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One-pot synthesis of quinoxaline-2-carboxylate derivatives using ionic liquid as reusable reaction media

H. M. Meshram *, P. Ramesh, G. Santosh Kumar, B. Chennakesava Reddy

Organic chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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ABSTRACT

The catalyst-free one-pot synthesis of quinoxaline-2-carboxylate is reported by the reaction of α-halo-β-ketoesters with 1,2-diamines using an ionic liquid as an environmentally benign solvent. The recovered ionic liquid was reused for four to five cycles. Moreover, the method is applicable for a variety of 1,2-diamines and α-halo-β-ketoesters.

Quinoxaline moiety is found in biologically active natural products, in many pharmaceuticals as well as in agrochemicals.[1] Some of the quinoxaline derivatives are found to exhibit a broad spectrum of biological activity.[1c] Many quinoxaline derivatives have a wide application in dyes,[2a] as an efficient electroluminescent material,[2b] as organic semiconductors,[2c] as dehydroannulenes[2d] and in chemically controllable switches.[2e] The quinoxaline ring is also found in antibiotics such as echinomycin, leromycin and actinomycin.[3] Due to the distinguished biological and physical properties of quinoxalines, there has been a tremendous interest to devise a simple and efficient method for the synthesis of more functionalized quinoxaline derivatives.

Commonly, a practicable method comprises the reaction of condensation of aryl 1,2-diamines with 1,2-dicarbonyl compounds,[4] 1,4-addition of 1,2-diamines to diazenylbutens[5] and oxidation-trapping of α-hydroxy ketones with 1,2-diamines.[6] Other reported methods accomplished the synthesis of quinoxalines by the reaction of 1,2-diamines with phenacyl bromides in solid-phase[7] or using heterogeneous catalyst such as $HClO_4$–SiO_2[8] and β-cyclodextrin (β-CD).[9] In addition to this, α-ketoesters,[10] 3-{[(*tert*-butoxy)carbonyl]diazenyl}but-2-enoats[11] and N=N polymer-bound 1,2-diaza-1,3-butadiene[12] have been reported for the synthesis of quinoxaline. Moreover, the attempted reaction of α-halo-β-ketoesters with 1,2-diamines also reported to give an uncyclized product.[11]

Although the reported methods provide good isolated yields, these methods suffer from tedious work-up, longer reaction time, use of metal catalyst and narrow scope of substrates. Moreover, some of the methods have drawbacks such as unsatisfactory yields, expensive and detrimental metal reagents. In view of this, there is still a need to develop a general, efficient and catalyst-free method for the synthesis of more functionalized quinoxaline derivatives.

Recently, ionic liquids have received much attention due to their unique properties such as non-volatility, non-flammability, reusability and great potential as environmentally benign media.[13] Some of the ionic liquids have been proved to act as catalysts because of their high polarity and the ability to solubilize both inorganic and organic compounds, which can result in the enhancement of the rate of the reaction. 1-Butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4 (Fig. 1) has gained more popularity and is used in various organic transformations such as vicinal diamines,[14] one-pot syntheses of 2*H*-indazolo[2,1-*b*]-phthalazine-triones[15] and hydrative cyclization of 1,6-diynes.[16] In continuation of our work in the development of green methodologies[17] and particularly in the development of non-metallic reagents[18], herein we wish to report an efficient and mild synthesis of quinoxalines from α-halo-β-ketoesters using ionic liquid as a reaction medium in the absence of catalyst. To the best of our knowledge this is the first report for the one-pot synthesis of functionalized quinoxalines.

Thus, the reaction of 1,2-phenylenediamine with α-halo-β-ketoesters in ionic liquid [bmim]BF_4 at rt gave the expected quin-

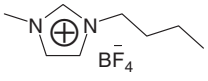

Figure 1. Chemical structure of representative ionic liquid (IL).

* Corresponding author. Tel.: +91 40 27160123 2642; fax: +91 40 27160512.
E-mail address: hmmeshram@yahoo.com (H.M. Meshram).

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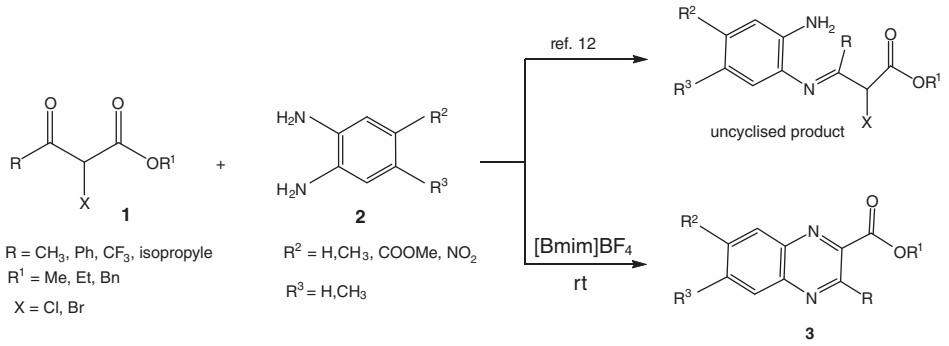


Scheme 1.

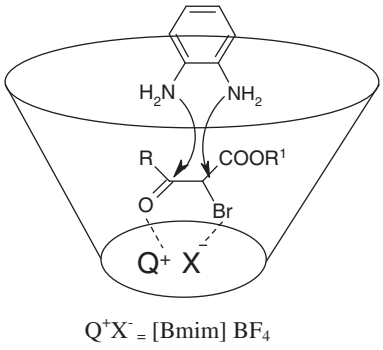


Figure 2. Plausible mechanistic pathway.

oxalines in high yield (93%) (Scheme 1). The reaction proceeded readily at rt and after work-up, the quinoxaline was the sole product. However, the reaction did not proceed in common organic solvents such as CH_2Cl_2, THF and CH_3CN. Though the reaction of 1,2-diamine and α-halo-β-ketoester is reported[11] to give an uncyclized product. The same reaction was forced to give the expected cyclized product in the present reaction conditions. This fact clearly indicated that in the present reaction, the ionic liquid plays the dual role of solvent and promoter[19] (Fig. 2). The reaction in ionic liquid is more advantageous, because ionic liquid can be recycled and reused in subsequent reactions. After the separation of the product by extraction of ionic liquid, it was thoroughly washed with ether and activated at 80 °C under reduced pressure. The reactivated ionic liquid was used for three cycles without any substantial loss in activity, while the reactivity gradually decreased for the next few cycles. For example, the reaction of 1,2-phenylenediamine with α-halo-β-ketoesters in ionic liquid [bmim]BF_4 afforded 93%, 92%, 92%, 85% and 80%, respectively, over five cycles. Encouraged by these results, we have extended this procedure[20] for different 1,2-phenylenediamines and α-halo-β-ketoesters (Table 1). Both the chloro and bromo ketoesters gave comparable results for the formation of quinoxaline. Similarly, the electronic effect

Table 1
Synthesis of quinoxaline-2-carboxylate derivatives using ionic liquid [bmim]BF_4

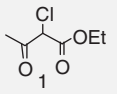
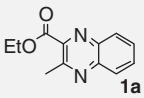
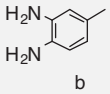
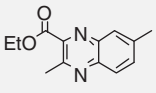
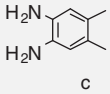
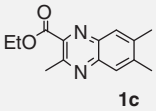
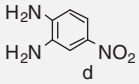
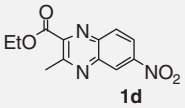
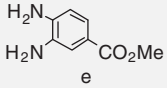
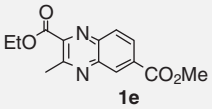
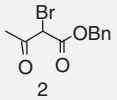
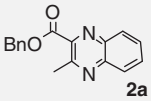
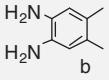
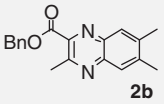
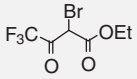
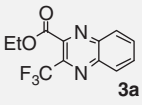
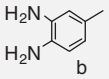
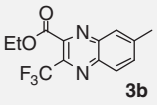
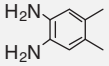
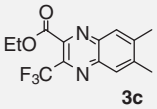
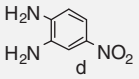
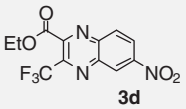
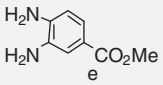
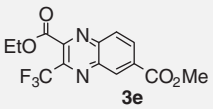
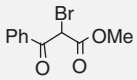
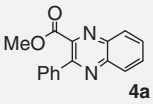
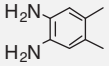
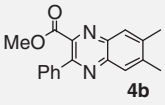
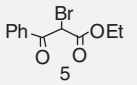
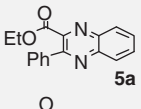
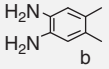
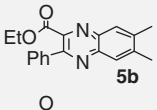
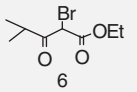
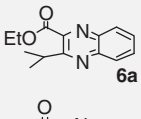
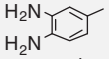
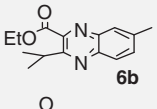
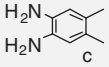
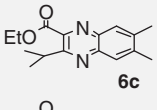
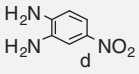
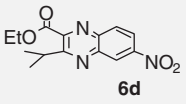
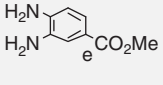
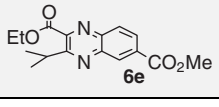
Entry	α-Halo, β-keto ester	1,2-Diamine	Product[a]	Time (min)	Yield[b] (%)
1	 1	 a	 **1a**	60	90
2		 b	 **1b**	56	92
3		 c	 **1c**	50	93
4		 d	 **1d**	80	87
5		 e	 **1e**	90	84
6	 2	 a	 **2a**	50	89

Table 1 (*continued*)

Entry	α-Halo, β-keto ester	1,2-Diamine	Product[a]	Time (min)	Yield[b] (%)
7		 b	 **2b**	59	91
8	 3	 a	 **3a**	45	93
9		 b	 **3b**	50	89
10		 c	 **3c**	40	94
11		 d	 **3d**	70	86
12		 e	 **3e**	80	82
13	 4	 a	 **4a**	45	92
14		 b	 **4b**	40	94
15	 5	 a	 **5a**	70	90
16		 b	 **5b**	50	92
17	 6	 a	 **6a**	80	87
18		 b	 **6b**	85	89[c]
19		 c	 **6c**	75	90
20		 d	 **6d**	95	87
21		 e	 **6e**	99	85

[a] Reaction conditions: α-halo, β-keto ester (1.1 equiv), 1,2-phenylene diamine (1 equiv), ionic liquid [bmim]BF_4 (2 mL) at rt.
[b] Isolated yields.
[c] Isomeric products.

of substituents on 1,2-diamine was studied in detail. The electron-donating substituents enhance the rate of reaction and gave the corresponding products in good yields (entries 3, 7, 10, 14, 16 and 19). It was interesting to note that the presence of methyl group at fourth position of 1,2-phenylenediamine (entries 2, 9 and 18) gave two isomeric products (80:20) depending on the course of cyclization. This phenomenon was not observed in the case of electron-withdrawing substituents. This fact may be attrib-

uted to the electron-donating nature of methyl group which may favour to increase the nucleophilic character of amine group. It was noticed that electron-withdrawing substituents suppress the reaction (entries 4, 5, 11, 12, 20 and 21) but favour the formation of only one desired product. In addition, the functionalities like ester remain unaffected. We believe that the procedure is simple, convenient and does not require any aqueous work-up, thereby avoiding the generation of waste, and may contribute to the area of green chemistry.

In summary, the ionic liquid was shown to be an effective and useful alternative reaction medium for the preparation of 2-carboxylate quinoxaline derivatives. The present procedure offers several unique advantages such as enhanced yields, shorter reaction times, operational simplicity, mild reaction conditions, ease of isolation of products and a greener aspect by avoiding the need for a catalyst.

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19. *General procedure*: A mixture of 1,2-phenylenediamine (1 mmol) and α-halo-β-ketoesters (1.1 mmol) in [bmim]BF_4 (2 mL) was stirred at rt for the appropriate time (see Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were concentrated under vacuum and the resulting product was directly charged on a silica gel (Merck, 60–120 mesh) column and eluted with a mixture of ethyl acetate/*n*-hexane (1:9) to afford the corresponding pure product. The residual ionic liquid was dried under vacuum and reused. All the products were prepared by following the same procedure and characterized by IR, mass and NMR.[20]
20. *Spectral data for new compounds:*
Compound **1b**: Semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (3H, t, *J* = 6.83 Hz), 2.62 (3H, s), 2.90 (3H, s), 4.51 (2H, q, *J* = 6.83 Hz), 7.54 (1H, d, *J* = 8.78 Hz), 7.78 (1H, s), 8.02 (1H, d, *J* = 8.78 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.2, 23.1, 70.0, 127.7, 129.0, 136.6, 142.1, 148.4, 154.0, 161.0. MS (ESI) *m*/*z* 243 (M+Na), 231 (M+1); IR (KBr) ν = 2924, 1724, 1669, 1629, 1451, 1409, 1259, 1083, 804 cm^{-1}. Compound **1d**: Solid. Mp 73–74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (3H, t, *J* = 7.17 Hz), 2.98 (3H, s), 4.55 (2H, q, *J* = 7.17 Hz), 8.16 (1H, d, *J* = 9.25 Hz), 8.60 (1H, dd, *J* = 2.45 Hz, *J* = 6.61 Hz), 9.07 (1H, d, *J* = 2.45 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 23.1, 60.8, 122.4, 122.7, 129.3, 141.5, 143.2, 152.6, 158.6, 161. MS (ESI) *m*/*z* 284 (M+Na), 262 (M+1). IR (KBr): 3098, 2921, 2849, 1746, 1576, 1535, 1350, 1300, 1153, 1114, 1030, 906. Compound **1e**: Solid. Mp 57–58 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (3H, t, *J* = 7.28 Hz), 2.98 (3H, s), 4.05 (3H, s), 4.55 (2H, q, *J* = 7.28 Hz), 8.07 (1H, d, *J* = 9.37 Hz), 8.40 (1H, d, *J* = 9.37 Hz), 8.87 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 23.1, 51.6, 70.0, 127.5, 130.2, 133.2, 141.1, 143.1, 150.9, 156.4, 161.0, 166.0. MS (ESI) *m*/*z* 297 (M+Na), 275 (M+1); IR (KBr) ν = 2925, 2854, 1719, 1617, 1553, 1445, 1318, 1236, 1086, 1020, 857, 758. Compound **3b**: Semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (3H, t, *J* = 6.83 Hz), 2.68 (3H, s), 4.53 (2H, q, *J* = 6.83 Hz), 7.78 (1H, t, *J* = 7.80 Hz), 8.01 (1H, d, *J* = 8.78 Hz), 8.13 (1H, d, *J* = 8.78 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.2, 61.0, 119.4, 129.3, 129.5, 138.2, 141.1, 142.0, 142.3, 161.0. MS (ESI) *m*/*z* 307 (M+Na), 285 (M+1); IR (KBr) ν = 2924, 2855, 1745, 1625, 1419, 1443, 1277, 1192, 1151, 1034, 827, 599 cm^{-1}. Compound **3c**: Solid. Mp 66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (3H, t, *J* = 7.17 Hz), 2.57 (6H, s), 4.52 (2H, q, *J* = 7.17 Hz), 7.98 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 18.8, 60.9, 119.8, 129.2, 129.7, 140.3, 140.9, 151.1, 151.8, 161.0. MS (ESI) *m*/*z* 299 (M+1); IR (KBr) ν = 3075, 2926, 2855, 1737, 1628, 1594, 1418, 1336, 1203, 1083, 806, 616. Compound **3d**: Semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (3H, t, *J* = 7.28 Hz), 4.57 (2H, q, *J* = 7.28 Hz), 8.44 (1H, d, *J* = 8.32 Hz), 8.72 (1H, d, *J* = 8.32 Hz), 9.13 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 70.0, 119.7, 124.4, 125.8, 141.9, 144.9, 145.1, 146.5, 146.7, 160.0. MS (ESI) *m*/*z* 338 (M+Na). IR (KBr): 2972, 2934, 1734, 1619, 1532, 1467, 1352 cm^{-1}. Compound **3e**: Semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (2H, t, *J* = 6.83 Hz), 4.04 (3H, s), 4.55 (2H, q, *J* = 6.83 Hz), 8.29 (1H, t, *J* = 7.80 Hz), 8.52 (1H, t, *J* = 7.80 Hz), 8.92 (1H, d, *J* = 8.78 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 51.5, 60.8, 119.8, 131.0, 133.6, 135.1, 142.0, 144.4, 145.2, 161.0, 165.9;. MS (ESI) *m*/*z* 351 (M+Na), 329 (M+1). IR (KBr) ν = 2926, 2853, 1737, 1628, 1594, 1550, 1418, 1201, 1054, 806, 616 cm^{-1}. Compound **6b**: Semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (6H, d, *J* = 6.79 Hz), 1.49 (3H, t, *J* = 7.17 Hz), 2.61 (3H, s), 3.65 (1H, m), 4.50 (2H, q, *J* = 7.17 Hz), 7.40 (1H, dd, *J* = 1.70, *J* = 6.79 Hz), 7.85 (1H, d, *J* = 8.49 Hz), 8.0 (1H, d, *J* = 8.49 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.3, 22.2, 32.4, 60.9, 127.87, 128.7, 136.6, 142.0, 148.4, 152.4, 161.2; MS (ESI) *m*/*z* 281 (M+Na), 259 (M+1). IR (KBr) ν = 2972, 2929, 1731, 1621, 1552, 1322, 1229, 1182, 1101, 1057, 828. Compound **6c**: Solid. mp 67–69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (6H, d, *J* = 6.24 Hz), 1.45 (3H, t, *J* = 7.28 Hz), 2.42 (3H, s), 2.44 (3H, s), 3.6 (1H, m), 4.44 (2H, q, *J* = 7.28 Hz), 7.77 (1H, s), 7.74 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 18.8, 22.1, 32.3, 60.9, 127.5, 129.1, 137.1, 141.9, 147.6, 150.0, 161.0. MS (ESI) *m*/*z* 295 (M+Na), 273 (M+1). IR (KBr): ν = 2970, 2931, 1732, 1552, 1459, 1320, 1230, 1182, 1103, 1055, 827. Compound **6d**: Semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (6H, d, *J* = 6.79 Hz), 1.51 (3H, t, *J* = 6.79 Hz), 3.68 (1H, m), 4.54 (2H, q, *J* = 6.79 Hz), 8.20 (1H, d, *J* = 9.06 Hz), 8.55 (1H, dd, *J* = 9.06 Hz, *J* = 11.33 Hz), 9.1 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.2, 32.2, 60.9, 122.4, 422.9, 141.5, 142.9, 152.6, 155.8, 161.0. MS (ESI) *m*/*z* 312 (M+Na), 290 (M+1). IR (KBr) ν = 2976, 2932, 2874, 1736, 1532, 1467, 1350, 1243, 1109, 1058, 849. Compound **6e**: Semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (2H, d, *J* = 7.28 Hz), 1.50 (3H, t, *J* = 7.28 Hz), 3.67 (1H, m), 4.0 (3H, s), 4.57 (2H, q, *J* = 7.28 Hz), 8.10 (1H, d, *J* = 8.32 Hz), 8.37 (1H, d, *J* = 8.32 Hz), 8.82 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.1, 32.3, 51.8, 60.9, 127.5, 130.4, 131.9, 133.4, 141.1, 143.1, 151.8, 154.5, 161.0, 165.9. MS (ESI) *m*/*z* 325 (M+Na). IR (KBr) ν = 2935, 2855, 1759, 1616, 1557, 1444, 1319, 1226, 1078, 1021, 850, 755.