

Dicationic Ionic Liquid as the Recyclable Catalyst for the Synthesis of Quinoxaline Derivatives

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ABSTRACT: *An efficient and eco-friendly protocol for the synthesis of quinoxaline derivatives employing a condensation reaction between 1,2-diketone and 1,2-diaminobenzene derivative has been developed. The reaction of 1,2-diketone and 1,2-diaminobenzene derivative was carried out in water at room temperature using 10 mol% of task-specific dicationic ionic liquid as a catalyst. The results show that the reactions catalyzed by the dicationic ionic liquid proceeded smoothly to give the corresponding products. High yields of the products, short reaction times, mild reaction conditions and simple experimental procedure make this protocol complementary to the existing methods. Further, the catalyst can be reused for several times without obvious loss of the catalytic activity.*

KEYWORDS: *Dicationic ionic liquid; Quinoxaline derivatives; Synthesis; Catalyst.*

INTRODUCTION

Quinoxaline and its derivatives are nitrogen-containing heterocyclic compounds displaying a broad spectrum of biological activities which have made them privileged structures in combinatorial drug discovery libraries [1-5]. They constitute the basis of many insecticides, fungicides, herbicides, as well as being important in human health and as receptor antagonists [6,7]. They have also found applications as dyes and building blocks in the synthesis of organic semiconductors, and they also serve as useful rigid subunits in macro cyclic receptors or molecular recognition and chemically controllable switches [8-10].

Many synthetic strategies have been developed for the preparation of quinoxaline derivatives. A variety of metal

reagents such as Pd(OAc)₂ or RuCl₂-(PPh₃)₃-TEMPO [11], MnO₂ [12,13], CuSO₄·5H₂O [14], Zn[(L) proline] in HOAc [15] and propylsulfonic acid functionalized nanozeolite clinoptilolite [16] have been reported as promoters for this preparation. Numerous methods are also available in the literature for the synthesis of quinoxaline derivatives including the Bi-catalyzed oxidative coupling of epoxides and ene-1,2-diamines [17], heteroannulation of nitroketene N,S-arylaminoacetals with POCl₃ [18], a solid -phase synthesis on Synphase TM Lanterns [19], cyclization of α -arylimino oximes of α -dicarbonyl compounds under reflux in acetic anhydride [20], condensation of *o*-phenylene diamines and 1,2-dicarbonyl compounds in MeOH/AcOH under

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microwave irradiation [21], and the molecular iodine-catalyzed cyclocondensation reaction in DMSO and CH₃CN [22,23]. However, the search for the new readily available and green catalysts is still being actively pursued.

Recently, ionic liquids have attracted extensive interest as green media in organic synthesis due to their favorable properties, for example, negligible volatility and high thermal stability. Although ionic liquids were initially introduced as an alternative green reaction medium, today they have marched far beyond this border, showing their significant role in controlling the reaction as catalysts. Brønsted acidic Task-Specific Ionic Liquids (TSILs) are one of the successful examples that ionic liquids used as reaction medium and catalysts in organic synthesis [24-28]. Recently, a novel dicationic acidic ionic liquid as halogen-free TSILs that bear dialkane sulfonic acid groups in acyclic diamine cations (Scheme 1) has been successfully applied to catalyze the Biginelli reaction [29]. The remarkable activity and reusability of this ionic liquid encouraged us to study its utility for the synthesis of quinoxaline derivatives. To the best of our knowledge in the open literature, the synthesis of quinoxaline derivatives catalyzed by the functionalized ionic liquid has not yet been reported. Herein, we have discovered that the dicationic acidic ionic liquid effectively promoted the synthesis of 2,3-disubstituted quinoxalines under relatively mild conditions (scheme 2).

EXPERIMENTAL SECTION

Melting points were determined on a Thomas Hoover capillary apparatus and were uncorrected. The IR spectra were recorded with a Bomem Michelson model 102 FT-IR. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX spectrometer at 500 MHz and 125 MHz, respectively, with CDCl₃ as solvent and TMS as an internal standard. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. Mass spectra were obtained with automated FININIGAN Trace Ultra-Trace DSQ GC/MS spectrometer. All starting chemicals (AR grade) were purchased from commercial suppliers and used without further purification.

The dicationic acidic ionic liquid was prepared according to the reported procedure in the literature [29]. The ionic liquid was identified by ¹H NMR and the resulting datum was compared with literature datum. ¹H NMR(500 MHz, CDCl₃): δ 1.85-1.95(q, 2×2H,

J=7.6Hz, N-C-CH₂-C-SO₃), 2.64(t, 2×2H, *J*=6.9Hz, N-C-CH₂-SO₃), 2.89(s, 4×3H, N-CH₃), 3.24(t, 2×2H, *J*=8.4Hz, N-CH₂-C-C-SO₃), 3.60(s, 4H, N-CH₂-CH₂-N); MS:m/z=556.89(M⁺), 361.07(M⁺-2H₂SO₄, 100).

General experimental procedures

A mixture of 1,2-diketone **1** (10mmol), 1,2-diaminobenzene derivative **2** (10mmol), and the dicationic ionic liquid (10 mol%) in water (25mL) was typically allowed to proceed for a certain time with the vigorous stirring at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the precipitated crude product was collected by filtration and recrystallized from ethanol to afford pure quinoxaline **3**. The filtrate containing dicationic ionic liquid could be reused directly in the next run without further purification. All products were known compounds, which were characterized by IR and ¹H NMR spectra data and their MPs compared with literature reports.

The spectral data for some of the selected representative compounds are given below.

2,3-Diphenyl-quinoxaline (3a)

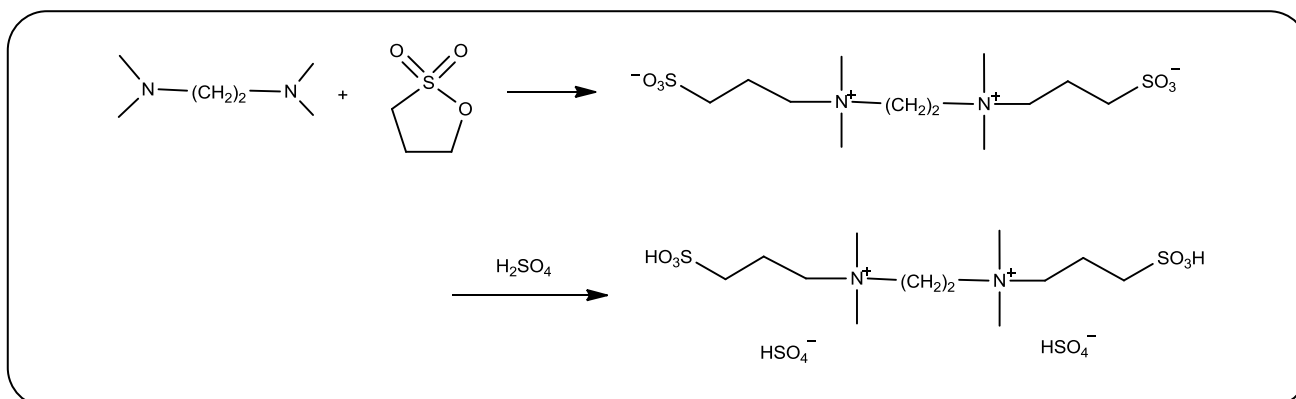
mp 122-124°C; ¹H NMR(500 MHz, CDCl₃): δ 8.21(dd, *J*=6.4, 3.44Hz, 2H), 7.76(dd, *J*=6.4, 3.42Hz, 2H), 7.53-7.56(m, 4H), 7.34-7.37(m, 6H); ¹³C NMR(125 MHz, CDCl₃): δ 153.4, 141.2, 141.2, 139.1, 130.0, 129.9, 129.80, 129.2, 128.8, 128.3, 128.3, 128.2; IR (KBr, cm⁻¹): 3065, 1441, 1395, 1344, 768, 696.

6-Methyl-2,3-diphenyl-quinoxaline (3b)

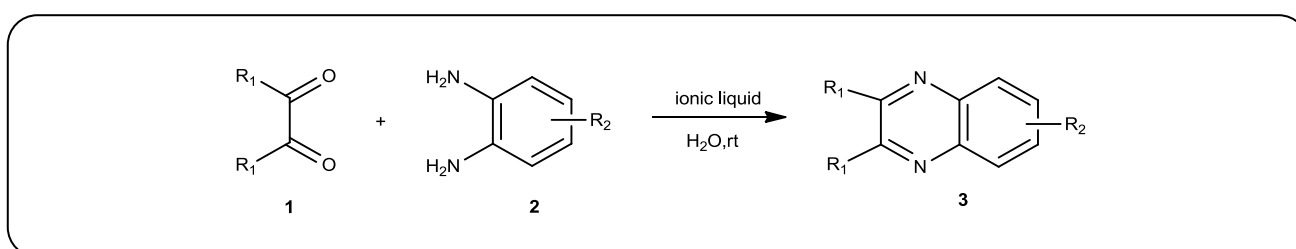
mp 135-137°C; ¹H NMR(500 MHz, CDCl₃): δ 8.07(d, *J*=8.6, 1H), 7.96(s, 1H), 7.53-7.55(m, 5H), 7.33-7.35(m, 6H), 2.63(s, 3H); ¹³C NMR(125 MHz, CDCl₃): δ 153.0, 152.3, 140.1, 139.9, 131.9, 130.6, 129.5, 129.0, 128.9, 128.3, 127.8, 127.6, 127.3, 126.9, 126.5; IR (KBr, cm⁻¹): 3055, 1615, 1488, 1448, 1341, 670.

6-Nitro-2,3-diphenyl-quinoxaline (3c)

mp 185-187°C; ¹H NMR(500 MHz, CDCl₃): δ 9.08(d, *J*=2.4, 1H), 8.53(dd, *J*=9.2, 2.51Hz, 1H), 8.30(d, *J*=9.2Hz, 1H), 7.55-7.57(m, 4H), 7.33-7.38(m, 6H); ¹³C NMR(125 MHz, CDCl₃): δ 143.3, 139.8, 137.9, 137.8, 130.7, 130.7, 130.5, 129.7, 129.6, 129.5, 129.4, 129.3, 128.6, 128.5, 128.2, 127.2, 127.1, 125.4, 124.3, 120.1; IR (KBr, cm⁻¹): 3439, 1614, 1520, 1397, 1340, 699.



Scheme 1: The preparation of dicationic ionic liquid.



Scheme 2: Synthesis of quinoxaline derivatives in the presence of dicationic ionic liquid.

2,3-Bis(4-methoxyphenyl)-quinoxaline (3d)

mp 146-148°C; ¹H NMR(500 MHz, CDCl₃): δ 8.13(dd, *J*=6.3, 3.42Hz, 2H), 7.73(dd, *J*=6.3, 3.40Hz, 2H), 7.50(d, *J*=8.6Hz, 4H), 6.88(d, *J*=8.6Hz, 4H), 3.84(s, 6H); ¹³C NMR(125 MHz, CDCl₃): δ 159.8, 152.7, 140.7, 131.4, 130.9, 129.2, 113.5, 55.0; IR (KBr, cm⁻¹): 2930, 2838, 1605, 1511, 1344, 1293, 1173, 833.

2,3-Bis(4-methoxyphenyl)-6-methylquinoxaline (3e)

mp 121-123°C; ¹H NMR(500 MHz, CDCl₃): δ 8.00(d, *J*=8.2Hz, 1H), 7.90(s, 1H), 7.46~7.56(m, 5H), 6.87(d, *J*=7.4Hz, 4H), 3.83(s, 6H), 2.59(s, 3H); ¹³C NMR(125 MHz, CDCl₃): δ 159.94, 152.8, 152.1, 141.1, 139.9, 131.8, 131.2, 131.1, 128.5, 127.8, 113.7, 55.3; IR (KBr, cm⁻¹): 2925, 2835, 1606, 1343, 1292, 1248, 1175, 833.

2,3-Di-*p*-tolylquinoxaline (3f)

mp 147-148°C; ¹H NMR(500 MHz, CDCl₃): δ 8.14-8.15(m, 2H), 7.73-7.76(m, 2H), 7.44(d, *J*=8.0Hz, 4H), 7.16(d, *J*=7.9, 4H), 2.38(s, 6H); ¹³C NMR(125 MHz, CDCl₃): δ 153.2, 140.8, 138.4, 136.1, 129.4, 129.3, 128.8, 128.6, 21.0; IR (KBr, cm⁻¹): 2914, 1608, 1467, 1397, 1339, 1217, 759.

6-Methyl-2,3-di-*p*-tolylquinoxaline (3g)

mp 134-136°C; ¹H NMR(500 MHz, CDCl₃): δ 8.03(d, *J*=8.5Hz, 1H), 7.92(s, 1H), 7.58(d, *J*=1.8Hz, 1H), 7.41(d, *J*=8.0, 4H), 2.60(s, 3H), 2.36(s, 6H); ¹³C NMR(125 MHz, CDCl₃): δ 153.0, 152.3, 140.9, 139.8, 139.3, 138.3, 138.2, 131.7, 129.4, 128.6, 128.3, 127.6; IR (KBr, cm⁻¹): 3428, 2913, 1611, 1448, 1337, 822.

6-Nitro-2,3-di-*p*-tolylquinoxaline (3h)

mp 168-169°C; ¹H NMR(500 MHz, CDCl₃): δ 9.04(d, *J*=2.3Hz, 1H), 8.49(dd, *J*=9.1, 2.31Hz, 1H), 8.25(d, *J*=9.2Hz, 1H), 7.45-7.49(m, 4H), 7.18(d, *J*=7.9, 4H), 2.39(s, 6H); ¹³C NMR(125 MHz, CDCl₃): δ 156.3, 155.7, 143.5, 140.0, 139.8, 135.4, 130.6, 129.8, 129.7, 129.2, 125.5, 123.0, 21.4; IR (KBr, cm⁻¹): 3428, 2918, 1611, 1523, 1402, 1343, 828.

2,3-Di-(furan-2-yl)quinoxaline (3i)

mp 131-133°C; ¹H NMR(500 MHz, CDCl₃): δ 8.12(dd, *J*=6.3, 3.41Hz, 1H), 7.72(dd, *J*=6.3, 3.41Hz, 1H), 7.61(s, 1H), 6.66(d, *J*=3.3Hz, 1H), 6.55(s, 1H); ¹³C NMR(125 MHz, CDCl₃): δ 150.7, 144.1, 142.5, 130.3, 129.02, 112.9, 111.8; IR (KBr, cm⁻¹): 3103, 1566, 1484, 1397, 1328, 755.

Table 1: Effect of solvent on the reaction. ^a

Entry	solvent	Yield (%) ^b
1	H ₂ O	95
2	C ₂ H ₅ OH	95
3	CH ₃ CN	96
4	CH ₂ Cl ₂	60
5	None	81

^a Reaction conditions: benzil (10 mmol), 1,2-diaminobenzene (10 mmol), dicationic ionic liquid (1.0 mmol), rt, reaction time (15 min).

^b Isolated yield

Table 2: Effect of amount of dicationic ionic liquid on the reaction. ^a

Entry	Catalyst (mmol)	Reaction time (min)	Yield (%) ^b
1	0	12h	0
2	0.2	15	58
3	0.4	15	75
4	0.8	15	90
5	1.0	15	95
6	2.0	15	95
7	4.0	15	93

^a Reaction conditions: benzil (10 mmol), 1,2-diaminobenzene (10 mmol), rt, water as a solvent. ^b Isolated yield

2,3-Di-(furan-2-yl)-6-methylquinoxaline (3j)

mp 112-114°C; ¹H NMR(500 MHz, CDCl₃): δ 8.01(d, J=8.6Hz, 1H), 7.791(s, 1H), 7.56~7.61(m, 3H), 6.55~6.62(m, 4H), 2.58(s, 3H); ¹³C NMR(125 MHz, CDCl₃): δ 150.6, 143.8, 143.7, 140.8, 140.4, 132.4, 128.33, 127.6, 112.5, 112.2, 111.5, 21.6; IR (KBr, cm⁻¹): 3106, 2918, 1485, 1323, 747.

RESULTS AND DISCUSSION

In the initial catalytic activity experiments, different solvents were screened for the reactions. Herein the reaction of benzil and 1,2-diaminobenzene was selected as the model. The results are summarized in Table 1. It was shown that the reaction could proceed effectively in polar organic solvents, for example, ethanol or acetonitrile as solvent (entries 2, 3). The chemical industry is under considerable pressure to replace many of the Volatile Organic Compounds (VOCs) that are currently used as solvents in organic synthesis. The reaction also proceeded under the solvent-free condition to give a yield of 81% (entry 5). The ionic liquid is viscous under the solvent-free

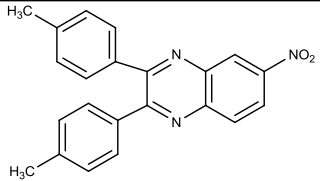
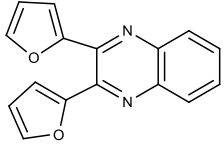
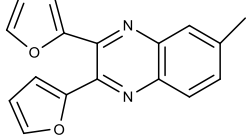
condition and the product need to be washed with water. With “green chemistry” becoming an important issue nowadays, developing the reactions in water and without the use of any harmful organic solvents is desirable. As water is a safe, economical and environmentally benign solvent, it is important to carry out the synthetic reactions in water to give the highest yield of 95% (entry 1) for the environmental and economic reason.

Subsequently, the same reaction of benzil and 1,2-diaminobenzene was employed as the model reaction to screen the effect of the catalytic amount of the dicationic ionic liquid on the reaction (Table 2). The results showed that no desirable product could be detected when the reaction proceeded at room temperature for 12h without any catalyst (entry 1), which indicated that the catalyst should be absolutely necessary for the reaction. With the amount of the ionic liquid increased, a ramp in the yield was clearly observed. The optimum amount of the ionic liquid was 1 mmol (10 mol% based on aniline) (entry 5), and increasing the amount of catalyst beyond this led to no substantial improvement in the yield.

Table 3: The synthesis of quinoxaline derives catalyzed by the dicationic ionic liquid. ^a

Entry	Product	Compound number	Time(min)	Yield (%) ^b
1		3a	15	95
2		3b	15	92
3		3c	20	87
4		3d	20	96
5		3e	20	94
6		3f	20	92
7		3g	20	92

Table 3: The synthesis of quinoxaline derives catalyzed by the dicationic ionic liquid. ^a

8		3h	20	84
9		3i	20	93
10		3j	20	92

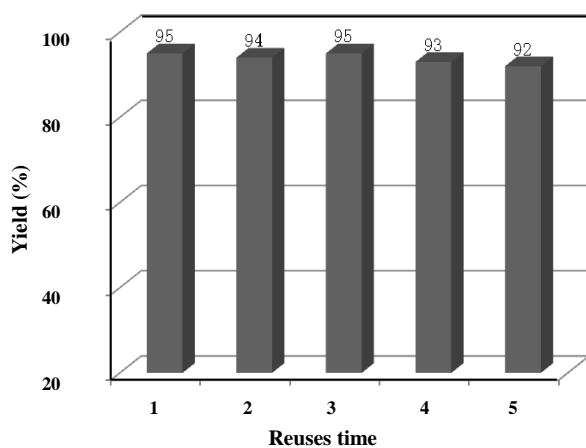


Fig. 1: Reusability of dicationic ionic liquid.

Compare with traditional solvents and catalysts, ionic liquids are easily reused, which is superior to the conventional solvents and catalysts. When optimizing the reaction condition, the recycling performance of the dicationic ionic liquid in the same model reaction was investigated. After the reaction, the products were isolated from the catalytic system by filtration. The filtrate (containing the catalyst) was reused in the next run without further purification. As shown in Fig. 1, the catalyst could be reused at least five times without appreciable decrease in catalytic activity.

The scope and the generality of the present method was then further demonstrated by condensation of various substituted o-phenylene diamines with 1,2-disubstituted 1,2-dicarbonyl compounds using the catalytic amount of

the dicationic ionic liquid at room temperature to give the corresponding 2,3-disubstituted quinoxalines in water. The results are summarized in Table 3. It can be seen that the reactions catalyzed by the dicationic ionic liquid proceeded smoothly to give the corresponding products. Compared to the past method, one additional important feature of the present protocol is the ability to tolerate variation in all components simultaneously.

CONCLUSIONS

In conclusion, we developed a convenient and efficient procedure for the synthesis of quinoxaline derivatives from the various 1,2-diketones and 1,2-diamines using the dicationic ionic liquid as a recyclable catalyst. High yields of the products, short reaction times, mild reaction conditions and simple experimental procedure make this protocol complementary to the existing methods. Further, the catalyst can be reused without obvious loss of the catalytic activity.

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