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Sulfonated Organic Salts: Recyclable Green Catalysts for the Facile and Rapid Route Synthesis of 2,3-Dissubstituted Quinoxaline Derivatives in Water

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Abstract: In this paper, we introduce Brønsted acidic ionic liquid (BAIL), (4-sulfobutyl) tris (4-sulfophenyl) phosphonium hydrogen sulfate as a green and efficient catalyst for the synthesis of 2,3-disubstituted quinoxaline derivatives via the one-pot condensation reaction of various *o*-phenylenediamine with 1,2-diketone derivatives. At all experiments, the desired products were synthesized successfully. The described novel synthesis method proposes several advantages of safety, mild condition, short reaction times, high yields, simplicity and easy workup compared to the traditional method of synthesis.

Key words: Ionic liquid · 2,3-Disubstituted quinoxaline · *o*-Phenylenediamine · 1,2-Diketone · Water solvent

INTRODUCTION

Ionic liquids (ILs) are molten salts that generally consist of bulky organic cations paired with inorganic anions. They have some unusual properties, such as non-flammability, a wide electrochemical window, high thermal stability, wide liquid range and the most important, negligible vapor pressure. This feature makes them as a replacement for ordinary organic solvents to reduce volatile organic compounds emissions. Therefore, ILs have widely been classified as "green solvents" [1]. There is growing interest in their use as clean solvents in various processes, e.g., pharmaceutical synthesis, catalysis and extraction [2-4]. They are nonvolatile with high ionic conductivity and therefore very promising in various electrochemical and industrial applications [5], including lithium ion batteries [4-6].

The synthesis and chemistry of quinoxalines have attracted considerable attention in the past ten years. 1,2 Some of them exhibit biological activities including anti-bacterial [7], anti-inflammatory [8], anti-cancer [9] (colon cancer therapies) [10], anti-viral [11], anti-HIV and anti-protozoal [12], anti-depressant [13] and as kinase inhibitors [14, 15]. They are also used in the agricultural field as fungicides, herbicides and insecticides [16]. Also, quinoxaline moieties are present in the structure of various antibiotics such as echinomycin, levomycin and actinoleutin, which are known to inhibit the growth of gram positive bacteria and they are active against various transplantable tumors [17, 18]. Several methods are available for the synthesis of quinoxaline derivatives which involve condensation of 1,4-addition of 1,2-diamines to diazenylbutenes [19], cyclization–oxidation of phenacyl bromides [20, 21], 1,2-diamines with α-diketones [22, 23] and oxidative coupling of epoxides with ene-1,2-diamines [24]. 2,3-Disubstituted quinoxalines have also been prepared via the condensation of *o*-phenylenediamines with 1,2-dicarbonyl compounds in MeOH/AcOH under microwave irradiation [25], Suzuki–Miyaura coupling reaction [26] and iodine catalyzed cyclo-condensation of 1,2-dicarbonyl compounds with substituted *o*-phenylenediamines in DMSO [27] or CH_3CN [28]. Improved methods have been reported for the synthesis of quinoxaline derivatives including a microwave procedure [25] and the use of

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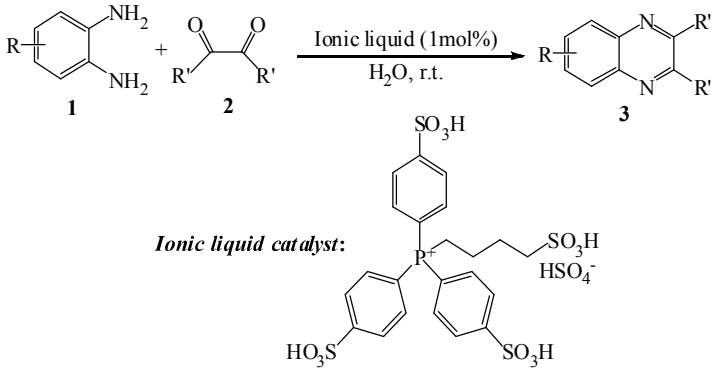


Fig. 1: Synthesis of 2,3-disubstituted quinoxaline using ionic liquid catalyst

$RuCl_2$-$(PPh_3)_3$-TEMPO [29], MnO_2 [30], zeolites [27], iodine [31], cerium ammonium nitrate [32], Montmorillonite K-10 [33] and $H_6P_2W_{18}O_{62}.24H_2O$; Wells-Dawson [34] as a catalyst.

Recently, Jianguo *et al*. [35] introduced a new catalyst with multi-SO_3H groups which have much higher activity than other reported catalysts with the additional advantage of reusability. In continuation of our investigations on the development of new synthetic methodologies [36], we herein report a new, facile and rapid route procedure for the synthesis of 2,3-disubstituted quinoxaline derivatives from one-pot condensation of various *o*-phenylenediamine with 1,2-diketone using this non-volatile ionic liquid with multi-SO_3H groups under ambient temperature (Fig. 1).

Experimental: NMR spectra were determined on a Fourier-transform (FT)- NMR Bruker AV-400 spectrometer in $CDCl_3$ are expressed in δ values relative to tetramethylsilane; coupling constants (*J*) are measured in Hz. Melting points were determined on a ELECTR THERMAL9100. Infrared spectra were recorded on a RAYLEIGH WQF-510 Fourier transform instrument. Commercially available reagents were used throughout without further purification.

General procedure for the synthesis of (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate (ionic liquid catalyst): The ionic liquid with multi-SO_3H groups was synthesized according to literature [35]. A black viscous liquid was formed in high purity and then the physical data (IR, ^{1}HNMR, ^{13}CNMR) of these known ionic liquid was found to be identical. Spectral data: IR (KBr): υ 3247, 3075, 2983, 1460, 1380, 1295, 957 cm^{-1}; ^{1}H NMR (400 MHz, D_2O): δ 1.74 (m, 2H), 1.87 (m, 2H), 2.13 (t, 2H, J = 6.7 Hz), 3.63 (t, 2H, J = 6.8 Hz), 7.57 (d, 6H, J = 6.8 Hz), 7.85 (d, 6H, J = 6.7 Hz); ^{13}C NMR (100 MHz, D_2O): δ 19.7, 22.5, 27.3, 55.1, 123.4, 127.9, 136.2, 151.3.

General procedure for the synthesis of 2,3-disubstituted quinoxaline derivatives: A mixture of *o*-phenylenediamine (1 mmol) and 1,2-diketone (1 mmol) was added to ionic liquid catalyst (1 mol%) in water (2 mL) and the reaction mixture was stirred at room temperature for an appropriate time. completion of the reactions was monitored by TLC (*n*-hexan/ethyl acetate 5:2). After completion of the reaction, the resulting solid crude product was filtered and then recrystallized from ethanol–water to achieve pure product. The formation of products was identical by comparing the melting points, IR and NMR data with authentic samples and literature data.

Spectral data for the selected of 2,3-disubstituted quinoxaline derivatives

2,3-Bis(4-methoxyphenyl)quinoxaline (Table 1, entry 3b): Yield: 95%; M.p 151-153°C (lit. [37] 151-152 °C); IR (KBr, cm^{-1}) 3069, 2970, 1617, 1560, 1445, 1357, 1271, 875, 755; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, J = 6.3 Hz, J = 3.1 Hz, 1H), 7.75 (dd, J = 6.4 Hz, J = 3.3 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.2 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 153.4, 142.4, 133.8, 132.1, 129.9, 129.2, 114.7, 57.1.

Dibenzo[a,c]phenazine (Table 1, entry 3e): Yield: 96%; M.p 227-229°C (lit. [38] 223-225 °C); IR (KBr, cm^{-1}) 3057, 2971, 1625, 1573, 1495, 1357, 1221, 967, 770; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (d, J = 7.6 Hz, 2H), 8.43 (d, J = 7.7 Hz, 2H), 8.17 (dd, J = 6.1 Hz, J = 3.5 Hz, 2H), 7. 67-7.57 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 143.7, 134.3, 132.1, 131.3, 130.5, 129.3, 127.7, 123.2.

6-Methyl-2,3-diphenylquinoxaline (Table 1, entry 3h): Yield: 94%; M.p 116-118°C (lit. [18] 117-118°C); IR (KBr, cm^{-1}) 3120, 3057, 2965, 1610, 1567, 1375, 987, 857; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.6 Hz, 1H), 7.98 (s, 1H), 7.71 (dd, J = 1.5 Hz, J = 1.4 Hz, 1H), 7.53 (t, J = 5.6 Hz, J = 5.1 Hz, 4H), 7.37 (d, J = 5.8, 6H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 153.1, 142.2, 141.4, 140.1, 139.5, 133.2, 130.6, 129.3, 128.7, 128.1, 127.8, 23.8.

6-Nitro-2,3-diphenylquinoxaline (Table 1, entry 3v): Yield: 96%; M.p 191-193°C (lit. [18] 193-194°C); IR (KBr, cm^{-1}) 3155, 3057, 2988, 1627, 1570, 1357, 951, 845; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 8.8 Hz, 1H), 8.25 (s, 1H), 7.86 (dd, J = 2.1 Hz, J = 1.8 Hz, 1H), 7.68 (t, J = 5.7 Hz, J = 5.6 Hz, 4H), 7.48 (d, J = 5.8, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.1, 143.1, 142.1, 139.7, 139.2, 137.1, 131.9, 130.5, 130.1, 129.7, 129.1, 128.3, 127.7.

RESULTS AND DISCUSSION

To institute the overview and possibility of our method, various aryl-1,2-diamines were reacted with some 1,2-diketones. The results are displayed in Table 1. As seen, the reactions proceeded efficiently and the individual quinoxalines were obtained in good to excellent yields and short reaction times. The effect of electron-releasing and electron-withdrawing substituents on the aromatic ring of aryl-1,2-diamines on the reaction was investigated. As Table 1 be evidence for, electron-releasing groups did not affected considerably on the yields and the reaction times (Table 1, entries 3h-3n, 3s-3u). Other than, aryl-1,2-diamine having electron-withdrawing groups on the aromatic ring (Table 1, entries 3v-3y) react faster and with better yield than electron-donating groups (Table 1, entries 3h-3n,

Table 1: Ionic liquids catalyzed synthesis of 2,3-disubstituted quinoxaline derivatives

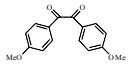
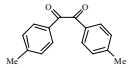
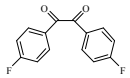
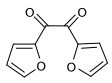
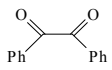
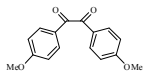
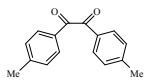
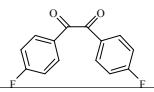
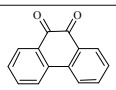
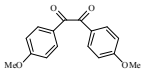
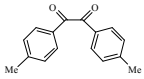
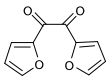
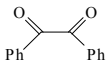
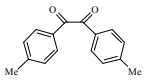
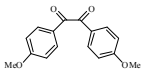
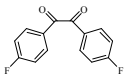
Entry	Diamine	1,2-Diketone	Time (min)	Yield (%)	M.p [Ref.]
3a			25	94	131-133 [18]
3b			17	95	151-153 [37]
3c			17	95	144-146 [27]
3d			13	97	137-139 [18]
3e			18	96	227-229 [38]
3f			20	96	235-237 [38]
3g			24	94	127-129 [39]
3h			17	94	116-118 [18]
3i			12	97	126-128 [37]
3j			13	96	137-139 [40]
3k			10	98	165-167 [18]

Table 1: Continue

Entry	Diamine	1,2-Diketone	Time (min)	Yield (%)	M.p [Ref.]
3l			13	97	208-210 [38]
3m			15	97	312-314 [38]
3n			17	95	118-120 [41]
3o			12	96	114-116 [32]
3p			10	94	155-157 [32]
3q			10	96	170-172 [42]
3r			12	94	121-123 [38]
3s			12	96	174-176 [43]
3t			10	96	138-140 [32]
3u			10	97	302-304 [44]
3v			10	96	191-193 [18]
3w			7	96	196-198 [37]
3x			5	98	174-176 [18]
3y			7	98	313-315 [45]

3s-3u). Moreover, it has been functional that the electronic properties of the aromatic ring of 1,2-diketones had insignificant effect on the yields and the reaction times.

The effect of solvent on the yield of 2,3-disubstituted quinoxaline derivatives is given in Table 2. The reaction of *o*-phenylenediamine with benzil was chosen as a model reaction for investigating the effect of solvent.

Table 2: Solvent effect in the synthesis of 2,3-diphenylquinoxaline (Table 1, entry 3a)[a]

Solvent	Solvent free	H_2O	C_2H_5OH	CH_3CN	Toluene	Benzene
Reaction time (min)	40	25	23	30	35	40
Yield (%)[b]	51	94	95	91	87	81

Reaction condition: [a] *o*-phenylenediamine (1 mmol), benzil (1 mmol), ionic liquid catalyst (1 mol%), solvent (2 mL); [b] Yields are related to the isolated pure products

Table 3: Reusability studies of catalyst for the synthesis of 2,3-diphenylquinoxaline (Table 1, entry 3a)[a]

Cycle	Fresh	1	2	3	4
Product isolated yield (%)[b]	94	94	93	92	90
Recycling catalyst yield (%)	98	97	95	92	90

Reaction condition: [a] *o*-phenylenediamine (1 mmol), benzil (1 mmol), ionic liquid catalyst (1 mol%), Water solvent (2 mL); [b] Yields are related to the isolated pure products

Table 4: Comparison of efficiency of various catalysts in synthesis of quinoxaline 3a

Entry	Catalyst	Condition	Time (min)	Yield (%)	[Ref.]
1	Ionic liquid with multi-SO_3H groups (1 mol%)	Water, r.t.	25	94	This work
2	I_2 (10 mol%)	DMSO, r.t.	35	95	[27]
3	PEG-400 (2gr), HDNIB, Na_2CO_3	CH_3CN, r.t.	180	90	[47]
4	PbO (4 mmol)	Ethanol, 60°C	55	95	[48]
5	$H_4SiW_{12}O_{40}$ (1 mol%)	Water, r.t.	60	92	[49]

From Table 2 we can know that water is obviously the best choice for these reactions. However, for this reaction, considering the laboratory not industry, the best results were achieved by carrying out the reaction at room temperature in ethanol for 23 min using 1 mol% of ionic liquid as a catalyst. But, in this paper water prefer to ethanol because water is green, safe and cheap compared with organic solvents.

The reusability of the catalysts is a significant advantage and makes them useful for commercial applications [46]. For this purpose, the reaction of *o*-phenylenediamine with benzil was chosen as the model reaction in the presence of ionic liquid catalyst. After completion of the reaction (monitored by TLC), CH_2Cl_2 was added to the mixture. The aqueous layer was separated and used without further purification. After washing the solid products with water completely, the water containing ionic liquid (ionic liquid is more soluble in water that than CH_2Cl_2) was evaporated under reduced pressure and the ionic liquid was recovered and reused. The recovered catalyst was reused in five runs without any loss of its activities (Table 3). The deactivation of the catalyst is low, although coke formation (reactant) was expected. The reaction was scaled up to 10 mmol of *o*-phenylenediamine and benzil in the presence of 10 mol% of catalyst at 25°C. The yield of the reaction was 94% after 25 min and 90% after the fifth run.

In order to show the merit of ILs in comparison with the other catalysts used for the similar reaction, some of the results are tabulated in Table 4. According to Table 4, the best yield and short reaction time is attributed to the high efficiency of the ionic liquid with multi-SO_3H groups as a catalyst.

CONCLUSION

In summary, a Brønsted acidic ionic liquid (BAIL) was prepared and used as homogeneous catalyst for the synthesis of 2,3-disubstituted quinoxaline derivatives from *o*-phenylenediamine and 1,2-diketone. The reactions proceeded efficiently with good yields. The catalyst can be separated from the product by changing the solvents. The catalyst is reusable. Simple workup and easy isolation under mild reaction conditions are the best features of the present methodology. The catalyst offers several advantages including mild reaction conditions, shorter reaction times, high yield of the products, cleaner reactions, lower catalytic loading, green acid catalyst as well as simple experimental and isolation procedures.

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