A selenium-catalysed synthesis of thiocarbamates from nitroarenes, carbon monoxide and thiols under mild conditions

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An improved method for the selenium-catalysed synthesis of thiocarbamates under mild conditions has been developed. With acetone as solvent, the one-pot selenium-catalysed carbonylation of nitroarenes and thiols with carbon monoxide proceeds smoothly at atmospheric pressure and ambient temperature.

Keywords: selenium, carbonylation, thiocarbamates, carbon monoxide

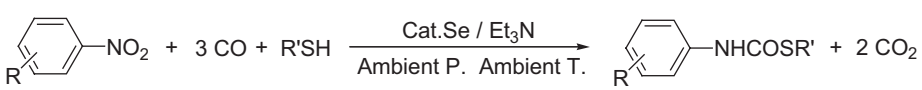
Thiocarbamates are frequently employed as bactericides[1] and antivirals[2] in medicine and as pesticides[3] and herbicides[4] in agricultural applications. Their biological activities as bioregulators[5] and enzyme inhibitors[6] are also well known. Numerous methods have been developed for the synthesis of such compounds. Carbonylation of amines and elemental sulfur with carbon monoxide, followed by alkylation with alkyl halides, provides an attractive process for their preparation;[7-9] however, multistep approaches are the primary problem of this method. An alternative approach to thiocarbamates is intramolecular rearrangements of various derivatives. However, these methods are extremely limited in starting materials.[10,11] Thiocarbamates can also be obtained by treating thiols with isocyanates, carbamoyl chlorides or carbamoylimidazolium salts or by treating chlorothioformates with amines; unfortunately, the necessary intermediates are typically prepared directly or indirectly from phosgene.[12,13] Although oxidative coupling of aryl thiols with amines and carbon monoxide is available, complex and expensive catalysts are limitations associated with this method.[14] In addition to above approaches, thiocarbamates synthesis has also been accomplished by selenium-catalysed[15] or palladium-catalysed[16] carbonylation of amines with disulfides, by carbonylation of aniline with thiols mediated by stoichiometric[17] or catalytic[18] selenium, and by the reaction of trichloroacetyl chloride with thiols and amines.[19] Cyclic thiocarbamates have been reported to have been formed by the reaction of amino thiols with carbon monoxide in the presence of selenium.[20]

Recently, we demonstrated a novel one-pot approach to thiocarbamates, *i.e.*, catalysed by selenium, carbonylation of nitroarenes with thiols proceeded efficiently, affording the corresponding thiocarbamates mostly in moderate to good yields.[21] However, with an autoclave as reactor, this approach proceeded at elevated temperature and with pressurised carbon monoxide, leading to higher cost and inconvenience for industrial production.

Due to the extensive applications of thiocarbamates, development of mild synthetic methods is of great importance. Thus, during the course of our ongoing investigations we made efforts to explore milder conditions for our above selenium-catalysed approach to thiocarbamates. We now report our facile one-pot selenium-catalysed synthesis of thiocarbamates under atmospheric pressure and ambient temperature conditions. With acetone as solvent, the facile one-pot selenium-catalysed carbonylation reaction of nitroarenes and thiols with carbon monoxide proceeds smoothly under atmospheric pressure and ambient temperature conditions, affording the corresponding thiocarbamates mostly in moderate to good yields (Scheme 1).

Our initial studies began with an investigation of selenium-catalysed carbonylation of nitrobenzene with propane-1-thiol at atmospheric pressure of carbon monoxide under various conditions. The results are summarised in Table 1. As shown in entries 1 and 2 (Table 1), no reaction occurred in the absence of either selenium or base, indicating that both selenium and base were necessary for the carbonylation. The carbonylation of nitrobenzene (5 mmol) with thiol (10 mmol) in the presence of 5 mol% or 10 mol% of the catalyst gave the product with similar yields (entries 3 and 4). This result showed that 5 mol% of catalyst was sufficient. Thus, further investigations were carried out in the presence of 5 mol% of selenium to explore the optimised reaction conditions. The effect of different bases, such as Et_3N, KOH, NaOH, NaOAc, and pyridine, on the selenium-catalysed carbonylation was first examined and Et_3N was shown to be superior to the others (entries 3, 5 and 8). When one equivalent of thiol with respect to nitrobenzene was used, only 53% yield of the desired thiocarbamate was obtained (entry 9), whereas two or three equivalents of propane-1-thiol afforded the product in yields of 79% and 80%, respectively (entries 3 and 10). The effects of solvents were also tested (entries 3, 11 and 14) and acetone was shown to be the best choice because of the very good yield (entry 3). Furthermore, the effect of reaction temperature was studied. The reaction was carried out in ambient temperature to provide a good yield (entry 3), while at 50 °C and at 70 °C, the yields were decreased to 42% and 29%, respectively (entries 15 and 16). The results obtained showed that the optimised reaction of nitrobenzene was carried out with 2 equiv. of thiol in acetone and Et_3N at ambient temperature in the presence of 5 mol% of selenium catalyst. After the reaction was completed, selenium could be easily separated from reaction mixture by simple filtration after its precipitation. The desired thiocarbamate was then purified by column chromatography or by recrystallisation from light petroleum ether.

Using the optimised reaction conditions, selenium-catalysed carbonylations of nitrobenzene with a series of thiols and aryl thiols were performed and the results are listed in Table 2.



Scheme 1

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Table 1 Carbonylation of nitrobenzene with propane-1-thiol under various conditions[a]

Entry	Se (mmol)	Base (2.5 mmol)	Thiol/mmol	Solvent (2 ml)	Reaction temperature	Yield/%[b]
1	0	Et_3N	10	Acetone	Ambient temperature	0
2	0.25	None	10	Acetone	Ambient temperature	0
3	0.25	Et_3N	10	Acetone	Ambient temperature	79
4	0.50	Et_3N	10	Acetone	Ambient temperature	80
5[c]	0.25	KOH	10	Acetone	Ambient temperature	0
6[c]	0.25	NaOH	10	Acetone	Ambient temperature	0
7[c]	0.25	NaOAc	10	Acetone	Ambient temperature	0
8	0.25	Pyridine	10	Acetone	Ambient temperature	31
9	0.25	Et_3N	5	Acetone	Ambient temperature	53
10	0.25	Et_3N	15	Acetone	Ambient temperature	80
11	0.25	Et_3N	10	None	Ambient temperature	14
12	0.25	Et_3N	10	Hexane	Ambient temperature	23
13	0.25	Et_3N	10	THF	Ambient temperature	32
14	0.25	Et_3N	10	DMF	Ambient temperature	22
15	0.25	Et_3N	10	Acetone	50 °C	42(15)[d]
16	0.25	Et_3N	10	Acetone	70 °C	29(23)[d]

[a]Reaction conditions: nitrobenzene, 5 mmol; atmosphere pressure of CO; ambient temperature; 15 h. [b]Isolated yield. [c]Additional 0.1 ml H_2O. [d]Diphenylurea.

The reaction proceeded smoothly under atmospheric pressure and ambient temperature. The structures of thiols evidently affected the reaction. Good yields were obtained when linear chain thiols were used (Table 2, entries 1, 2, 4, 6 and 7); and bulky thiols gave lower yields (Table 2, entries 3, 8, 9). No reaction took place when *tert*-butanethiol was used due to its steric bulkiness (Table 2, entry 5). When aryl thiols were used, much lower yields of the corresponding thiocarbamates were obtained due to their weak nucleophilicity. The aryl thiols with electron-donating groups such as 4-methoxybenzenethiol were more reactive than those with electron-withdrawing groups such as 4-chlorobenzenethiol (Table 2, entries 11, 13).

To expand the scope of reaction substrates, various substituted nitroarenes were employed under the same mild conditions. As summarised in Table 3, the reaction can proceed smoothly with many different nitroarenes, affording the desired thiocarbamates with yields ranging from 42 to 81% with the exception of 2-chloronitrobenzene. In addition to nitroarenes, as an example of nitroheteroaromatics, we have performed a carbonylation of 2-methoxy-5-nitropyridine with propane-1-thiol and found that the reaction worked well, affording the corresponding thiocarbamate in 77% isolated yield in 15 h (Table 3, entry 13). Both steric hindrance and electron effects of nitroarenes seemed to influence the reaction. The electron-rich ones (Table 3, entries 6–13) showed higher reactivity than the electron-deficient ones (Table 3, entries 1–5). Steric hindrance seemed to be the reason that the nitroarenes with substituents in the *ortho*-position (Table 3, entries 1, 6, 11) were less reactive than those with substituents in the *para*-position (Table 3, entries 3, 8, 12). The combined effect of electronic and steric factors was the most probable reason that 2-chloronitrobenzene failed to undergo this reaction (Table 3, entry 1).

Table 2 Selenium-catalysed carbonylation of nitrobenzene with different thiols[a]

Entry	R	R'	Product	Yield/%[b]
1	H	Ethyl	**1a**	77
2	H	Propyl	**1b**	79
3	H	Isopropyl	**1c**	52
4	H	Butyl	**1d**	76
5	H	*tert*-Butyl	**1e**	0
6	H	Pentyl	**1f**	72
7	H	Hexyl	**1g**	70
8	H	Cyclohexyl	**1h**	61
9	H	Benzyl	**1i**	61
10	H	Phenyl	**1j**	21
11	H	4-Chlorophenyl	**1k**	14
12	H	4-Methylphenyl	**1l**	30
13	H	4-Methoxyphenyl	**1m**	42

[a]Reaction conditions: nitrobenzene, 5 mmol; thiol, 10 mmol; Se, 0.25 mmol; Et_3N, 2.5 mmol; acetone, 2 ml; atmosphere pressure of CO; ambient temperature; 15 h. [b]Isolated yield.

Table 3 Selenium-catalysed carbonylation of propane-1-thiol with different nitroarenes[a]

Entry	R	R'	Product	Yield/%[b]
1	2-Chloro	Propyl	**2a**	0
2	3-Chloro	Propyl	**2b**	57
3	4-Chloro	Propyl	**2c**	42
4	4-Bromo	Propyl	**2d**	43
5	4-Acetyl	Propyl	**2e**	52
6	2-Methyl	Propyl	**2f**	54
7	3-Methyl	Propyl	**2g**	71
8	4-Methyl	Propyl	**2h**	73
9	4-Ethyl	Propyl	**2i**	73
10	4-Isopropyl	Propyl	**2j**	72
11	2-Methoxy	Propyl	**2k**	74
12	4-Methoxy	Propyl	**2l**	81
13	2-Methoxy-5-nitropyridine	Propyl	**2m**	77

[a]Reaction conditions: nitroarenes, 5 mmol; thiol, 10 mmol; Se, 0.25 mmol; Et_3N, 2.5 mmol; acetone, 2 ml; atmosphere pressure of CO; ambient temperature; 15 h. [b]Isolated yield.

In conclusion, we have developed a facile one-pot method for the synthesis of thiocarbamates from nitroarenes, carbon monoxide and thiols through selenium-catalysed carbonylation reaction at atmospheric pressure and ambient temperature. This procedure offers many advantages including simple starting materials, cheap catalyst, one-pot synthesis, very mild reaction conditions, simple experimental procedures and simple workup, which make it an attractive strategy for larger scale production.

Experimental

Elemental selenium (99.99%) and carbon monoxide (99.9%) used as purchased. Nitroarenes, thiols, triethylamine and acetone were reagent grade and used without further purification. Melting points were determined on a Taike X-4 apparatus (Beijing, China) and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker DRX 400 spectrometer at ambient temperature, with $CDCl_3$ as solvent and Me_4Si as internal standard.

General procedure for the selenium-catalysed synthesis of thiocarbamates (**1a–d**, **1f–m** *and* **2b–2m**)

To a 500-ml three-neck round-bottom flask was added selenium (0.25 mmol). The flask was sealed, subjected to a vacuum and flushed with carbon monoxide three times in turn. Carbon monoxide was then introduced again into the flask and the flask was connected to a bag containing carbon monoxide. Into the flask the mixture of nitroarene

(5 mmol), thiol (10 mmol), triethylamine (2.5 mmol), and acetone (2 ml) was injected. The reaction proceeded at ambient temperature with vigorous stirring for 15 h. After the apparatus was opened, the reaction mixture was dissolved in THF and stirred for another 30 min to precipitate selenium which could be recovered by filtration. The filtrate was concentrated and the residue was purified either by column chromatography or by recrystallisation from light petroleum ether to give the product thiocarbamate.

N-Phenylthiocarbamic acid S-ethyl ester (**1a**): M.p. 67–68 °C (lit.[18] 67–68 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43–7.09 (m, 6H), 2.99 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.4 Hz, 3H).

N-Phenylthiocarbamic acid S-propyl ester (**1b**): M.p. 83–84 °C (lit.[18] 83–84 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.07 (m, 6H), 2.95 (t, *J* = 8.0 Hz, 2H), 1.68 (m, 2H), 0.99 (t, *J* = 8.0 Hz, 3H).

N-Phenylthiocarbamic acid S-isopropyl ester (**1c**): M.p. 112–113 °C (lit.[18] 112–113 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.09 (m, 6H), 3.72 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 6H).

N-Phenylthiocarbamic acid S-butyl ester (**1d**): M.p. 73–74 °C (lit.[18] 73–74 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.42–7.08 (m, 6H), 2.98 (t, *J* = 8.0 Hz, 2H), 1.64 (m, 2H), 1.42 (m, 2H), 0.93 (t, *J* = 8.0 Hz, 3H).

N-Phenylthiocarbamic acid S-pentyl ester (**1f**): M.p. 47–48 °C (lit.[18] 47–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.59 (brs, 1H), 7.41–7.05 (m, 5H), 2.95 (t, *J* = 8.0 Hz, 2H), 1.64 (m, 2H), 1.33 (m, 4H), 0.87 (t, *J* = 8.0 Hz, 3H).

N-Phenylthiocarbamic acid S-hexyl ester (**1g**): M.p. 69 °C (lit.[18] 69 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.41–7.08 (m, 6H), 2.96 (t, *J* = 8.0 Hz, 2H), 1.65 (m, 2H), 1.38 (m, 2H), 1.29 (m, 4H), 0.88 (t, *J* = 8.0 Hz, 3H).

N-Phenylthiocarbamic acid S-cyclohexyl ester (**1h**): M.p. 115–116 °C (lit.[18] 115–116 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.03 (m, 6H), 3.54 (t, *J* = 3.6 Hz, 1H), 2.05–1.27 (m, 10H).

N-Phenylthiocarbamic acid S-benzyl ester (**1i**): M.p. 97–98 °C (lit.[18] 97–98 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.31–6.99 (m, 11H), 4.13 (s, 2H).

N-Phenylthiocarbamic acid S-phenyl ester (**1j**): M.p. 122–123 °C (lit.[18] 122–123 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.08 (m, 11H).

N-Phenylthiocarbamic acid S-4-chlorophenyl ester (**1k**): M.p. 147–148 °C (lit.[18] 147–148 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.10 (m, 10H).

N-Phenylthiocarbamic acid S-4-methylphenyl ester (**1l**): M.p. 131–132 °C (lit.[18] 131–132 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.08 (m, 10H), 2.38 (s, 3H).

N-Phenylthiocarbamic acid S-4-methoxyl-phenyl ester (**1m**): M.p. 109–110 °C (lit.[18] 109–110 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–6.93 (m, 10H), 3.81 (s, 3H).

N-(3-chlorophenyl)thiocarbamic acid S-propyl ester (**2b**): M.p. 52–53 °C (lit.[21] 52–53 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.26–7.05 (m, 4H), 2.95 (t, *J* = 8.0 Hz, 2H), 1.69 (m, 2H), 1.00 (t, *J* = 8.0 Hz, 3H).

N-(4-chlorophenyl)thiocarbamic acid S-propyl ester (**2c**): M.p. 92 °C (lit.[21] 91–92 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.22 (m, 5H), 2.95 (t, *J* = 8.0 Hz, 2H), 1.68 (m, 2H), 0.99 (t, *J* = 8.0 Hz, 3H).

N-(4-bromophenyl)thiocarbamic acid S-propyl ester (**2d**): M.p. 74–75 °C (lit.[21] 75–76 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.43 (m, 4H), 7.11 (s, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 1.68 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H).

N-(4-acetylphenyl)thiocarbamic acid S-propyl ester (**2e**): M.p. 110–111 °C (lit.[21] 110–111 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93(d, *J* = 8.0 Hz, 2H), 7.75 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.59(s, 3H), 1.69 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

N-(2-methylphenyl)thiocarbamic acid S-propyl ester (**2f**): M.p. 63–64 °C (lit.[21] 62–63 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.19–7.00 (m, 4H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.66 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

N-(3-methylphenyl)thiocarbamic acid S-propyl ester (**2g**): Yellow oil (lit.[21] yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–6.89 (m, 5H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.67 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

N-(4-methylphenyl)thiocarbamic acid S-propyl ester (**2h**): M.p. 77–78 °C (lit.[21] 77–78 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.09 (m, 5H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 1.67 (m, 2H), 1.00 (t, *J* = 4.0 Hz, 3H).

N-(4-ethylphenyl)thiocarbamic acid S-propyl ester (**2i**): M.p. 60–61 °C (lit.[21] 60–61 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 2.94 (d, *J* = 7.2 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.68 (m, 2H), 1.20 (t, *J* = 7.6 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H).

N-(4-isopropylphenyl)thiocarbamic acid S-propyl ester (**2j**): M.p. 72–73 °C (lit.[21] 72–73 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.16 (s, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.88 (m, 1H), 1.68 (m, 2H), 1.22 (d, *J* = 7.2 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 3H).

N-(2-methoxylphenyl)thiocarbamic acid S-propyl ester (**2k**): Colourless oil (lit.[21] colourless oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.69 (s, 1H), 7.01–6.82 (m, 3H), 3.81 (s, 3H), 2.94 (t, *J* = 7.2 Hz, 2H), 1.68 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

N-(4-methoxylphenyl)thiocarbamic acid S-propyl ester (**2l**): M.p. 72–73 °C (lit.[21] 71–72 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.30 (d, *J* = 8.8 Hz, 2H), 7.23 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.94 (t, *J* = 7.2 Hz, 2H), 1.67 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

N-(6-methoxypyridine-3-yl)thiocarbamic acid S-propyl ester (**2m**): M.p. 66–67 °C (lit.[21] 66–67 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.79(d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H), 2.94 (t, *J* = 7.2 Hz, 2H), 1.67 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

Supplementary material such as copies of ^{1}H NMR spectra of the thiocarbamates can be available by contacting us.

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