12.7; 31.0; 61.2; 118.4; 124.3; 127.4; 128.7; 133.6; 136.3; 138.7; 149.4; 198.7. ESI-MS: 369 ($[M + H]^+$). Anal. calc. for $C_{20}H_{18}BrNO$ (368.27): C 65.23, H 4.93, N 3.80; found: C 65.26, H 4.96, N 3.79.

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