

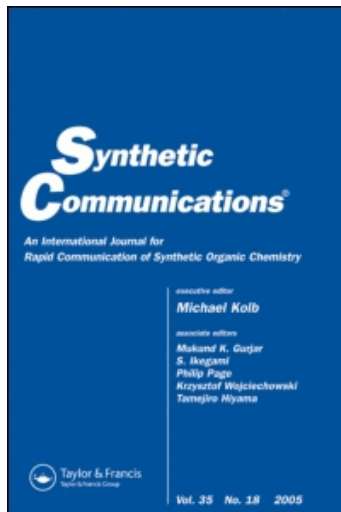
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Efficient, Ecofriendly, and Practical Process for the Synthesis of Quinoxalines Catalyzed by Amberlyst-15 in Aqueous Media

Ju-Yan Liu^a; Jing Liu^a; Jia-Di Wang^a; De-Quan Jiao^a; Hai-Wang Liu^a

^a College of Chemistry and Life Science, Tianjin Key Laboratory of Structure and Performance for Functional Molecule, Tianjin Normal University, Tianjin, China

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EFFICIENT, ECOFRIENDLY, AND PRACTICAL PROCESS FOR THE SYNTHESIS OF QUINOXALINES CATALYZED BY AMBERLYST-15 IN AQUEOUS MEDIA

Ju-Yan Liu, Jing Liu, Jia-Di Wang, De-Quan Jiao, and Hai-Wang Liu

College of Chemistry and Life Science, Tianjin Key Laboratory of Structure and Performance for Functional Molecule, Tianjin Normal University, Tianjin, China

Amberlyst-15/H₂O has been used as an efficient and environmentally friendly catalytic system for the synthesis of quinoxalines. The present methodology offers several advantages, such as excellent yields, short reaction time, and simple workup.

Keywords: Amberlyst-15; 1,2-diamine; 1,2-diketone; quinoxaline; water

INTRODUCTION

The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons and benzene, which are widely used in organic synthetic processes, poses a serious threat to the environment. Recently, performing organic reactions in aqueous media has attracted much attention because water is considerably safer, nontoxic, more environmentally friendly, and less expensive than organic solvents.^[1] Water also exhibits unique reactivity and selectivity that cannot be attained in conventional organic solvents.^[2] There is no doubt that the use of water as a reaction medium could have an outstanding impact on organic synthesis, including at a process scale.

Nitrogen-containing compounds are of significant importance in human life, but they are also useful as biologically active substances, dyes, and fine chemicals.^[3] For instance, quinoxaline is an important ring system. Its derivatives possess well-known biological activities including antibacterial, antiviral, anti-inflammatory, antiprotozoal, anticancer, and anthelmintic activities and can act as kinase inhibitors.^[4] Besides this, they have found widespread applications in dyes,^[5] efficient electroluminescent materials,^[6] organic semiconductors,^[7] building blocks for the synthesis of anion receptors, and DNA cleaving agents.^[8] Therefore, various synthetic strategies have been developed for the preparation of substituted quinoxalines,

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Address correspondence to Ju-Yan Liu, College of Chemistry and Life Science, Tianjin Key Laboratory of Structure and Performance for Functional Molecule, Tianjin Normal University, Tianjin, China. E-mail: hsxyljy@mail.tjnu.edu.cn

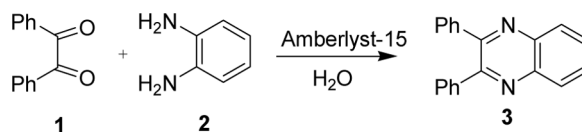
and the most common method relies on the condensation of 1,2-aryldiamine with 1,2-diketone in refluxing ethanol or acetic acid for 2–12 h, giving 34–85% yields.^[9] Improved approaches have been reported for the synthesis of quinoxaline derivatives including the Bi-catalyzed oxidative coupling,^[10] solid-phase synthesis,^[11] microwave irradiation,^[12] and the use of $\text{RuCl}_2\text{-(PPh}_3)_3$ –2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO),^[13] MnO_2 ,^[14] POCl_3 ,^[15] zeolites,^[16] I_2 ,^[17] sulfamic acid (SA),^[18] montmorillonite K-10,^[19] polyaniline-sulfate salt (SSA),^[20] *p*-TsOH,^[21] $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$,^[22] InCl_3 ,^[23] MnCl_2 ,^[24] $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,^[25] $\text{Zn}[(\text{L})\text{proline}]$,^[26] ceric ammonium nitrate (CAN),^[27] and $\text{Ga}(\text{OTf})_3$ ^[28] as catalysts or activators. Many of these methods suffer from one or more limitations, such as the use of toxic organic solvents, long reaction times, use of expensive or corrosive reagents, tedious workup processes, special apparatus, and harsh reaction conditions. Thus, the development of new catalytic methods is highly desirable.

In recent years, heterogeneous catalysts have attracted much attention as promoters for various chemical transformations as well as procedures related to fine-chemical synthesis.^[29–31] One of those heterogeneous catalysts is amberlyst-15. It possesses unique properties such as environmental compatibility, reusability, nontoxicity, noncorrosiveness, and physical and chemical stability. Amberlyst-15 can conveniently be handled and removed by simple filtration after the reaction. Because of these advantages, amberlyst-15 has been explored as a powerful catalyst for various organic reactions under mild conditions.^[32] In this article, we report a green and efficient protocol for the synthesis of quinoxaline derivatives in good to excellent yields by the condensation of 1,2-diamines with 1,2-dicarbonyl compounds catalyzed by amberlyst-15 in water.

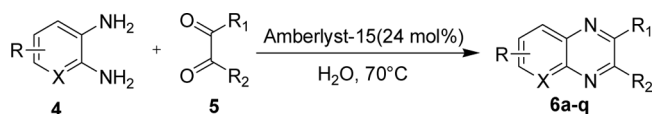
RESULTS AND DISCUSSION

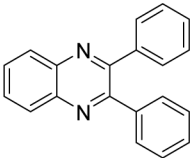
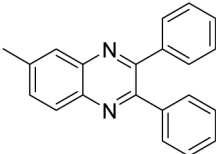
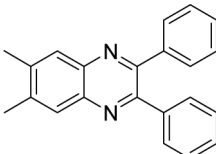
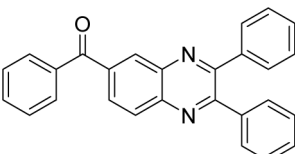
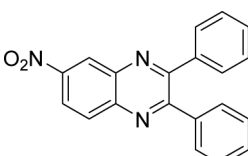
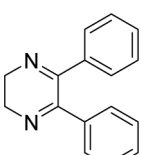
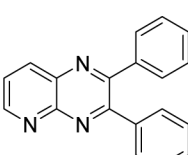
The catalytic activity of amberlyst-15 was first tested for the condensation of α -diaminobenzene with benzil in water. Initially, the reaction was conducted at room temperature in the presence of 1 equiv of amberlyst-15 and afforded the product in 70% yield over 45 min (Table 1, entry 1). To our satisfaction, rapid conversion was observed when the reaction was carried out with heating at 70 °C. In these cases,

Table 1. Amberlyst-15-catalyzed synthesis of 2,3-diphenylquinoxaline



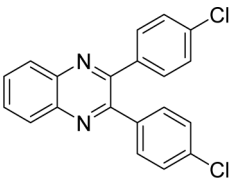
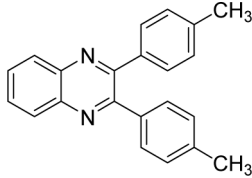
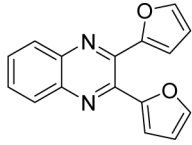
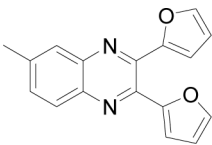
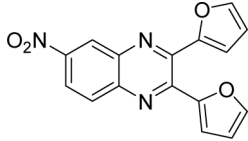
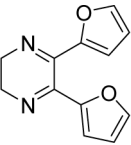
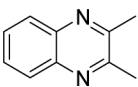
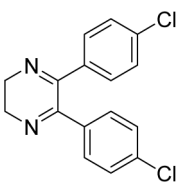
Entry	Amberlyst-15 (mol%)	Temperature (°C)	Time (min)	Solvent	Isolated yield (%)
1	100	25	45	H ₂ O	70
2	100	60	23	H ₂ O	93
3	47	60	25	H ₂ O	93
4	24	70	19	H ₂ O	>99
5	20	70	26	H ₂ O	90
6	No	70	60	H ₂ O	0

Table 2. Amberlyst-15/H₂O catalytic synthesis of quinoxalines at 70 °C

Entry ^a	Product ^b	Time (min)	Isolated yield	Mp (°C) (lit. ^[ref])	
1		6a	19	>99	125–126 (124 ^[18])
2		6b	14	>99	110 (109 ^[18])
3		6c	12	>99	170–171 (172 ^[18])
4		6d	28	92	149 (150–151 ^[28])
5		6e	54	71	185 (183 ^[18])
6		6f	15	>99	161 (158 ^[18])
7		6g	52	70	135–136 (135 ^[18])

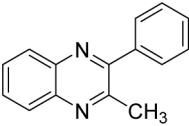
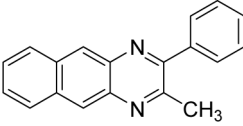
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Table 2. Continued

Entry ^a	Product ^b	Time (min)	Isolated yield	Mp (°C) (lit. [ref])
8		12	>99	198 (195–196 ^[26])
9		15	96	145 (142–143 ^[21])
10		17	98	133 (131 ^[27])
11		11	>99	117 (119–120 ^[27])
12		50	78	106–107 (108 ^[28])
13		15	>99	83–84 (81 ^[28])
14		18	>99	105 (103 ^[18])
15		11	>99	134 (133–135 ^[28])

(Continued)

Table 2. Continued

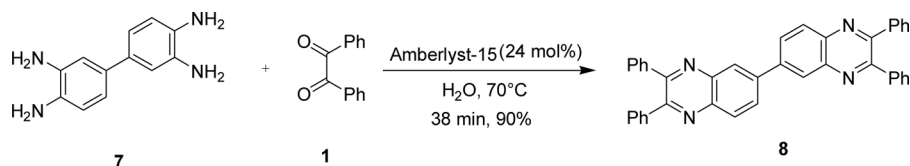
Entry ^a	Product ^b	Time (min)	Isolated yield	Mp (°C) (lit. [ref])
16		10	>99	57 (56 ^[27])
17		14	97	132 (134 ^[27])

^aAll reactions were performed at 1 mmol scale using 24 mol% of amberlyst-15 in 15 mL of water.

^bAll products were well characterized using ¹H NMR, ¹³C NMR, and elemental analysis.

lower temperature could also be applied but resulted in a longer reaction period (Table 1, entry 3). We have also investigated the efficiency of the catalyst in less than a stoichiometric amount. The condensed product was obtained using 24 mol% of amberlyst-15 in excellent yield. Lower catalyst loading could be used with only a marginal drop in reaction rate (Table 1, entry 5). In the absence of catalyst, the reaction did not yield any product at 70 °C even after a long reaction time (60 min). This result suggests that amberlyst-15 plays a critical role in this reaction.

To demonstrate the limitations and scope of this method, we examined the reaction with various structurally diverse 1,2-diamines and 1,2-dicarbonyl compounds under optimized conditions, and the results are summarized in Table 2. The reaction proceeded very cleanly at 70 °C, and no undesirable side reactions were observed. As shown in Table 2, a series of aromatic, aliphatic, and heterocyclic α -diamines reacted with several α -dicarbonyls smoothly to afford a wide range of substituted quinoxalines in good to excellent yields. The nature of the substituents in the diamine part affect the conversion rate; aromatic diamines with electron-donating groups on the aromatic ring (Table 2, entries 2 and 3) react faster than *o*-phenylenediamine (Table 2, entry 1), and an electron-withdrawing substituent (i.e., NO₂, benzoyl) deactivated aryl diamines (Table 2, entries 4, 5, and 12). On the other hand, the substituents at the 1,2-diketones had no significant effect on the yield of products (Table 2, entries 8 and 9). Furthermore, the electron-deficient heterocyclic substrate 2,3-diaminopyridine gave the corresponding 2,3-diphenylpyrido[2,3-*b*]pyrazine in



Scheme 1. Synthesis of bisquinoxaline compound **8** using amberlyst-15 as the catalyst.

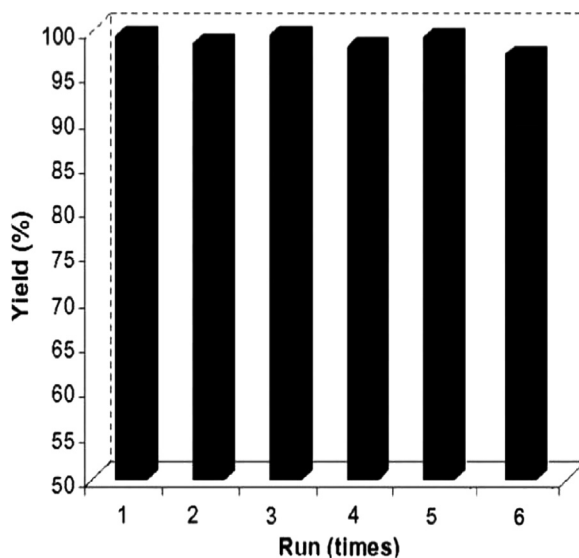


Figure 1. Recycling of amberlyst-15 in the reaction between *o*-phenylenediamine and benzil.

70% yield without polymerization under these reaction conditions (Table 2, entry 7).^[33] To check the versatility of this method, we also investigated compounds such as furil and 1-phenyl-1,2-propanedione and obtained the corresponding products in excellent yields (Table 2, entries 10, 11, 16, and 17). The generality of this catalytic system was also confirmed by the employment of other dicarbonyls (i.e., diacetyl) and other diamines (i.e., 1,2-ethylenediamine) as shown in Table 2 (entries 6, 13–15).

This reaction was further explored for the synthesis of bisquinoxaline compound **8** by the condensation of 3,3'-diaminobenzidine **7** and 2 equiv of benzil under similar conditions. Compound **8** was obtained in excellent yield (Scheme 1).

One of the special features of amberlyst-15 is its insolubility in water and organic solvents, which makes its recovery very convenient. It should be noted that the workup involves simple filtration, and the catalyst could be recycled after washing with ether and air drying. The recycling of amberlyst-15 was studied in the reaction of *o*-phenylenediamine and benzil. Amberlyst-15 is recyclable and could be reused without significant loss of its catalytic activity. Even after five runs, the catalytic activity of amberlyst-15 was almost the same as that of the freshly used catalyst (Fig. 1).

To evaluate the possibility of applying this methodology in a large-scale reaction, we carried out the reaction of equimolar amounts of *o*-phenylenediamine with benzil starting from 10.8 g (100 mmol) of diamine. The yield in the 2,3-diphenylquinoxaline (98%) was almost the same as that of the small-scale (1 mmol) run.

CONCLUSION

In conclusion, we have developed a rapid, practical, and efficient protocol for the synthesis of quinoxalines from 1,2-diketone and 1,2-diamine using amberlyst-15

in aqueous media. The attractive features of this procedure are the simple manipulation, good conversions, clean reaction profiles, recyclability of catalyst, and applicability to large-scale reactions, all of which make it a useful and attractive strategy for the preparation of various quinoxaline derivatives by simply changing different substrates.

EXPERIMENTAL

General

All chemicals were purchased from Aldrich Co. and used as received. All products were identified by their spectra and physical data. Melting points were determined on a X-4 apparatus and are uncorrected. NMR spectra were taken with a Varian 400 spectrometer using tetramethylsilane (TMS) as an internal standard (CDCl₃ solution). Elemental analysis were conducted on an MT-3 analyzer. All of the obtained quinoxalines are known compounds and were characterized by comparison of thin-layer chromatography (TLC), spectral, and physical data with data of authentic samples.^[18–28]

General Procedure for the Synthesis of Quinoxaline Derivatives

A catalytic amount of amberlyst-15 (24 mol%, 0.05 g) was added to a mixture of an appropriate 1,2-diketone (1 mmol) and 1,2-diamine (1 mmol) in water (15 mL), and the mixture was stirred vigorously at 70 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, ethyl acetate (10 mL) was added, and the heterogeneous mixture was filtered. The filter cake was washed with diethylether, and the catalyst was recovered. The organic phase was washed with water (2 × 15 mL) and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure to provide the crude product, which was washed with cold methanol and dried to afford pure product. In the cases of entries 5, 7, and 12, the crude products were purified by silica-gel column chromatography (15% ethyl acetate in petroleum ether) to give the pure quinoxalines.

Physical and Spectral Data of the Selected Products

2,3-Diphenylquinoxaline (6a). Mp 125–126 °C (EtOH); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.20 (m, 2H), 7.78 (m, 2H), 7.54 (m, 4H), 7.37 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz) 153.51, 141.27, 139.19, 130.05, 129.98, 129.26, 128.88, 128.32. Anal. calcd. for C₂₀H₁₄N₂: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.99; H, 5.15; N, 9.89.

2,3,2',3'-Tetraphenyl-[6,6']biquinoxaliny (8). Mp > 296 °C (EtOH); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.61 (s, 2H), 8.35 (d, *J* = 8.6 Hz, 2H), 8.20 (dd, *J* = 8.7 Hz, *J* = 1.7 Hz, 2H), 7.56 (m, 8H), 7.39 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz) 154.21, 153.77, 141.46, 141.29, 140.99, 139.09, 129.98, 129.91, 129.56, 129.00, 128.38, 127.52. Anal. calcd. for C₄₀H₂₆N₄: C, 85.38; H, 4.66; N, 9.96. Found: C, 85.19; H, 4.75; N, 10.09.

ACKNOWLEDGMENT

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