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A facile one-pot phosgene-free synthesis of naphthalen-1-ylcarbamates by selenium-catalyzed carbonylation of 1-nitronaphthalene with carbon monoxide

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ABSTRACT

With selenium as catalyst and triethylamine as cocatalyst, a facile one-pot phosgene-free synthesis of naphthalen-1-ylcarbamates by selenium-catalyzed redox carbonylation of 1-nitronaphthalene with alcohols and carbon monoxide was achieved. The effects of temperature, pressure, time, and the content of catalyst, triethylamine and alcohol on the reaction were studied. It turned out that the reaction proceeded efficiently under optimized conditions with a series of alcohols to afford the corresponding naphthalen-1-ylcarbamates in fair to good yields.

1. Introduction

Carbamates are useful compounds with a wide range of applications in the production of commodity chemicals like polyurethanes, coating, adhesives, plastics and fibers [1]. They also find utilizations in agrochemical industry as herbicides, fungicides and pesticides [2–4] and in pharmaceutical industry as drug intermediates [5–7]. In addition, carbamates are often used as protecting groups for amine functionality in organic synthesis [8,9]. The conventional process for the preparation of carbamates usually consists of three separate steps as hydrogenation of a nitro aromatic, subsequent phosgenation of the resulting aromatic amine, and then addition of alcohol to the resulting isocyanate. This classical method needs to be sufficiently improved due to its multistep approach, employing extremely toxic phosgene and producing large amounts of corrosive HCl as a side product [10–12]. Therefore, in recent years, great efforts have been made to replace phosgene-based technology with environmentally benign routes for the preparation of carbamate compounds. One of the most attractive approaches is the one-pot procedure of catalytically reductive carbonylation of nitro compounds with carbon monoxide in the presence of alcohol using group VIII transition metal complexes [11,12] such as palladium [13], ruthenium [14] and rhodium [14,15] as catalysts. However, the high cost and low availability of the transition metal catalyst system together with the energy consumable separation process made this approach very uneconomical. During the last decades, nonmetal selenium has been found to be an efficient and economical catalyst for the carbonylation of nitro aromatics [16,17], amines [17,18] and alcohols [17,19], etc. Although in some cases selenium may remain present as traces in the corresponding products, it is still an attractive catalyst for carbonylation reaction due to selenium's low cost, high efficacy and easy availability. As a result of research in this regard, some carbamates were synthesized by selenium-catalyzed carbonylation of nitro compounds with alcohols in the presence of carbon monoxide [17,20–22], but their variety is very limited. Therefore, further pursue for diversely functionalized carbamates is still an interesting topic.

In this paper, we report for the first time a facile one-pot phosgene-free synthesis of naphthalen-1-ylcarbamates from selenium-catalyzed carbonylation of 1-nitronaphthalene with a series of alcohols in the presence of carbon monoxide (Scheme 1). The main factors affecting the reaction such as reaction temperature, pressure, reaction time, and the content of catalyst, triethylamine and alcohol were examined carefully. It was demonstrated that with triethylamine as cocatalyst, the selenium-catalyzed carbonylation of 1-nitronaphthalene proceeded efficiently under optimized conditions with a series of alcohols to afford the corresponding naphthalen-1-ylcarbamates in fair to good yields.

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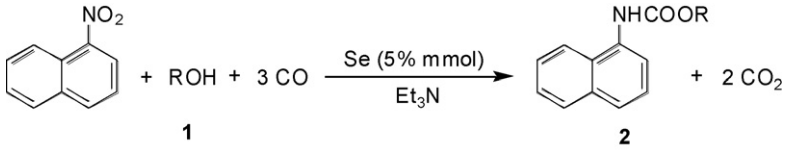

Scheme 1. Selenium-catalyzed carbonylation of 1-nitronaphthaene with alcohols to naphthalen-1-ylcarbamates.

2. Experimental

2.1. Materials and instruments

Selenium power (99.95%) and carbon monoxide (99.9%) were used as purchased. All other chemicals were A. R. grade and used without further purification. Melting points were determined on a Keyi XT4 apparatus (Beijing, China) and were uncorrected. ^{1}H NMR spectra were measured on a Bruker DPX 400 spectrometer in $CDCl_3$ with Me_4Si as internal standard.

2.2. General procedure for the selenium-catalyzed carbonylation to naphthalen-1-ylcarbamates

All the selenium-catalyzed carbonylation reactions were carried out in a 100 ml stainless steel autoclave equipped with magnetic stirrer. 1-Nitronaphthalene (5 mmol), selenium (0.25 mmol), triethylamine (10 mmol) and alcohol (25 mmol) were added to the autoclave in turn. After being sealed, the reactor was flushed three times with carbon monoxide. Then carbon monoxide was introduced into the autoclave to the desired pressure. Subsequently, the reactor was immersed in an oil bath preheated to the required temperature with stirring. Upon completion, the reactor was cooled to room temperature and the residual gas was released. The reaction mixture was stirred for 30 min to precipitate selenium, which was then collected by suction. The filtrate was concentrated and the residual was purified either by column chromatography (silica gel, ethyl acetate–petroleum ether, 1:10–1:15) or by crystallization from petroleum ether to give naphthalen-1-ylcarbamates. The purity and structure of the product was checked by ^{1}H NMR.

3. Results and discussion

3.1. Preparation of naphthalen-1-ylcarbamates

To demonstrate the scope and efficiency of the selenium-catalyzed carbonylation reaction, a series of alcohols were tried under optimized conditions (Table 1). As shown in Table 1, the selenium-catalyzed carbonylation reaction can tolerate structurally diverse alcohols, affording the corresponding naphthalene-1-ylcarbamates mostly in fair to good yields. The reaction proceeded well and completed in 6 h with short chain alcohols (entries 1–4), affording the corresponding carbamates in good yields except for the branched isopropanol (entry 4). This is mostly due to the greater steric hindrance of isopropanol, resulting in lower reactivity than the straight alcohols. For alcohols with longer chain, the carbonylation reaction needs 10 h to complete, but the yields are equally good (entries 5, 6, 8 and 9, 11–14). It is also demonstrated that the greater the steric hindrance of the alcohols, the lower their reactivity, accordingly, the lower the yields of corresponding products. For example, with highly branched *tert*-butyl alcohol (entry 7) or *tert*-pentyl alcohol (entry 10), no desired products were obtained.

3.2. Effect of reaction conditions

Taking selenium-catalyzed carbonylation of 1-nitronaphthalene with ethanol as a model reaction, the main factors affecting the carbonylation reaction such as temperature, time, pressure of carbon monoxide, and the content of alcohol, triethylamine and selenium were studied systematically.

Table 1
The selenium-catalyzed carbonylation of 1-nitronaphthalene in alcohol media to naphthalen-1-ylcarbamates.[a].

Entry	R	Alcohol	Conversion[b] (%)	Product	mp (°C)		Product yield[c] (%)
					Found	Lit.	
1[d]	Methyl	**1a**	100	**2a**	118–119	124 [23]	89
2[d]	Ethyl	**1b**	100	**2b**	78	75–76 [24]	86
3[d]	Propyl	**1c**	100	**2c**	72	76 [25]	81
4[d]	Isopropyl	**1d**	100	**2d**	103	105 [26]	52
5[e]	Butyl	**1e**	100	**2e**	66	72 [25]	77
6[e]	Sec-butyl	**1f**	100	**2f**	93	97–98 [25]	48
7[e]	Tert-butyl	**1g**	15	**2g**	–	98–99 [27]	0
8[e]	Pentyl	**1h**	100	**2h**	67	68 [28]	80
9[e]	Isopentyl	**1i**	100	**2i**	60	67–68 [25]	74
10[e]	Tert-pentyl	**1j**	12	**2j**	–	71–72 [25]	0
11[e]	Hexyl	**1k**	100	**2k**	58	59 [29]	81
12[e]	Cyclohexyl	**1l**	100	**2l**	126–127	128–129 [28]	84
13[e]	Heptyl	**1m**	100	**2m**	57–58	60–61 [25]	57
14[e]	Octyl	**1n**	100	**2n**	65	66 [25]	46

[a] *Reaction conditions*: 1-nitronaphthalene, 5 mmol; alcohol, 25 mmol; selenium, 0.25 mmol; triethylamine, 10 mmol; CO pressure, 2.0 MPa; temperature, 160 °C.
[b] Based on 1-nitronaphthalene.
[c] Isolated yields.
[d] 6 h.
[e] 10 h.

Table 2
Effect of reaction temperature on selenium-catalyzed carbonylation of 1-nitronaphthalene.[a].

Entry	Temperature (°C)	Conversion[b] (%)	Product yield[c] (%)	Amine yield[c] (%)
1	120	62	54	2
2	140	78	68	9
3	160	100	86	14
4	180	100	83	15
5	200	100	81	18

[a] *Reaction conditions*: 1-nitronaphthalene, 5 mmol; ethanol, 25 mmol; selenium, 0.25 mmol; triethylamine, 10 mmol; CO, 2.0 MPa; time, 6 h.
[b] Based on 1-nitronaphthalene.
[c] Isolated yield.

3.2.1. Effect of temperature

In order to gain insight into the effect of temperature on the synthesis of naphthalen-1-ylcarbamates, the carbonylation reaction was conducted at different temperatures and the results were summarized in Table 2.

The results revealed that the conversion of 1-nitronaphthalene and the yields of naphthalen-1-ylcarbamate were gradually increased with the increase of the reaction temperature from 120 to 160 °C (entries 1–3). It turned out that 1-nitronaphthalene was completely consumed and the product yield reached maximum in 6 h at 160 °C (entry 3). With higher temperature than 160 °C, the yield of naphthalene-1-ylcarbamates decreased. Meanwhile, an increase of the sideproduct naphthalen-1-amine was detected (entries 4 and 5).

3.2.2. Effect of time

Next, we examined the effect of time on the carbonylation reaction and the results are shown in Table 3.

The result showed a fast rise both in the conversion of 1-nitronaphthalene and in the product yield within the initial reaction period (entries 1 and 2). The reaction reached a completion within 6 h with yields of 86% for naphthalen-1-ylcarbamate and 14% for naphthalen-1-amine, respectively (entry 3). There was no distinct increase in the product yield with longer reaction period than 6 h (entries 4 and 5) most probably because the reaction reached an equilibrium in 6 h. With longer chain alcohols, it was necessary to lengthen the reaction time to achieve satisfactory results.

3.2.3. Effect of CO pressure

The effect of CO pressure on the reaction is shown in Table 4. From the results it can be deduced that within certain reaction period higher pressure of CO results in faster conversion of the starting material and higher yield of the corresponding product (entries 1 and 2). It is also demonstrated that the optimum pressure is 2.0 MPa with a yield of 86% and a 100% conversion (entry 3).

Table 3
Effect of reaction time on selenium-catalyzed carbonylation of 1-nitronaphthalene.[a].

Entry	Time (h)	Conversion[b] (%)	Product yield[c] (%)	Amine yield[c] (%)
1	2	43	41	2
2	4	78	68	9
3	6	100	86	14
4	8	100	85	14
5	10	100	86	14

[a] *Reaction conditions*: 1-nitronaphthalene, 5 mmol; ethanol, 25 mmol; selenium, 0.25 mmol; triethylamine, 10 mmol; temperature, 160 °C; CO, 2.0 MPa.
[b] Based on 1-nitronaphthalene.
[c] Isolated yield.

Table 4
Effect of CO pressure on selenium-catalyzed carbonylation of 1-nitronaphthalene.[a].

Entry	CO pressure (MPa)	Conversion[b] (%)	Product yield[c] (%)	Amine yield[c] (%)
1	1.0	62	58	3
2	1.5	83	74	8
3	2.0	100	86	14
4	3.0	100	86	13

[a] *Reaction conditions*: 1-nitronaphthalene, 5 mmol; ethanol, 25 mmol; selenium, 0.25 mmol; triethylamine, 10 mmol; temperature, 160 °C; time, 6 h.
[b] Based on 1-nitronaphthalene.
[c] Isolated yield.

Table 5
Effect of alcohol content on selenium-catalyzed carbonylation of 1-nitronaphthalene.[a].

Entry	Alcohol (mmol)	Conversion[b] (%)	Product yield[c] (%)	Amine yield[c] (%)
1	5	50	46	3
2	10	84	78	4
3	25	100	86	14
4	50	100	85	14

[a] *Reaction conditions*: 1-nitronaphthalene, 5 mmol; selenium, 0.25 mmol; triethylamine, 10 mmol; temperature, 160 °C; CO, 2.0 MPa; time, 6 h.
[b] Based on 1-nitronaphthalene.
[c] Isolated yield.

3.2.4. Effect of alcohol content

Results in Table 5 show the influence of alcohol content on the carbonylation reaction.

It can be seen from Table 5 that the conversion of 1-nitronaphthalene and the product yield increased evidently with the increase of alcohol amount from 5 mmol to 25 mmol (entries 1–3). Alcohol here acts as both substrate and solvent, so excessive amount of alcohol is appropriate for the carbonylation reaction. The conversion of 1-nitronaphthalene and the yield of corresponding naphthalen-1-ylcarbamate achieved maximum when the molar ratio of alcohol to 1-nitronaphthalene reached 5 (entry 3). Further increase of alcohol amount failed to gain any increase in product yield (entry 4).

3.2.5. Effect of triethylamine content

The influence of triethylamine as cocatalyst on the carbonylation reaction is shown in Table 6.

The reaction failed to proceed in the absence of triethylamine (entry 1), while the substrate conversion and the product yield increased observably with addition of triethylamine (entries 2 and 3), which indicates that triethylamine is indispensable for this selenium-catalyzed carbonylation reaction. The role of triethylamine here is believed to promote the formation of the active carbonyl selenide (SeCO) which is usually formed *in situ* by the reaction of selenium with CO in basic conditions. When the molar ratio

Table 6
Effect of triethylamine content on selenium-catalyzed carbonylation of 1-nitronaphthalene.[a].

Entry	Triethylamine (mmol)	Conversion[b] (%)	Product yield[c] (%)	Amine yield[c] (%)
1	0	0	0	0
2	1	31	28	1
3	5	69	64	4
4	10	100	86	14
5	15	100	86	13

[a] *Reaction conditions*: 1-nitronaphthalene, 5 mmol; ethanol, 25 mmol; selenium, 0.25 mmol; temperature, 160 °C; CO, 2.0 MPa; time, 6 h.
[b] Based on 1-nitronaphthalene.
[c] Isolated yield.

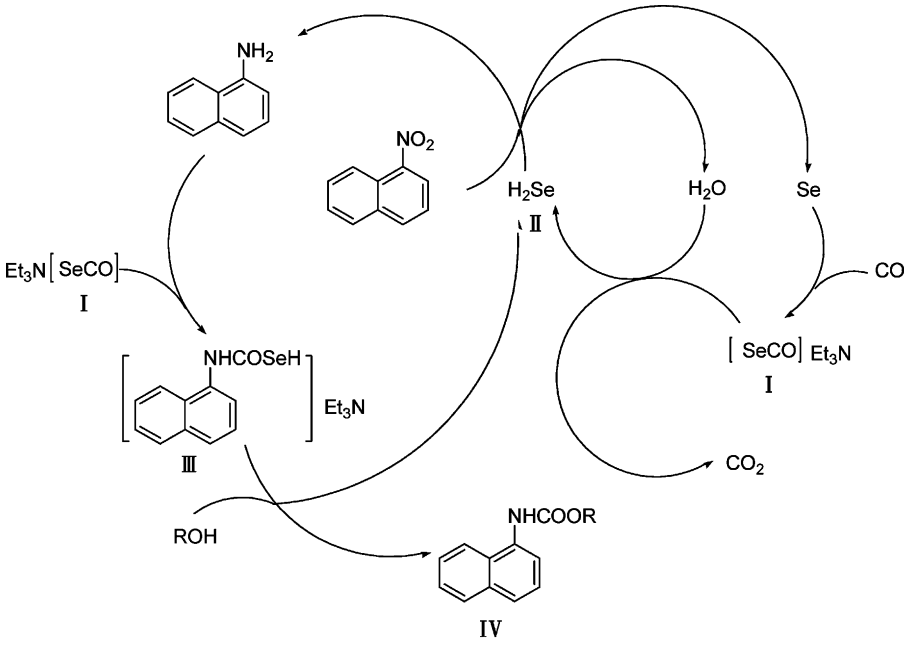

Fig. 1. A proposed reaction pathway to naphthalen-1-ylcarbamates.

of triethylamine to 1-nitronaphthalene reached 2, 100% conversion and maximum product yield could be achieved (entry 4).

3.2.6. Effect of selenium content

Table 7 shows the representative results of the effect of selenium amount on the carbonylation reaction. When no selenium was used, the reaction could not proceed at all (entry 1). With the increase of selenium content, the conversion and the product yield increased accordingly (entries 2 and 3). The reaction reached completion and gave naphthalen-1-ylcarbamate in 86% yield when selenium content reached 0.25 mmol (entry 4).

3.3. A possible reaction pathway to naphthalen-1-ylcarbamates

A plausible pathway for the selenium-catalyzed carbonylation was shown in Fig. 1. Firstly, the reaction was initiated by the formation of carbonyl selenide **I** [17], which was generated *in situ* from the reaction of carbon monoxide and selenium in the presence of triethylamine. Then, **I** reacted with small amount of water present as impurities in the reagents to form hydrongen selenide **II** with the release of carbon dioxide [30]. As the next step, 1-nitronaphthalene was reduced to the corresponding naphthalen-1-amine by the *in situ* formed **II** [31] and **II** was oxidized to selenium and ready for the next catalytic cycle. The subsequent nucleophilic attack of naphthalen-1-amine on **I** produced selenocarbamicacid salts **III**. Then **III** underwent nucleophilic attack of alcohol to afford the desired naphthalen-1-ylcarbamates **IV** with the formation of hydrogen selenide **II**. Hydrogen selenide was then oxidized to selenium again by 1-nitronaphthalene for the coming catalytic cycle.

Table 7
Effect of selenium content on the carbonylation of 1-nitronaphthalene.[a].

Entry	Se (mmol)	Conversion[b] (%)	Product yield[c] (%)	Amine yield[c] (%)
1	0	0	0	0
2	0.05	31	29	1
3	0.10	60	55	4
4	0.25	100	86	14

[a] *Reaction conditions*: 1-nitronaphthalene, 5 mmol; ethanol, 25 mmol; triethylamine, 10 mmol; temperature, 160 °C; CO, 2.0 MPa; time, 6 h.
[b] Based on 1-nitronaphthalene.
[c] Isolated yield.

4. Conclusion

In summary, a facile one-pot phosgene-free synthesis of naphthalen-1-ylcarbamates has been developed. With cheap and easily available selenium as catalyst, triethylamine as cocatalyst, the carbonylation reaction of 1-nitronaphthalene proceeded well with a series of alcohols in the presence of carbon monoxide under optimized conditions to afford the corresponding naphthalen-1-ylcarbamates in fair to good yields.

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