

Research Article

Oxidative Carbonylation of Aromatic Amines with CO Catalyzed by 1,3-Dialkylimidazole-2-selenone in Ionic Liquids

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1,3-Dialkylimidazole-2-selenone as a novel substituted selenium heterocyclic catalyst was used to catalyze oxidative carbonylation of aromatic amines with carbon monoxide in the presence of air to symmetrical ureas in up to 97% yield in ionic liquids.

1. Introduction

In recent years, attention has been paid to a very promising nonphosgene process for the synthesis of various ureas, namely, the reductive carbonylation of nitrocompounds or the oxidative carbonylation of aromatic amines catalyzed by noble metals, including rhodium, ruthenium, and palladium [1–7]. However, oxidative carbonylation of amines or reductive carbonylation of nitrocompounds by selenium catalysts instead of noble metals has been reported to give symmetrical ureas [8–10]. Though these reactions possess these advantages such as the easily available catalyst and phase-transfer catalyst properties [11, 12], selenium-catalyzed carbonylation reactions have a disadvantage that the volatile selenium-containing intermediates (H_2Se) generated in the reaction produce unbearable and toxic odour. The use of selenium-containing catalyst is a trend in selenium-catalyzed reaction for safety and green chemistry purposes.

In the course of our ongoing investigations on the selenium-catalyzed carbonylation reaction, we have discovered that symmetrical ureas could be obtained from the carbonylation of nitrobenzene or substituted nitroarene under solvent-free conditions [13] or under atmospheric pressure [14] or in ionic liquids [15].

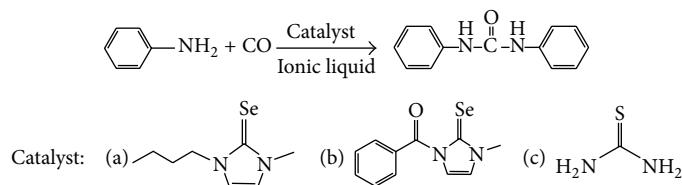
Recently, we also have reported the synthesis of 1,3-dialkylimidazole-2-selenones using 1,3-dialkylimidazolium salts with selenium in water or in ethanol or acetone [16, 17]. Keeping this result in mind, we reported 1,3-dialkylimidazole-2-selenone catalyzed oxidative carbonylation of aromatic

amines with carbon monoxide in the presence of oxygen in ionic liquids (Scheme 1).

2. Experimental

Imidazolin-2-selenones were synthesized according to the literature [17]. The organic solvents were all of reagent grade and were used without further purification. Ionic liquids were synthesized according to the literature [18]. Selenium (99.5%) and carbon monoxide (99%) and organic amines were all used as purchased. Melting points were determined on a Taike X-4 apparatus (Beijing, China) and are uncorrected. 1H and ^{13}C NMR spectra were obtained on a Bruker DRX 400 spectrometer. Chemical shifts were reported in parts per million relative to tetramethylsilane (δ units), with dimethylsulfoxide ($DMSO-d_6$) as solvent.

2.1. General Procedure. 5 mmol of aniline, 0.46 mmol of selenium-containing catalyst, and 0.25 g $[BMIM]BF_4$ were sealed in a 100 mL stainless steel autoclave. The reactor was pressurized with 0.2 Mpa oxygen and 1.1 Mpa carbon monoxide and then placed in an oil bath preheated to 90°C; after 6 h of the reaction time, the apparatus was degassed, and the 1,3-diaryl urea was separated from $[BMIM]BF_4$ by adding acetone and water to the reaction mixtures. Purification by column chromatography on silica gel or recrystallization gave the urea product. Products were identified by NMR measurements and/or comparison with authentic samples.



SCHEME 1

TABLE 1: The study of the reaction in different conditions.

Entry ^a	Catalyst a (mmol)	IL (g)	Base	Temperature (°C)	Yield (%) ^f
1	0.46	0.25	—	90	94
2 ^b	0.46	0.25	—	90	34
3 ^c	0.46	0.25	—	90	25
4 ^d	0.46	0.25	—	90	5
5	0.46	0	—	90	19
6	0.46	0.25 ^e	—	90	19
7	0.46	0.25	Et ₃ N	90	<3
8	0.46	0.25	K ₂ CO ₃	90	<5
9	0.46	0.25	—	60	34
10	0.46	0.50	—	60	57
11	0.46	0.25	HOAc	90	57

^aReaction conditions: aniline (5.0 mmol); IL is [BMIM]BF₄; Pair = 0.2 Mpa, Pair + Pco = 1.3 Mpa; ^bcatalyst is selenium; ^ccatalyst is **b**; ^dcatalyst is **c**; ^eIL is [BMIM]Cl; ^fisolated yields.

3. Results and Discussion

Aniline was treated with 1-butyl-3-methyl-imidazole-2-selenone and carbon monoxide and air in the presence of [BMIM]BF₄ at 90°C for 6 h. Oxidative carbonylation of aniline efficiently led to N,N-diphenylurea in 94% yield (Table 1, entry 1). We found that the reaction catalyzed by different catalysts exhibited different yields of urea (Table 1, entries 1–4) and **a** is the best catalyst in the reaction. The reaction proceeded very slowly in the absence of ionic liquid (Table 1, entry 5) and the efficiency of use of [BMIM]BF₄ is better than that of use of [BMIM]Cl (Table 1, entries 1 and 6). It is well known that the base plays an important role during selenium-catalyzed reaction [23, 24]. In the reaction, both Et₃N and K₂CO₃ increase the reaction efficiency but no reaction occurs (Table 1, entries 7–8). The reaction occurred without use of a base (Table 1). The yield of N,N-diphenylurea increased when adding amount of the [BMIM]BF₄ or raising the reaction temperature (Table 1, entries 1, 8–9). When HOAc was used in the reaction, the yield of N,N-diphenylurea is up to 57%; the reason may be decomposition of containing selenium catalyst under acidic condition (Table 1, entry 11).

To test the reusability of the catalyst and the ionic liquid, the oxidative carbonylation of aniline was performed using 1-butyl-3-methyl-imidazole-2-selenone as catalyst in the presence of CO and air (Pair = 0.2 Mpa, Pair + Pco = 1.3 Mpa) in ionic liquid at 90°C for 6 h (Table 2). After the reaction was complete, the 1,3-diaryl urea was separated from [BMIM]BF₄ by adding acetone and water to the reaction mixture; the resultant liquor containing the catalyst and ionic

TABLE 2: Reusability of the catalysts in the reaction.

Entry ^a	Cycle	Yield ^b
1	0	94
2	1	96
3	2	99
4	3	92

^aReaction conditions: catalyst **a** (0.46 mmol), [BMIM]BF₄ (0.25 g), aniline (5.0 mmol), Pair = 0.2 Mpa, Pair + Pco = 1.3 Mpa; temperature = 90°C; reaction time = 6 h; ^bisolated yields.

liquid was reused with a fresh charge of aniline. Catalyst exhibited better activity than it did in the original runs. The yield of the symmetrical urea increased upon recycling the catalyst, suggesting that unchanged substrates might have participated in the subsequent reaction (Table 2).

In a fashion similar to the synthesis of symmetrical ureas, the oxidative carbonylation of aniline was investigated, and the results are summarized in Table 3. It is noteworthy that all aromatic amines could undergo the same type of reactions under the conditions as stated in Table 3 (entries 1–6). Increasing steric hindrance on the phenyl rings of the substrate obviously dropped to the product yield (17%) (Table 3, entry 3). 1-Naphthylamine and 2-aminopyridine gave the corresponding ureas in 41% and 40% (Table 3, entries 5–6). When aniline and 4-methylaniline were used as the substrate, the yields of the intended products were obtained in 94% and 97% (Table 3, entries 1 and 2), but using 4-acetylaniline as the substrate, the product yield decreased in 7% rapidly (Table 3, entry 4).

TABLE 3: The synthesis of symmetrical ureas from organic amines.

Entry ^a	Substrates	Products	[BMIM]BF ₄ (g)	T (°C)	Yield (%) ^c
1 [19]			0.25	90	94
2 [19]			0.25	90	97
3 [19]			0.25	90	17
4 [19]			0.25	90	7
5 [20]			0.25	90	41
6 [21]			0.25	90	40
7 [3]			0.25	60	70
8 [3]			—	60	73
9 ^b [22]	CH ₃ CH ₂ NH ₂	CH ₃ CH ₂ NHCONHCH ₂ CH ₃	—	60	52
10			—	60	0
11 [22]	(CH ₃)(CH ₂) ₃ NH ₂	(CH ₃)(CH ₂) ₃ NHCONH(CH ₂) ₃ CH ₃	—	60	91
12 [22]	(CH ₃) ₂ CHNH ₂	(CH ₃) ₂ CHNHCONHCH(CH ₃) ₂	—	60	97
13 [19]			—	60	98

^aReaction conditions: catalyst **a** (0.10 g), [BMIM]BF₄ (0.25 g), amine (5.0 mmol); Pair + Pco = 1.3 Mpa; reaction time = 6 h; ^b65–75% aqueous solution; ^cisolated yields.

Aliphatic amines exhibited a higher activity than aromatic amines in a lower temperature (60°C). Without use of the ionic liquid, the reaction occurs satisfactorily (Table 3, entries 8-9). Complete conversions were achieved for aliphatic amines over a period of 6 h, and the symmetrical ureas were obtained in moderate to good yields (52–98%) after workup (Table 3, entries 7–12). When dimethylamine aqueous solution (65–75%) was used as the substrate, the product yield was 52% (Table 3, entry 9), but the reaction did not proceed in the presence of piperidine (Table 3, entry 10). Long-chain aliphatic amines and cyclohexanemethylamine afforded the symmetrical ureas in 91–98% yields (Table 3, entries 11–13).

4. Conclusion

In conclusion, we have found a synthetic method for the symmetrical ureas from amines and selenium-containing

catalyst and carbon monoxide through oxidative carbonylation reaction. The odour that exists in elemental selenium-catalyzed carbonylation reactions was not present in this catalytic system. The in situ generated inorganic selenium compounds (such as H₂Se) that are mainly responsible for the unbearable and toxic odour in selenium-catalyzed carbonylation reactions can be avoided because of selenium-containing catalyst (the chemical loading of selenium). Although the mechanism for formation of symmetrical ureas using selenium-containing catalyst has not been clarified, the reason may be the result of selenium-containing catalysts directly involved in the reaction and avoiding the generation of toxic gases. Further studies regarding the mechanism are underway.

Data of Some Products

N,N'-Diphenylurea: ¹H NMR (DMSO-d₆, 400 MHz): 8.68 (s, 2H), 7.47 (m, 4H), 7.29 (m, 4H), 6.98 (m, 2H);

^{13}C NMR (DMSO- d_6 , 400 MHz): $\delta = 152.5, 139.7, 128.8, 121.9, 118.2$.

N,N'-Bis(4-methylphenyl)urea: ^1H NMR (DMSO- d_6 , 400 MHz): 8.50 (s, 2H), 7.33 (d, 4H), 7.07 (d, 4H), 2.24 (s, 6H); ^{13}C NMR (DMSO- d_6 , 400 MHz): $\delta = 152.6, 137.2, 130.5, 129.2, 118.2, 20.4$.

N,N'-Bis(2-methylphenyl)urea: ^1H NMR (DMSO- d_6 , 400 MHz): 8.24 (s, 2H), 7.82 (d, 2H), 7.18–7.13 (m, 4H), 6.95 (m, 2H), 2.26 (s, 6H); ^{13}C NMR (DMSO- d_6 , 400 MHz): $\delta = 152.9, 137.5, 130.2, 127.7, 126.1, 122.7, 121.5, 18.0$.

N,N'-Bis(4-methoxyphenyl)urea: ^1H NMR (DMSO- d_6 , 400 MHz): 9.26 (s, 2H), 8.17 (d, 4H), 7.89 (d, 4H), 2.77 (s, 6H); ^{13}C NMR (DMSO- d_6 , 400 MHz): $\delta = 195.7, 151.5, 143.6, 130.7, 130.1, 129.1, 117.3, 25.7$.

N,N'-Dimethylurea: ^1H NMR (DMSO- d_6 , 400 MHz): 5.50 (s, 2H), 3.19 (q, 4H), 1.11 (t, 6H); ^{13}C NMR (DMSO- d_6 , 400 MHz): $\delta = 158.8, 34.5, 15.1$.

N,N'-Diisopropylurea: ^1H NMR (DMSO- d_6 , 400 MHz): 5.36 (d, 2H), 3.68 (m, 2H), 1.02 (d, 12H); ^{13}C NMR (DMSO- d_6 , 400 MHz): $\delta = 156.6, 40.38, 22.8$.

Conflict of Interests

The authors would like to declare that they do not have any commercial or associative interests that represent a conflict of interests in connection with the submitted paper.


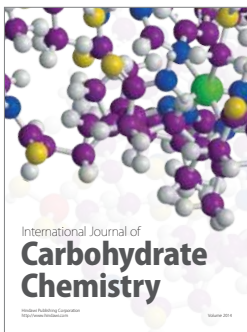
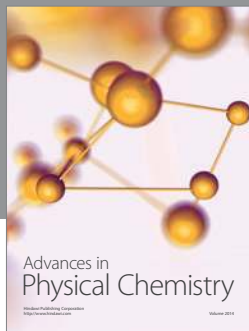
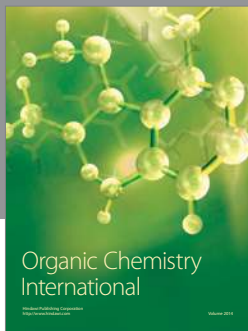
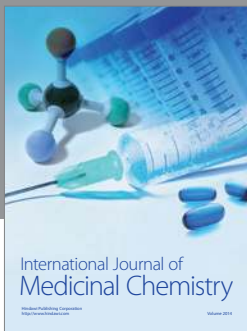
Acknowledgments

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