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Brönsted acid hydrotrope combined catalyst for environmentally benign synthesis of quinoxalines and pyrido[2,3-*b*]pyrazines in aqueous medium

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ABSTRACT

A new Brönsted acid hydrotrope combined catalyst (BAHC) has been developed and applied in acid catalyzed synthesis of pyrido[2,3-*b*]pyrazines and quinoxalines in an aqueous medium at ambient temperature with excellent yields. Interestingly, the catalyst can be easily recovered after the reactions and reused. Furthermore, BAHC catalyst worked well and avoids the use of organic solvents. We have reported herein the synthetic pathway which has less disastrous effect in the atmosphere and human survival.

Annulated pyrazines, such as quinoxaline and pteridine derivatives are very important nitrogen-containing heterocycles found in biological systems and are widely used as pharmaceuticals.[1] The quinoxaline anticancer drugs CQS (chloroquinoxaline sulfonamide) and XK469 were both found to have activity against solid tumors. (2-Quinoxalinyloxy)phenoxypropanoic acid derivatives, such as Assure® are well documented as herbicides and are used to control annual and perennial grass weeds in broadleaf crops (Fig. 1).[2] It is noteworthy that, by virtue of their thermal stability, intense luminescence, and other desirable properties, they have been widely used in organic semiconductors and electroluminescent materials.[3]

Generally, pyrido[2,3-*b*]pyrazines and quinoxalines are synthesized by the condensation of aryl 1,2-diamines with 1,2-dicarbonyl compounds in MeOH/AcOH[4] and also by several modified procedures using β-cyclodextrin (β-CD),[5] ionic liquids,[6] molecular iodine,[7] heteropolyacid,[8] cellulose sulfuric acid,[9] TiO_2,[10] hypervalent iodine(III) sulfonate in PEG,[11] polyaniline-sulfate salt,[12] DABCO,[13] CAN,[14] $HClO_4$–SiO_2,[15] and MnO_2.[16] Although some of these methods afford good to high yields of the corresponding quinoxalines, many of them suffer from various disadvantages such as use of strong acids, high temperatures, long reaction times, moisture sensitivity as well as high cost, and toxicity of the reagents.

Organic reactions in aqueous media have attracted increasing interest offering many practical and economical advantages. From a viewpoint of ecological advantage and greenness of water, it is desirable to use water as a reaction solvent since it is safe, harmless, and environmentally benign.[17] However, the limited aqueous solubility of organic compounds poses a unique problem. The low solubility of organic reactants in water can often be overcome by using hydrotropes which are the class of compounds, though amphiphilic in character, have hydrophobic regions and thus differ from classical surfactants; yet they display substantial ability to solubilize, non-polar compounds in water.[18] The self aggregation of hydrotropes has been considered to be a prerequisite for a huge number of applications in various fields such as drug solubilization, separation sciences, and nanocarriers for poorly soluble drugs.[19] There is also growing interest for the use of hydrotropes as a reaction media in organic synthesis.[20] The key focus of the use of

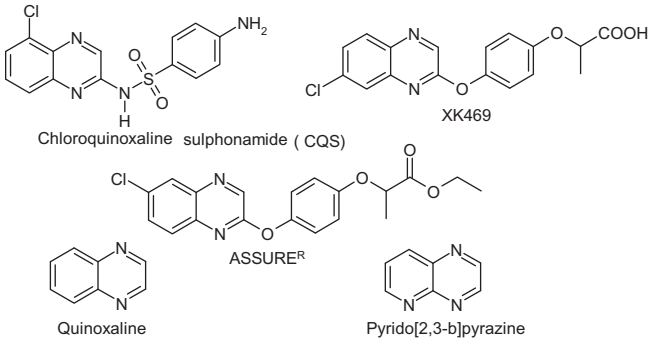

Figure 1. Pyrido[2,3-*b*]pyrazine and quinoxaline bicyclic heterocycles.

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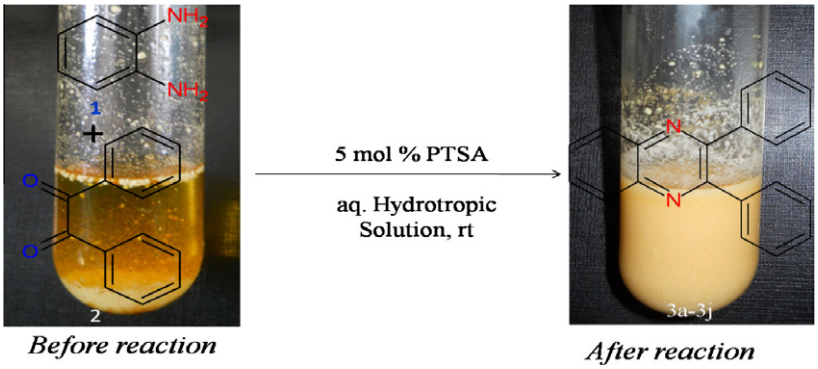
hydrotropes as a reaction media depends on the nature of hydrotrope used and its minimum hydrotropic concentration (MHC) above which there is maximum solubility of reactants. As hydrotropes increase the solubility of compounds in many fold excess, this effect is attributed to a direct interaction between the reactants which are practically insoluble in water. Secondly, the product precipitates on dilution with water from hydrotropic solution, which leads to the product formation in crystalline form with an improved purity, and the mother liquor can be used to concentrate the hydrotrope for recycling. This technique avoids the use of highly inflammable and expensive organic solvents that are normally used in organic synthesis. These interactive properties of hydrotropes and our ongoing efforts in the development of newer methods for organic synthesis,[21] rendered us to explore the use of the Brönsted acid hydrotrope combined catalyst for the synthesis of medicinally important pyrido[2,3-*b*]pyrazines and quinoxalines in aqueous medium.

In order to optimize the reaction conditions, initially, the condensation of *o*-phenylene diamine **1** and benzil **2** was studied as a model reaction at room temperature (Scheme 1).

In the absence of any catalyst the product **3a** was produced in water with very low yield after 10 h (Table 1, entry 1), but, on addition of a catalytic amount (5 mol %) of *p*-toluene sulfonic acid (PTSA) the yield increased to 70% in 3 h (Table 1, entry 2). On the other hand, the hydrotrope aided acid catalysis was studied in the model reaction using PTSA as Brönsted acid catalyst in aqueous NaPTS (sodium *p*-toluene sulfonate) solution as a hydrotrope. The reaction which proceeded sluggishly in the aqueous NaPTS (5 mL, 20% w/v) solution (Table 1, entry 3), showed a remarkable enhancement of the reactivity when the reaction was carried out in the presence of 5 mol % PTSA combined with aqueous NaPTS (5 mL, 20% w/v) solution, and the corresponding product was obtained in 90% within 20 min (Table 1, entry 4). On the completion of reaction as monitored by TLC, the reaction mixture was diluted with cold water and product was separated out (Scheme 1). The filtration of reaction mixture afforded the corresponding product of high purity.[23] From these observations, it was revealed that most of the substrates and catalyst molecules were concentrated in the hydrophobic reaction environment and enabled the rapid organic reaction in water.

With these results in hand, we have determined the hydrotropic concentration for maximum solubilization of the reactants in water to give maximum yield of the product. Thus the model reaction was carried out with various concentrations (% w/v) of NaPTS in water at ambient temperature. By changing the concentration, a dramatic effect on the conversion rate of quinoxaline was observed. As shown in Table 1, a linear relationship was observed with concentration. The yield of the product was highest at 40% of hydrotropic concentration since this concentration was suitable for the maximum solubilization of organic compounds (Table 1, entry 7). On the other hand, further increase in concentration resulted in a decrease in the product yield due to decreased solubility of substrates in solution (Table 1, entry 8).

After the optimization of hydrotropic concentration, various hydrotropes such as, NaXS (sodium xylene sulfonate) and NaBS (sodium benzene sulfonate) were used for model reaction with 5 mol % PTSA. Results revealed that PTSA is more active when combined with NaPTS as compared to NaXS and NaBS (Table 1, entries 7, 9, and 10). The higher activity of NaPTS was rationalized on the basis of an overall planar structure of hydrophobic and hydrophilic regions giving rise to self associated configuration, offering a good micro-environment of lower polarity and stabilizes the reactants through a cooperative mechanism.[18]



Scheme 1. Synthesis of quinoxalines in aqueous hydrotropic solution.

Table 1
Screening of various reaction conditions for the synthesis of quinoxalines[a]

Entry	Hydrotrope	Hydrotrope concentration (% w/v)	Catalyst (mol %)	Time (min)	Yield[b] (%)
1	H_2O	—	—	10 h	Trace
2	H_2O	—	5	3.0 h	70
3	NaPTS	20	—	1.5 h	82
4	NaPTS	20	5	20	90
5	NaPTS	10	5	30	80
6	NaPTS	30	5	15	92
7	NaPTS	40	5	7	96
8	NaPTS	50	5	15	90
9	NaXS	40	5	10	93
10	NaBS	40	5	12	89

[a] Reaction conditions: Benzil (1.0 mmol), *o*-phenylenediamine (1.0 mmol), PTSA (5 mol %), aqueous hydrotropic solution (5 mL), RT.
[b] Isolated yields.

Table 2
Synthesis of quinoxaline and pyrido[2,3-*b*]pyrazine derivatives in BAHC[a]

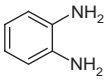
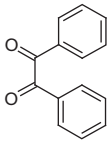
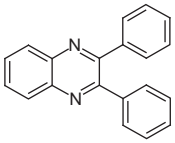
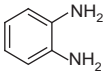
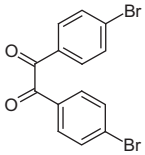
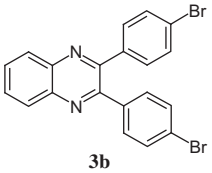
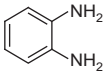
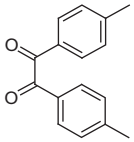
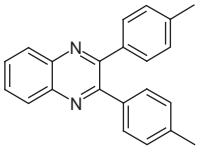
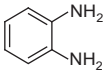
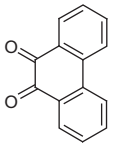
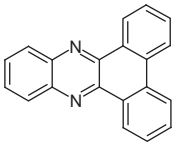
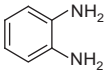
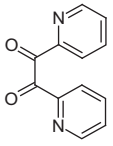
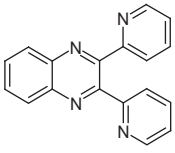
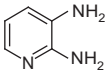
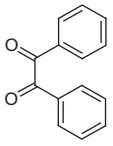
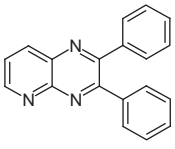
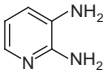
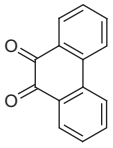
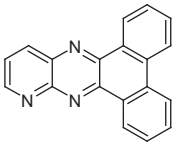
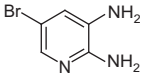
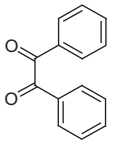
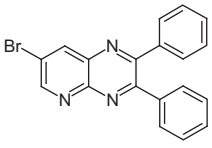
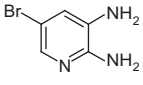
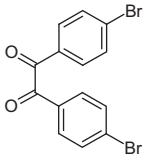
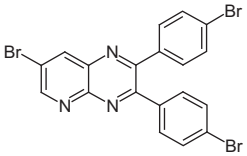
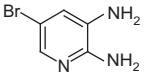
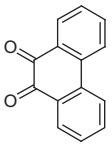
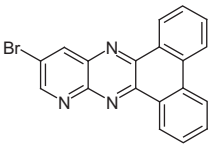
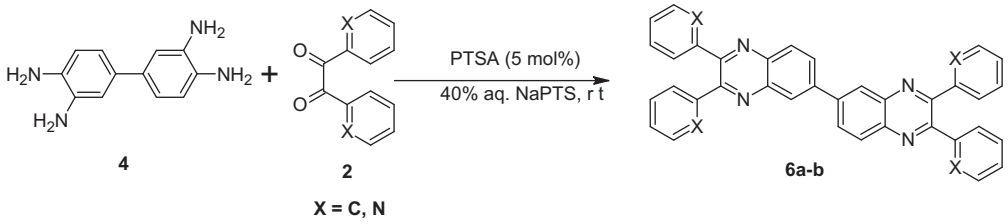
Entry	1,2-Diamine	1,2-Diketone	Product[b]	Time (min)	Yield[c] (%)
1			 **3a**	7	96
2			 **3b**	20	91
3			 **3c**	10	91
4			 **3d**	7	93
5			 **3e**	15	92
6			 **3f**	25	80
7			 **3g**	25	86
8			 **3h**	15	92
9			 **3i**	25	92

Table 2 (*continued*)

Entry	1,2-Diamine	1,2-Diketone	Product[b]	Time (min)	Yield[c] (%)
10			 **3j**	10	93

[a] Reaction conditions: Diketone (1.0 mmol), diamine (1.0 mmol), PTSA (5 mol %), 40% aq NaPTS (5 mL), RT.
[b] All products were analyzed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.
[c] Isolated yields.



Scheme 2. Synthesis of quinoxalines 2,3,2′,3′-tetra aryl[6,6′]biquinoxalinyl in BAHC.

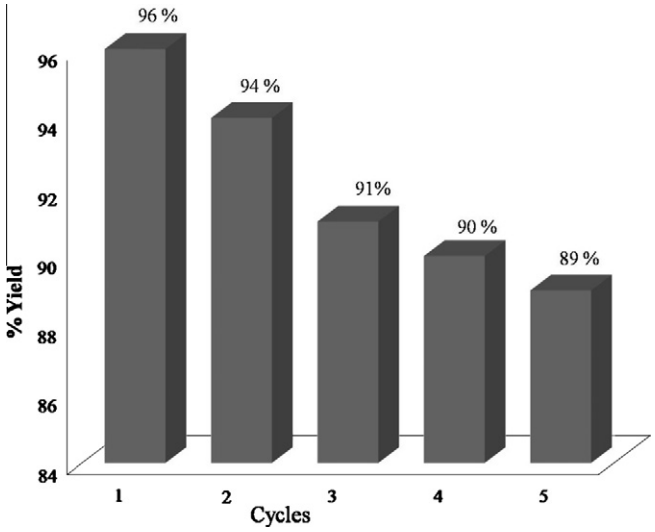


Figure 2. Recyclability of BAHC.

After the selection of an appropriate hydrotrope and optimized conditions, a series of diketones were treated with various 1,2-diamines in 40% aqueous NaPTS solution at ambient temperature with 5 mol % PTSA (Table 2). The reactions proceeded at room temperature within a short time to afford the desired products in excellent yields.[23]

Next, we have extended this protocol for the tetra amines such as 3,3′,4,4′-tetraamino-1,1′-biphenyl **4**. It underwent condensation with diketones **2** in the presence of 5 mol % PTSA in 40% aq NaPTS (5 mL) affording the sterically hindered product 2,3,2′,3′-tetra aryl[6,6′]biquinoxalinyl **6a–b** in 83% and 81% yields, respectively in 20 min (Scheme 2).

Another striking feature of BAHC catalyst was easy recovery from the reaction mixture. As PTSA and hydrotrope are more soluble in water than in organic solvents, almost 100% of BAHC was quite easily recovered from the aqueous solution after the reaction was completed. The reaction mixture was quenched with water and the precipitated product was simply separated by filtration. The BAHC was in the aqueous layer, and only removal of water gave the catalyst which could be used in the next reaction. To assess the reusability of BAHC, recycling experiments were carried out with *o*-phenylenediamine and benzil as substrates over the four reaction cycles. After each experiment, the aqueous solution of BAHC was recovered by filtration, washed thoroughly with diethyl ether, concentrated and then subjected to a new run with fresh reactants under identical reaction conditions. The results shown in Figure 2 indicated that BAHC could be reused for at least five runs with a modest change in yield of the product.

The plausible mechanism of the product formation is conceptualized in Figure 3.[22] The water molecules hydrate the hydrotrope head groups decreasing the electrostatic interaction between these groups. The two head groups move apart and displace the water molecules interacting hydrophobic chains. This may be the driving force for two hydrophobic chains to interact and force the diamine to interact with diketone which is activated by acid. The eliminated water molecules then get easily absorbed by the hydrophilic head groups. As a result, of the overall effect there is a rate enhancement of the reaction.

In conclusion, we have presented a simple, efficient, and green protocol for the synthesis of quinoxaline and pyrido[2,3-*b*]pyrazine derivatives in a novel Brönsted acid hydrotrope combined catalysts (BAHC) in water at ambient temperature. The merits of the present method are easy work-up, faster reactions, and satisfactory yields which avoids hazardous organic solvents and toxic catalysts. The BAHC could be reused for at least five runs with a modest change in the product yield.

Acknowledgments

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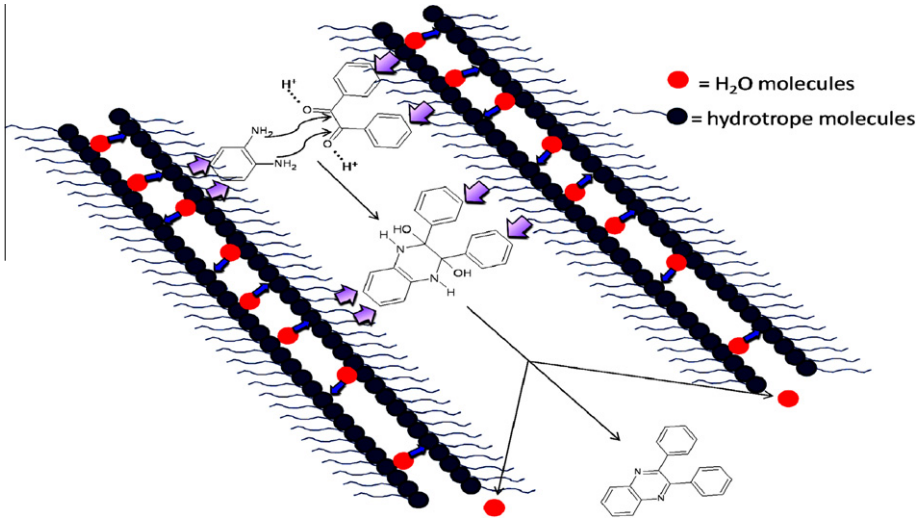

Figure 3. Conceptual picture of quinoxaline formation.

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23. *General procedure for the synthesis of quinoxaline and pyrido[2,3-b]pyrazine*: In a small Schlenk tube, 1,2-diamine (1 mmol), 1,2-diketone (1 mmol), PTSA (5 mol %), and 40% aq NaPTS (5 ml) were taken and the reaction mixture was stirred at room temperature. The reaction process was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was diluted with water (20 mL). The filtrate was washed with water and dried affording the corresponding products.
Spectral data of representative compounds: *Compound* ***3d***: Yellow solid; mp 228–229 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.73–7.89 (6H, m), 8.31–8.37 (2H, m), 8.59 (2H, d, J = 8.7 Hz), 9.42 (2H, dd, J = 7.8 Hz, 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 122.93, 126.27, 127.95, 129.44, 129.77, 130.32, 132.06, 142.19, 142.45; MS (ESI): m/z 280; elemental analysis (calcd C = 85.6, H = 4.3, N = 9.9: observed C = 86.0, H = 4.2, N = 9.8).
Compound ***3e***: White solid; mp 178–179 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.21–7.25 (2H, m), 7.80–7.85 (4H, m), 8.00 (2H, d, J = 7.0 Hz), 8.22 (2H, dd, J = 6.6 Hz, 3.3 Hz), 8.34 (2H, d, J = 4.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 122.80, 124.20, 129.40, 130.28, 136.49, 141.14, 148.27, 152.41, 157.53; MS (ESI): m/z 284; elemental analysis (calcd C = 76.0, H = 4.2, N = 19.7: observed C = 76.2, H = 4.3, N = 19.4).
Compound ***3g***: Yellow solid; mp 217–219 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.71–7.85 (5H, m), 8.55 (2H, d, J = 7.8 Hz), 8.67 (1H, dd, J = 8.4 Hz, 1.8 Hz), 9.29–9.36 (2H, m) 9.54 (1H, dd, J = 7.8 Hz, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 123.90, 126.21, 127.32, 129.50, 129.86, 130.82, 132.10, 132.50, 138.13, 145.09, 152.42, 154.31; MS (ESI): m/z 281; elemental analysis (calcd C = 81.1, H = 3.9, N = 15.0: observed C = 81.1, H = 4.0, N = 14.9).
Compound ***3i***: White solid; mp 236–237 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.41–7.45 (2H, m), 7.53–7.56 (6H, m), 8.65 (1H, d, J = 2.4 Hz), 9.18 (1H, d, J = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 121.34, 124.65, 124.91, 131.37, 131.66, 131.72, 131.84, 136.37, 136.64, 139.20, 148.10, 153.80, 154.86, 155.56; MS (ESI): m/z 517; elemental analysis (calcd C = 43.8, H= 2.0, Br = 46.1, N = 8.0. observed C = 43.7, H = 2.1, Br = 46.1, N = 8.1).
Compound ***3j***: White solid; mp 235–238 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.72–7.87 (4H, m), 8.56 (2H, d, J = 8.1 Hz), 8.81–8.83 (1H, m), 9.25–9.29 (2H, m), 9.47 (1H, d, J = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 120.64, 122.97, 123.10, 126.70, 127.31, 128.21, 128.32, 129.29, 129.54, 131.30, 131.47, 132.59, 137.49, 139.49, 144.22, 155.50; MS (ESI): m/z 359; elemental analysis (calcd C = 63.3, H = 2.8, Br = 22.2, N = 11.6: observed, C = 63.5, H = 2.8, Br = 22.2, N = 11.5).
Compound ***6b***: Yellow solid; mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.84–7.90 (4H, m) 8.07–8.10 (4H, m), 8.27–8.38 (8H, m), 8.65 (2H, d, J = 1.8 Hz); MS (ESI): m/z 566; elemental analysis (calcd C = 76.3, H = 3.9, N = 19.8: observed, C = 76.4, H = 3.8, N = 19.7).