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Biomimetic synthesis of quinoxalines in water

B. Madhav, S. Narayana Murthy, V. Prakash Reddy, K. Rama Rao, Y. V. D. Nageswar *

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500 607, India

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ABSTRACT

Various quinoxalines have been synthesized for the first time in the presence of β-cyclodextrin in water. Biomimetic catalysis of β-cyclodextrin is explained by using ^{1}H NMR spectroscopy.

Quinoxalines and their derivatives are very important class of nitrogen containing heterocycles, having various biological activities such as anti-viral, anti-bacterial, anti-biotic, anti-inflammatory and kinase inhibition.[1] They are potential building blocks for the synthesis of organic semiconductors,[2] electroluminescent material,[3] cavitands,[4] dehydroannulenes,[5] and dyes.[6] Quinoxalines serve as useful rigid subunits in macrocyclic receptors[7] for molecular recognition and chemically controllable switches.[8]

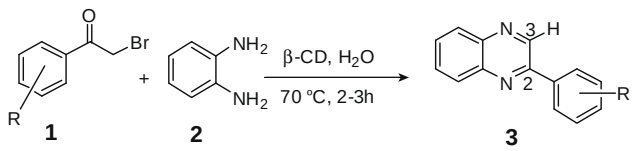
Consequently many methods have been developed for the synthesis of quinoxaline derivatives, which include condensation of 1,2-diamines and 1,2-dicarbonyl compounds,[9] oxidative cyclization of α-hydroxy ketones with 1,2-diamines,[10] oxidative coupling of epoxides with ene-1,2-diamines,[11] 1,4-addition of 1,2-diamines to diazenylbutenes,[12] cyclization-oxidation of phenacyl bromides with 1,2-diamines by $HClO_4{\cdot}SiO_2$[13] and by using solid phase synthesis.[14]

In comparison with broad spectrum utility of quinoxalines in many fields, their preparation methods are limited in number. However, these established procedures suffered from many drawbacks such as drastic reaction conditions, expensive reagents and complicated work-up. Therefore, there is a clear need for the development of generally applicable and environmentally benign mild methodology for the synthesis of quinoxaline derivatives. In continuation of our interest in the use of cyclodextrins as mild and efficient biomimetic catalysts in promoting various transformations,[15] we have been attempting the synthesis of biologically important class of heterocycles. We report herein the preparation of quinoxalines (**3**) from phenacyl bromides (**1**) and benzene-1,2-diamine (**2**) in water, using β-cyclodextrin (β-CD) as a catalyst.

Cyclodextrins (CDs) 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. We describe, herein, the remarkable catalytic activity of β-cyclodextrin in the reaction of benzene-1,2-diamines towards a variety of phenacyl bromides, to give exclusively substituted quinoxalines (Scheme 1).

In general, a model reaction was carried out by the addition of benzene-1,2-diamine with β-CD complex of phenacyl bromide, formed in water at 50 °C, and by stirring the reaction mixture at 70 °C to give the corresponding quinoxaline.[17] Similarly a variety of phenacyl bromides were reacted with benzene-1,2-diamine in the presence of β-CD at 70 °C resulting in the corresponding quinoxalines in quantitative yields (87–92%). This method is equally effective with phenacyl bromides bearing electron-withdrawing and electron-donating substituents in the aromatic ring (Table 2). All these reactions have proceeded efficiently and produced high yields without the formation of any side products. This is because of the activation of phenacyl bromide by the complexation with β-cyclodextrin. All the products were isolated and characterized by ^{1}H NMR, ^{13}C NMR, mass and by comparison with the known compounds. β-CD can also be recovered and reused.

The reaction also takes place without β-CD but longer reaction times (48 h) are required and the isolated yields of the products



Scheme 1. Biomimetic synthesis of quinoxalines in water.

Table 1
Catalyst optimization study

Entry	Catalyst (%)	Time (h)	Yield (%)
1	0	48	25
2	10	40	35
3	20	30	40
4	50	12	62
5	70	6	74
6	100	2	90

* Corresponding author. Tel.: +91 40 27191654; fax: +91 40 27160512.
E-mail address: dryvdnageswar@gmail.com (Y.V.D. Nageswar).

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Table 2
Synthesis of quinoxalines in the presence of β-CD in water[a]

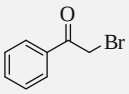
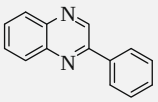
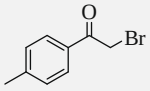
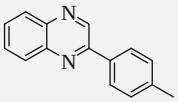
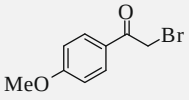
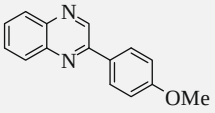
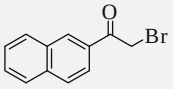
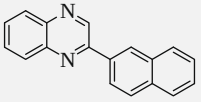
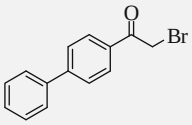
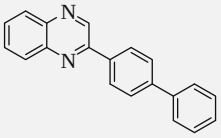
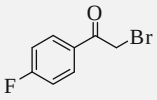
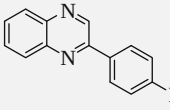
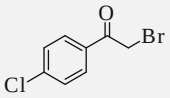
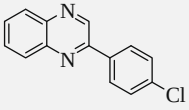
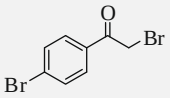
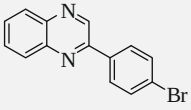
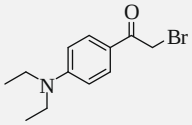
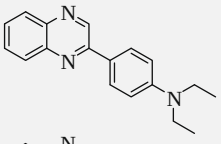
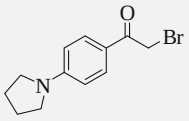
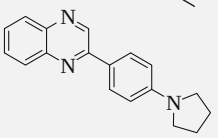
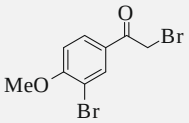
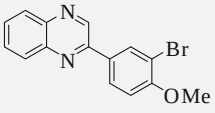
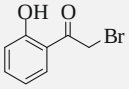
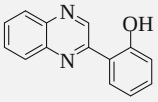
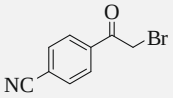
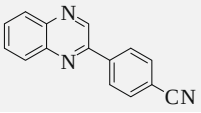
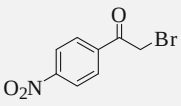
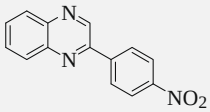
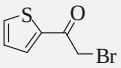
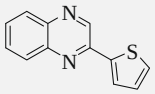
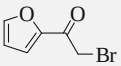
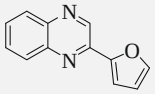
Entry	Substrate	Product	Time (h)	Yield[b] (%)
1			2.0	90
2			2.4	87
3			2.0	92
4			2.2	91
5			2.3	89
6			2.4	89
7			2.3	90
8			2.2	90
9			2.1	92
10			2.2	87
11			2.4	89
12			2.0	90
13			2.4	90

Table 2 (*continued*)

Entry	Substrate	Product	Time (h)	Yield[b] (%)
14			2.5	83
15			2.3	91
16			2.3	87

[a] Reaction conditions: phenacyl bromide (1 equiv), benzene-1,2-diamine (1 equiv), β-CD (1 equiv) and water (15 mL).
[b] Yields of the isolated products.

obtained are very low (~25%). The catalytic amount of β-CD (0.1 equiv) had no impact on the reaction. Increasing the amount of β-CD at 70 °C has improved the yield of the product gradually. These experiments (Table 1) indicate the substantial role of cyclodextrin. To prove the role of cyclodextrin, NMR studies were carried out on β-CD, β-CD complex of phenacylbromide (**1**) and freeze-dried reaction mixture.

Here, β-CD appears to be involved in activating the phenacyl bromide by forming host-guest complex and promotes the reaction. The complexation of phenacyl bromide with β-CD was confirmed by isolation of β-CD–phenacyl bromide complex and study of ^{1}H NMR. NMR spectroscopy is one of the most important techniques used for characterization of inclusion complexes. The formation of inclusion complex results in the shift changes in the resonances of the protons of host cyclodextrin and the guest.[16] A comparison of the ^{1}H NMR spectra (D_2O) of β-CD, β-CD:phenacyl bromide (**1**) complex and freeze-dried reaction mixture of β-CD:phenacyl bromide (**1**) complex with the benzene-1,2-diamine at 1 h was studied (Fig. 1). It is observed from Figure 1 that there is an upfield shift of H_3 (0.041 ppm) and H_5 (0.055 ppm) protons of cyclodextrin in the β-CD:phenacyl bromide (**1**) complex as compared to β-CD, indicating the formation of an inclusion complex of phenacyl bromide (**1**) with β-CD from the secondary side of cyclodextrin. In this biomimetic synthesis of quinoxalines,[18] β-cyclodextrin plays a significant role by forming an inclusion complex with phenacyl bromide from the secondary side and activating the molecule to undergo cyclocondensation with benzene-1,2-diamine as shown in Figure 2.

In conclusion, we have presented an elegant and simple methodology for the synthesis of quinoxaline derivatives from benzene-1,2-diamine and phenacyl bromides in the presence of β-cyclodextrin in water. This straightforward methodology may find wide spread applications in organic and medicinal chemistry.

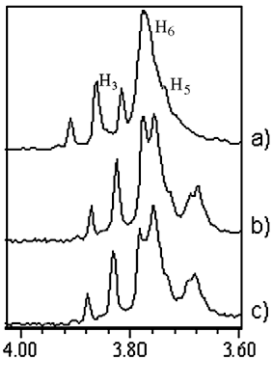


Figure 1. ^{1}H NMR Spectra (200 MHz, D_2O) of (a) β-CD, (b) β-CD:phenacyl bromide (**1**) complex and (c) the freeze-dried reaction mixture after 1 h.

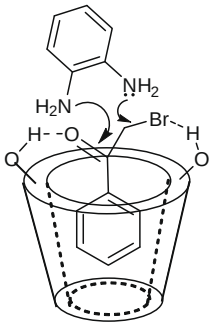


Figure 2. Plausible mechanistic pathway.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.033.

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17. *General Procedure for the synthesis of quinoxalines. Typical example: 2-phenylquinoxaline* (Table 2, entry 1): β-CD (1.135 g, 1 mmol) was dissolved in water (15 mL) by warming to 50 °C until a clear solution was formed. Then, phenacyl bromide (0.198 g, 1 mmol) dissolved in methanol (2 mL) was added dropwise followed by benzene-1,2-diamine (0.108 g, 1 mmol) and the mixture was stirred at 70 °C until the reaction was complete (as monitored by TLC) (Table 2). The mixture was extracted with ethyl acetate, and the extract was filtered. The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the resulting product 2-phenylquinoxaline was further purified by column chromatography. The aqueous layer was cooled to 5 °C to recover β-CD by filtration. Bright yellow solid; yield 0.185 g, (90%); mp 75–78 °C; R_f (20% EtOAc/*n*-hexane) 0.5; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.52–7.61 (m, 3H, ArH), 7.73–7.83 (m, 2H, ArH), 8.13–8.22 (m, 4H, ArH), 9.33 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.3, 129.0, 129.1, 129.5, 129.6, 130.1, 130.2, 136.7, 141.5, 142.2, 143.3, 151.7; MS (ESI): *m*/*z* 207 $(M+H)^+$.
18. *Data for the representative examples of synthesized compounds:*
2-(Naphthalen-2-yl)quinoxaline (Table 2, entry 4): Solid; yield 91%; dark yellow solid; mp 135 °C; R_f (20% EtOAc/*n*-hexane) 0.45; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.51–7.56 (m, 2H, ArH), 7.69–8.19 (m, 7H, ArH), 8.36–8.41 (m, 1H, ArH), 8.65(s, 1H, ArH), 9.50(s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.1, 127.8, 127.9, 128.8, 128.9, 129.5, 129.7, 130.5, 135.3, 140.1, 140.2, 140.8, 141.0, 142.3, 142.7, 143.0, 151.0; MS (ESI): *m*/*z* 257 $(M+H)^+$.
2-(Biphenyl)quinoxaline (Table 2, entry 5): Pale yellow solid; yield 89%; mp 130–131 °C; R_f (20% EtOAc/*n*-hexane) 0.46; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35–7.54 (m, 3H, ArH), 7.70–7.82 (m, 6H, ArH), 8.11–8.30 (m, 4H, ArH), 9.38 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$ ppm) δ 127.1, 127.8, 127.9, 128.8, 128.9, 129.5, 129.7, 130.5, 135.3, 140.1, 141.0, 142.3, 142.7, 143.0, 151.4; MS (ESI): *m*/*z* 283 $(M+H)^+$.
2-(4-Bromophenyl)quinoxaline (Table 2, entry 8): Pale yellow solid, 90%, mp 138 °C; R_f (20% EtOAc/*n*-hexane) 0.48; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.64–7.85 (m, 4H, ArH), 8.03–8.2 (m, 4H, ArH), 9.32 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.0, 129.0, 129.6, 129.9, 130.5, 132.4, 135.5, 141.4, 142.2, 142.6, 150.6; MS (ESI): *m*/*z* 285 $(M+H)^+$.
N,N-Diethyl-4-(quinoxalin-2-yl)benzenamine (Table 2, entry 9): Dark yellow solid; yield 92%; mp 82–85 °C; R_f (20% EtOAc/*n*-hexane) 0.45; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.17–1.22 (m, 6H, CH_3), 3.34–3.44 (m, 4H, CH_2), 6.4–6.8 (m, 2H, ArH), 7.6–7.8 (m, 2H, ArH), 7.99–8.10 (m, 4H, ArH), 9.28 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.0, 12.0, 43.8, 44.3, 110, 111.3, 111.6, 111.7, 128.2, 128.8, 128.9, 129.0, 129.05, 129.8, 130.8, 140.7, 142.5, 143; MS (ESI): *m*/*z* 278 $(M+H)^+$.
2-(4-(Pyrrolidin-1-yl) phenyl)quinoxaline (Table 2, entry 10): Yellow solid; yield 87%; mp 180–185 °C; R_f (20% EtOAc/*n*-hexane) 0.4; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.05 (m, 4H, $2CH_2$), 3.39 (m, 4H, $2CH_2$), 6.69 (d, J = 8.68 Hz, 2H, ArH), 7.62–7.79 (m, 2H, ArH), 8.03–8.27 (m, 4H, ArH), 9.28 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.4, 47.7, 110.6, 112.3, 127.9, 128.3, 128.8, 129.3, 130.4, 130.6, 140.4, 140.5, 140.6, 140.7, 143.3, 149.6, 150.8; MS (ESI): *m*/*z* 276 $(M+H)^+$.
2-(3-Bromo-4-methoxyphenyl)quinoxaline (Table 2, entry 11): Pale yellow solid; yield 89%; mp 95–100 °C; R_f (20% EtOAc/*n*-hexane) 0.4; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.85 (s, 3H, OCH_3), 6.98–7.14 (m, 2H, ArH), 7.80–8.02 (m, 2H, ArH), 8.20–8.28 (m, 3H, ArH), 9.25 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 114.5, 128.9, 129.0, 129.3, 130.2, 141.0, 142.2, 142.9, 151.3, 161.5; MS (ESI): *m*/*z* 315 $(M+H)^+$.
2-(Quinoxalin-2-yl)phenol (Table 2, entry 12): Pale yellow solid; yield 90%; mp 200–205 °C; R_f (20% EtOAc/*n*-hexane) 0.37; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.96–7.17 (m, 2H, ArH), 7.36–7.45 (m, 1H, ArH), 7.70–7.88 (m, 2H, ArH), 7.96–8.22 (m, 3H, ArH), 9.5 (s, 1H, C_3–H), 10.2 (brs, 1H, OH). ^{13}C (75 MHz, $CDCl_3$) δ 117.2, 118.8, 119.6, 126.7, 127.6, 129.0, 129.8, 131.2, 133.0, 138.4, 140.2, 142.2, 152.2, 160.9; MS (ESI): *m*/*z* 223 $(M+H)^+$.
4-(Quinoxalin-2-yl)benzonitrile (Table 2, entry 13): Pale yellow solid; yield 90%; mp 193–195 °C; R_f (20% EtOAc/*n*-hexane) 0.28; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82–7.88 (m, 4H, ArH), 8.13–8.20 (m, 2H, ArH), 8.33–8.36 (d, J = 8.309, 2H, ArH), 9.35 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.8, 118.4, 127.5, 128.0, 129.0, 129.8, 130.7, 130.9, 132.9, 140.6, 141.6, 142.3, 142.3, 149.6; MS (ESI): *m*/*z* 232 $(M+H)^+$.
2-(4-Nitrophenyl)quinoxaline (Table 2, entry 14): Pale yellow solid; yield 83%; mp 185–190 °C; R_f (20% EtOAc/*n*-hexane) 0.2; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82–7.86 (m, 2H, ArH), 8.16–8.21 (m, 2H, ArH), 8.4 (s, 4H, ArH), 9.4 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.3, 128.0, 128.2, 130.3, 130.9, 140.0, 152.3, 160.0; MS (ESI): *m*/*z* 252 $(M+H)^+$.
2-(Thiophen-2-yl)quinoxaline (Table 2, entry 15): Pale yellow solid; yield 91%; mp 130–135 °C; R_f (20% EtOAc/*n*-hexane) 0.48; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.17 (d, J = 4.53, 1H, thiophene H), 7.52 (d, J = 4.53, 1H, thiophene H), 7.65–7.75 (m, 2H, ArH), 7.84 (d, J = 3.02, 1H, thiophene H), 8.09 (d, J = 8.309, 2H, ArH), 9.2 (s, 1H, C_3–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.4, 127.0, 126.4, 127.0, 128.5, 128.5, 129.0, 129.0, 129.3, 130.0, 130.5, 141.0, 141.8, 142.1; MS (ESI): *m*/*z* 213 $(M+H)^+$.
2-(Furan-2-yl)quinoxaline (Table 2, entry 16): Solid; yield 87%; mp 95–98 °C; R_f (20% EtOAc/*n*-hexane) 0.45 L; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.58–6.59 (m, 1H, ArH), 7.28 (d, J = 3.5 Hz, 1H, Furan H), 7.65–7.7 (m, 3H, ArH), 8.0–8.08 (m, 2H, Furan H), 9.5 (s, 1H, C_3–H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.2, 112.8, 129.5, 129.6, 130.8, 141.6, 142.4, 142.4, 144.2, 145.4, 151.3; MS (ESI): *m*/*z* 197 $(M+H)^+$.