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NOVEL SYNTHESIS OF *S*-ALKYL THIOCARBAMATES FROM AMINES, CARBON MONOXIDE, ELEMENTAL SULFUR, AND ALKYL HALIDES IN THE PRESENCE OF A SELENIUM CATALYST

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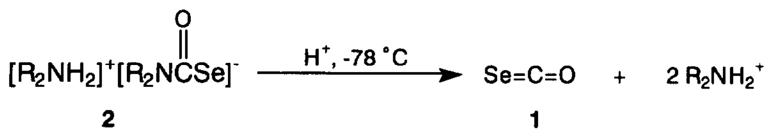
Abstract : Carbonyl selenide easily reacted with elemental sulfur at low temperature to form carbonyl sulfide in a good yield, and reaction of ammonium salts of selenocarbamates with elemental sulfur brought about ready transformation to those of thiocarbamates. On the basis of the high catalytic activity of selenium for carbonylation of amines with carbon monoxide in addition to these important findings, a convenient new method for synthesis of *S*-alkyl thiocarbamates was developed through the carbonylation of amines with carbon monoxide and elemental sulfur in the presence of a selenium catalyst under mild conditions followed by alkylation of ammonium salts of the thiocarbamates with alkyl halides.

INTRODUCTION

The synthesis of urea derivatives from amines, carbon monoxide, and oxygen in the presence of a selenium catalyst is an elegant efficient reaction under very mild conditions.[1] In this carbonylation system, carbonyl selenide (Se=C=O, **1**), generated *in situ* from the reaction of selenium with carbon monoxide, plays an important role as a key active intermediate and causes the effective carbonylation of amines under ordinary pressure at room temperature.

About fifteen years ago, we developed a practical convenient method for the synthesis of carbonyl selenide (**1**), which method involved acid-catalyzed decomposition of ammonium salts of selenocarbamates **2** (Eq. 1),[2] readily prepared from secondary amines, carbon monoxide, and selenium. This finding provided an easy access to carbonyl selenide (**1**) and encouraged our research on the reactivities of **1** toward various reagents.[3]

Recently, we reported an efficient reaction of **1** with elemental sulfur at low temperature to form carbonyl sulfide (**3**) in a good yield and established a useful synthesis of *S*-alkyl thiocarbamates **4**.[4]



$$\underset{\mathbf{2}}{[R_2NH_2]^+[R_2N\overset{\overset{O}{\|}}{C}Se]^-} \xrightarrow{H^+,\ -78\ ^\circ C} \underset{\mathbf{1}}{Se{=}C{=}O} + 2\,R_2NH_2^+ \quad (1)$$

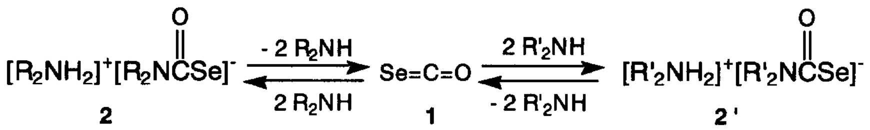
In this paper, we wish to report full details of the novel reactions of carbonyl selenide (**1**) or ammonium salts of selenocarbamates **2** with elemental sulfur and also to describe a new useful synthesis of *S*-alkyl thiocarbamates **4**, used as effective herbicides, by the carbonylation of amines with carbon monoxide and elemental sulfur in the presence of a selenium catalyst followed by alkylation of ammonium salts of thiocarbamates **5** with alkyl halides.

RESULTS AND DISCUSSION

At the outset, we examined the reaction of carbonyl selenide (**1**) with elemental sulfur at low temperature. Carbonyl selenide (**1**), generated from acid-catalyzed decomposition of an ammonium salt of selenocarbamate,[5] readily reacted with elemental sulfur in the presence of triethylamine over the range of -45 °C to 5 °C for 1 h to give carbonyl sulfide (**3**) in an 88% yield, as *S*-butyl *N,N*-diethylthiocarbamate (**4m**), and elemental selenium was recovered quantitatively (eq. 2). Therefore, carbonyl sulfide (**3**) was easily prepared by the reaction of carbonyl selenide (**1**) with elemental sulfur even at low temperature.

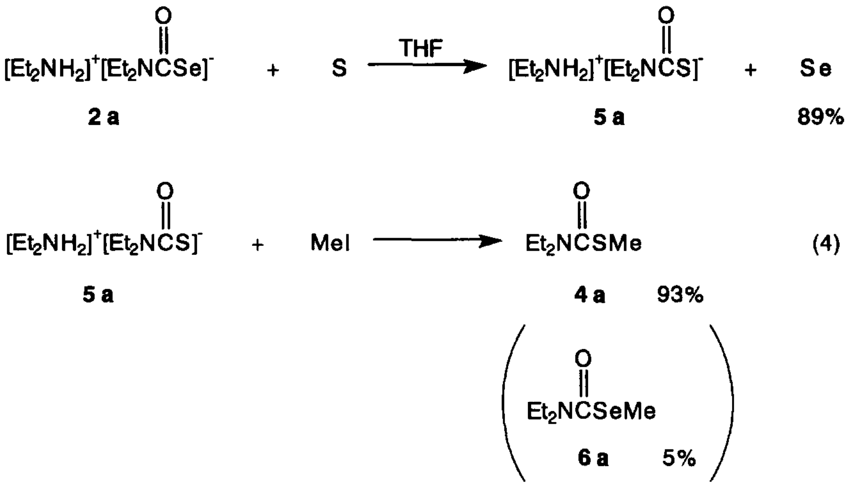
$$\underset{\mathbf{1}}{Se{=}C{=}O} + S \xrightarrow[-45\ -\ 5\ ^\circ C]{Et_3N,\ THF} \underset{\mathbf{3}\ \ 88\%}{S{=}C{=}O} + \underset{100\%}{Se} \quad (2)$$

Next, diethylammonium *N,N*-diethylselenocarbamate (**2a**), prepared from diethylamine, carbon monoxide, and selenium, was treated with dipropylamine at 20 °C for 2 h. Quenching the reaction mixture with methyl iodide gave a 47:53 mixture of *Se*-methyl *N,N*-diethylselenocarbamate (**6a**) and *Se*-methyl *N,N*-dipropylselenocarbamate (**6d**). A similar reaction of dipropylammonium *N,N*-dipropylselenocarbamate (**2b**) with diethylamine followed by quenching with methyl iodide gave a 49:51 mixture of **6a** and **6d**. A direct nucleophilic attack of an amine on the carbonyl carbon of **2** is not likely because of the steric hindrance of the dialkyl group.[6] Thus, these results strongly suggest an equilibrium between an ammonium salt of selenocarbamate **2** and **2'** through **1** (Eq. 3).



$$\underset{\mathbf{2}}{[R_2NH_2]^+[R_2N\overset{\overset{O}{\|}}{C}Se]^-} \underset{2\,R_2NH}{\overset{-2\,R_2NH}{\rightleftarrows}} \underset{\mathbf{1}}{Se{=}C{=}O} \underset{-2\,R'_2NH}{\overset{2\,R'_2NH}{\rightleftarrows}} \underset{\mathbf{2'}}{[R'_2NH_2]^+[R'_2N\overset{\overset{O}{\|}}{C}Se]^-} \quad (3)$$

On the basis of the present findings, a new reaction of an ammonium salt of selenocarbamate **2** with elemental sulfur to form an ammonium salt of thiocarbamate **5** and selenium was developed. Thus, the reaction of freshly prepared diethylammonium *N,N*-diethylselenocarbamate (**2 a**) with elemental sulfur at 30 °C for 2 h followed by alkylation with methyl iodide gave *S*-methyl *N,N*-diethylthiocarbamate (**4 a**) (93%, GLC yield), *Se*-methyl *N,N*-diethylselenocarbamate (**6 a**) (5%, GLC yield), and elemental selenium (89%) (Eq. 4).



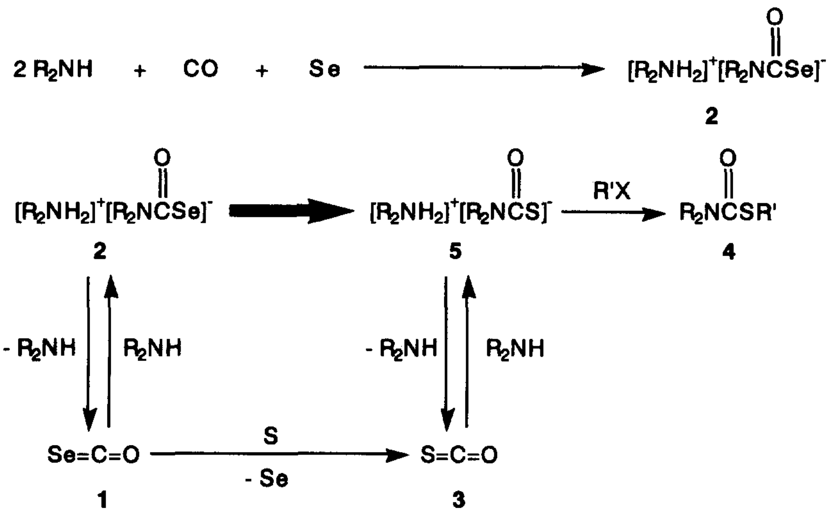
$$\underset{\textbf{2a}}{[Et_2NH_2]^+[Et_2N\overset{O}{\overset{\|}{C}}Se]^-} + S \xrightarrow{THF} \underset{\textbf{5a}}{[Et_2NH_2]^+[Et_2N\overset{O}{\overset{\|}{C}}S]^-} + \underset{89\%}{Se}$$

$$\underset{\textbf{5a}}{[Et_2NH_2]^+[Et_2N\overset{O}{\overset{\|}{C}}S]^-} + MeI \longrightarrow \underset{\textbf{4a}\quad 93\%}{Et_2N\overset{O}{\overset{\|}{C}}SMe} \quad \left(\underset{\textbf{6a}\quad 5\%}{Et_2N\overset{O}{\overset{\|}{C}}SeMe}\right) \qquad (4)$$

A variety of *S*-alkyl thiocarbamates (**4a-l**) were synthesized through efficient transformation of ammonium salts of selenocarbamates **2** into those of thiocarbamates **5** in the presence of elemental sulfur under mild conditions (Scheme 1 and Table 1).[7,15] For example, a diethylammonium *N,N*-diethylselenocarbamate (**2 a**) was prepared from diethylamine, carbon monoxide, and selenium at 30 °C, 1 atm for 2 h. Into the resulting solution containing **2 a** was then added two mole equivalents of elemental sulfur,[16] and the mixture was stirred at 30 °C for an additional 4 h followed by alkylation with methyl iodide. *S*-Methyl *N,N*-diethylthiocarbamate (**4 a**) was isolated in an 88% yield.

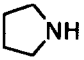
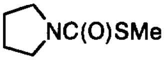
As shown in Table 1, from secondary amines, the corresponding *S*-alkyl thiocarbamates (**4a-h**) were generally afforded in good to excellent yields (Entries 1-8). However, the reaction of a primary amine (butylamine) provided **4 i** in a low yield (Entry 9), and that of an aromatic amine (aniline) did not give the corresponding product at all, even in the presence of a tertiary amine as a co-catalyst[17] (Entry 10).

A conceivable route for the synthesis of *S*-alkyl thiocarbamates **4** is proposed in Scheme 2. The first nucleophilic attack of an amine on elemental sulfur may form an adduct **7**, which then reacts with carbonyl selenide (**1**), generated through equilibrium with an ammonium salt of selenocarbamate **2**, to give an intermediate **8**. The elimination of **7** ' and elemental selenium from



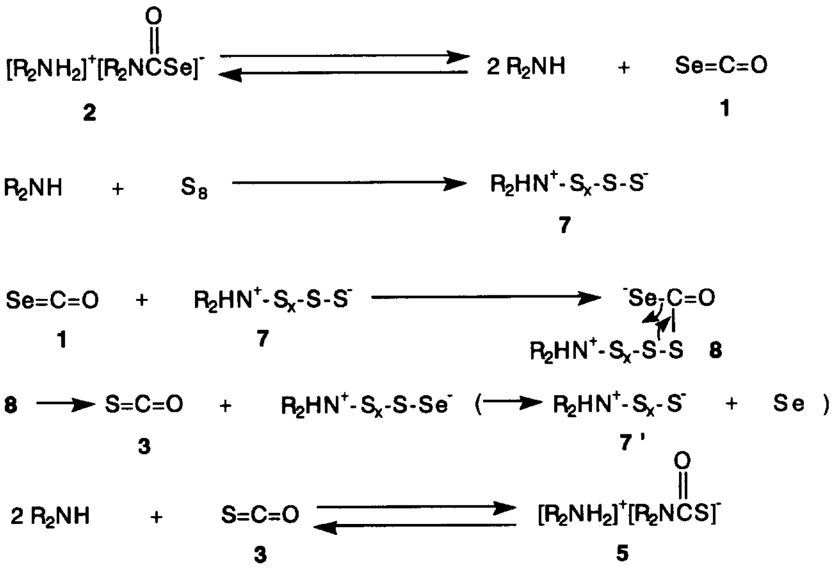
Scheme 1

Table 1. Synthesis of *S*-Alkyl Thiocarbamates **4**

entry	amine	alkyl halide	product		yield, %[a]
1	Et_2NH	MeI	$Et_2NC(O)SMe$	**4a**	88
2		EtBr	$Et_2NC(O)SEt$	**4b**	70
3		$PhCH_2Br$	$Et_2NC(O)SCH_2Ph$	**4c**	96
4	Pr_2NH	MeI	$Pr_2NC(O)SMe$	**4d**	93
5		EtI	$Pr_2NC(O)SEt$	**4e**	97
6	Bu_2NH	MeI	$Bu_2NC(O)SMe$	**4f**	80
7	 NH	MeI	 NC(O)SMe	**4g**	99
8	 NH	MeI	 NC(O)SMe	**4h**	80
9	$BuNH_2$	MeI	$BuNHC(O)SMe$	**4i**	40
10	$PhNH_2$	MeI	———		0[b]

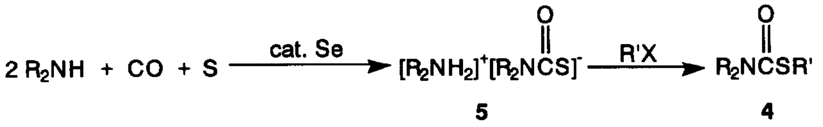
a) Isolated yield based on selenium used.
b) Et_3N (50 mmol) and MeI (100 mmol) were used.

8 may provide carbonyl sulfide (**3**), which reacts with two equivalents of amine to give finally an ammonium salt of thiocarbamate **5** through the equilibrium. It seems plausible that the reaction of carbonyl selenide (**1**) with elemental sulfur giving carbonyl sulfide (**3**) and recovered elemental selenium brought about easy transformation of an ammonium salt of selenocarbamate **2** into that of thiocarbamate **5** in the presence of elemental sulfur.



Scheme 2

Furthermore, facile transformation of **2** into **5**, quantitative recovery of selenium, and ready formation of **2** from amine, carbon monoxide, and elemental selenium prompted us to examine the possibility of the useful synthesis of *S*-alkyl thiocarbamates **4** under similar conditions (1 atm, room temperature) in the presence of a catalytic amount of selenium (eq. 5).



$$2\,R_2NH + CO + S \xrightarrow{\text{cat. Se}} \underset{\mathbf{5}}{[R_2NH_2]^+[R_2N\overset{O}{\overset{\|}{C}}S]^-} \xrightarrow{R'X} \underset{\mathbf{4}}{R_2N\overset{O}{\overset{\|}{C}}SR'} \quad (5)$$

In order to examine the effect of a catalytic amount of selenium, some control experiments were performed. In the presence and the absence of the selenium catalyst, yields of *S*-methyl *N,N*-

diethyl thiocarbamate (**4 a**) as a function of reaction time (h) are shown in Fig. 1. The results clearly show the high catalytic activity of selenium.

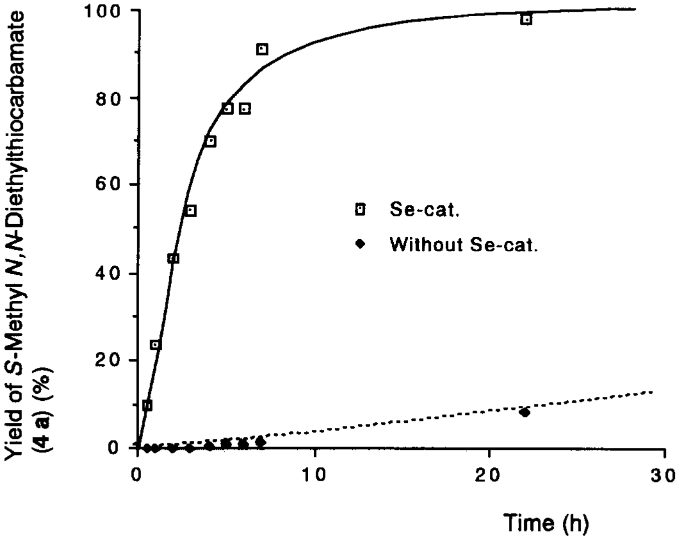


Fig. 1. Yields of **4 a** as a function of reaction time in the presence and absence of a catalytic amount of selenium. The solid line indicates yields of **4 a** in the reaction of diethylamine (50 mmol) with carbon monoxide (1 atm) and sulfur (20 mmol) using a selenium catalyst (10 mol%) at 30 °C, and the dotted line shows those of **4 a** without a selenium catalyst.

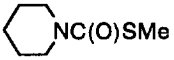
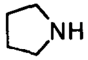
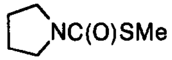
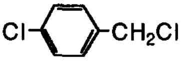
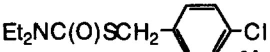
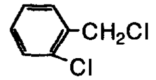
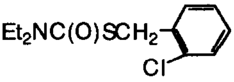
Table 2. Effect of Different Amounts of Selenium Catalyst

entry	Se, mol%	yield, %[a]
1	0	5
2	1	59
3	2.5	85
4	5	100

a) GLC yield of **4 a** based on sulfur used (1 atm, 30 °C, 20 h).

The amount of elemental selenium was found to bring about a remarkable effect on the synthesis of **4a** as shown in Table 2. Use of 5 mol% of selenium catalyst resulted in the quantitative formation of **4a** (Entry 4). However, in the absence of the selenium catalyst, **4a** was obtained only in a fairly low yield (Entry 1).

Table 3. Selenium-Catalyzed Synthesis of *S*-Alkyl Thiocarbamates **4**

entry	amine	alkyl halide	product		yield, %[a]	
					Se,	Without Se
1	Et_2NH	MeI	$Et_2NC(O)SMe$	**4a**	79	5
2		EtI	$Et_2NC(O)SEt$	**4b**	79[b]	
3		$PhCH_2Br$	$Et_2NC(O)SCH_2Ph$	**4c**	100[b]	
4	Pr_2NH	MeI	$Pr_2NC(O)SMe$	**4d**	87	24
5		EtI	$Pr_2NC(O)SEt$	**4e**	82[b]	
6	Bu_2NH	MeI	$Bu_2NC(O)SMe$	**4f**	87	0
7		MeI		**4g**	92	15
8		MeI		**4h**	83	59
9	$BuNH_2$	MeI	$BuNHC(O)SMe$	**4i**	69	40
10	$PhNH_2$	MeI	$PhNHC(O)SMe$	**4j**	41[c]	0[c]
11	Et_2NH			**4k**	90	
12	Et_2NH			**4l**	92	

a) Isolated yield based on amine used. Amine (20 mmol), S (11 mmol), Se (1 mmol), and alkyl halide (16 mmol) were used.
b) Amine (10 mmol), S (5.5 mmol), Se (0.5 mmol), and alkyl halide (8 mmol) were used. c) Et_3N (50 mmol) and MeI (100 mmol) were used.

Therefore, various *S*-alkyl thiocarbamates (**4a-l**) were synthesized from amines, carbon monoxide, elemental sulfur, and alkyl halides in the presence of the selenium catalyst (10 mol%) as shown in Table 3. Most of the *S*-alkyl thiocarbamates **4** from secondary amines were formed in good to excellent yields (Entries 1-8), and yields of those from primary amines were just moderate (Entries 9, 10). Furthermore, the preparation of **4j** from an aromatic amine required triethylamine as a co-catalyst (Entry 10).[17] However, *in the absence of the selenium catalyst*, *S*-alkyl thiocarbamates **4** were not obtained at all (Entries 6, 10) or were produced only in low yields (Entries 1, 4, 7, 9). In the case of the synthesis of *S*-methyl pyrrolidinecarbothioate (**4h**) from pyrrolidine, **4h** was afforded in a considerably good yield, even in the absence of the selenium catalyst, because of the high basicity and nucleophilicity of pyrrolidine.[18]

A series of *S*-alkyl thiocarbamates **4** is well known as useful herbicides. For instance, *S*-ethyl *N,N*-dipropylthiocarbamate (Eptam®) (**4e**) exhibits outstanding effectiveness and selectivity for control of annual grasses and many broadleaf weeds,[8,19] and *S*-4-chlorobenzyl *N,N*-diethylthiocarbamate (Benthiocarb®) (**4k**) for rice crops and *S*-2-chlorobenzyl *N,N*-diethylthiocarbamate (Orthobencarb®) (**4l**) for wheat and barley have been produced on a large scale as important herbicides.[20] These compounds (**4e**, **4k**, **4l**) were easily prepared in excellent yields by this method (Entries 5, 11, 12).

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EXPERIMENTAL SECTION

General Comments : Melting points were determined on a Yanaco MICRO MELTING POINT APPARATUS and were uncorrected. Gas chromatography (GLC) was performed on a Shimadzu GC-7A. ^{1}H-NMR spectra were obtained on a JEOL JNM-EX270 or JEOL JNM-FX90Q spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (δ-units). Infrared (IR) spectra were recorded on a JASCO A-3 spectrometer. Mass spectra were recorded on a JEOL JMS-DX303HF spectrometer. THF was dried over sodium wire and purified by distillation prior to use. Amines were commercially purchased, dried over potassium hydroxide, and distilled. Alkyl halides were use as purchased. Elemental selenium (99.9%) from Nacalai Tesque Co., Ltd., powdered sulfur (99.5%) from Yoneyama Chem. Co., Ltd., and carbon monoxide (99.9%) from Sumitomo Seika Co., Ltd. were used.

Reaction of Carbonyl Selenide (1) with Elemental Sulfur: Into a THF (5 mL) solution of elemental sulfur (0.16 g, 5 mmol) and triethylamine (0.14 mL, 1 mmol) cooled at -196 °C in a liquid nitrogen bath, isolated carbonyl selenide (**1**)[2] (5 mmol) in THF (5 mL) solution was added dropwise under a nitrogen atmosphere. The mixture was stirred over the range of -45 °C to 5 °C for 1 h. Carbonyl sulfide (**3**) was then formed, and elemental selenium (100%) was recovered by filtration. Generated **3** was quenched by a THF solution (4 mL) of diethylamine (1.24 mL, 12 mmol) at -90 °C, and the solution was stirred for 1 h below -20 °C. Alkylation by butyl iodide (1.37 ml, 12 mmol) gave *S*-butyl *N,N*-diethylthiocarbamate (**4m**) in an 88% yield (GLC yield).

Equilibrium between Ammonium Salt of Selenocarbamate 2 and 2' : A THF (20 mL) solution of diethylammonium *N,N*-diethylselenocarbamate (**2a**) prepared from diethylamine (0.52 mL, 5 mmol) and elemental selenium (79 mg, 1 mmol) with carbon monoxide,[21] and dipropylamine

(0.69 mL, 5 mmol) was stirred at 20 °C for 2 h under a nitrogen atmosphere. Quenching the resulting mixture with methyl iodide (0.93 mL, 15 mmol) and stirring for 4 h gave a 47 : 53 mixture of *Se*-methyl *N,N*-diethylselenocarbamate (**6a**) (0.46 mmol) and *Se*-methyl *N,N*-dipropylselenocarbamate (**6d**) (0.52 mmol) by GLC analysis. A similar reaction of dipropylammonium *N,N*-dipropylselenocarbamate (**2b**) with diethylamine gave a 49 : 51 mixture of **6a** (0.49 mmol) and **6d** (0.50 mmol).

Reaction of Isolated Ammonium Salt of Selenocarbamate (2a) with Elemental Sulfur : A mixture of diethylamine (2.6 mL, 25 mmol), elemental selenium (0.79 g, 10 mmol), and THF (20 mL) was stirred at room temperature for 4 h under carbon monoxide (1 atm), and a homogeneous solution of diethylammonium *N,N*-diethylselenocarbamate (**2a**) was obtained. The solvent (THF) and excess diethylamine were evaporated by a vacuum pump at room temperature to give a white solid (**2a**) that was sensitive upon exposure to air or to heat. THF (20 mL) was poured on **2a**, and then powdered sulfur (0.32 g, 10 mmol) was added under a nitrogen atmosphere. The resulting solution was kept at 30 °C for 2 h. After the reaction, methyl iodide (1.3 mL, 20 mmol) was added dropwise at 0 °C, and the reaction mixture was stirred for 4 h at room temperature. *S*-Methyl *N,N*-diethylthiocarbamate (**4a**) (1.37 g, 93%) and *Se*-methyl *N,N*-diethylselenocarbamate (**6a**) (0.10 g, 5%) were obtained (GLC yields). Elemental selenium (0.71 g, 89%) was recovered by filtration.

Typical Procedure for *S*-Alkyl Thiocarbamate (4a-j) Synthesis Based upon the Reaction of Ammonium Salts of Selenocarbamates with Elemental Sulfur : Into a solution of freshly distilled THF (20 mL) containing diethylamine (2.5 mL, 24 mmol) was added 0.79 g (10 mmol) of elemental selenium, and the mixture was vigorously stirred at 30 °C for 2 h under carbon monoxide (1 atm). Powdered sulfur (0.64 g, 20 mmol) was then added in one portion under a nitrogen atmosphere to the homogeneous solution of diethylammonium *N,N*-diethylselenocarbamate (**2a**).[16] The resulting solution was kept at 30 °C for 4 h, accompanied by deposition of elemental selenium. After addition of methyl iodide (1.0 mL, 16 mmol) at 0 °C, the mixture was stirred at room temperature for 4 h. After filtration of the precipitates containing recovered elemental selenium, the filtrate was purified by short-column chromatography (silica gel) to give *S*-methyl *N,N*-diethylthiocarbamate (**4a**) in 88% yield (based on selenium used) (1.29 g).

Typical Procedure for Selenium-Catalyzed Synthesis of *S*-Alkyl Thiocarbamates (4a-l) : Powdered sulfur (0.32 g, 10 mmol) and elemental selenium (79 mg, 1 mmol) were added to a solution of freshly distilled THF (20 mL) containing diethylamine (2.1 mL, 20 mmol), and the mixture was vigorously stirred at 30 °C for 7 h under atmospheric pressure of carbon monoxide. Powdered sulfur (32 mg, 1 mmol) was then added in one portion under a nitrogen atmosphere to the resulting homogeneous pale yellow solution.[22] After a while, elemental selenium began to precipitate, and the solution was stirred at 30 °C for an additional 4 h. After the addition of methyl iodide (1.0 mL, 16mmol) dropwise at 0 °C, the mixture was stirred at room temperature for 4 h. After filtration of the precipitates followed by evaporation of THF, *S*-methyl *N,N*-diethylthiocarbamate (**4a**) was obtained in 79% yield (based on amine used) (1.16 g) by distillation. The physical properties and spectroscopic characteristics of all isolated *S*-alkyl thiocarbamates (**4a-l**) were consistent with those of authentic samples or published data (**4a,b**,[8] **4c**,[23] **4d-g**,[8] **4h,i**,[24] **4j**,[25] **4k,l**[23]).

***S*-Methyl *N,N*-diethylthiocarbamate** (**4a**). Oil; bp 112 °C (14 mmHg) (lit.,[8] 132.5-133.0 °C, 87 mmHg); IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 1.17 (t, J=7 Hz, 6H), 2.31 (s, 3H), 3.38 (q, J=7 Hz, 4H); MS, m/z (%), 147 (M$^+$, 21), 100 (85), 72 (100); exact MS calcd. for $C_6H_{13}NOS$ 147.0718, found 147.0735. Anal. Calcd : C, 48.95; H, 8.90; N, 9.51; S, 21.77%. Found : C, 49.02; H, 9.03; N, 9.29; S, 22.07%.

***S*-Ethyl *N,N*-diethylthiocarbamate** (**4b**). Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 1.17 (t, J=7 Hz, 6H), 1.29 (t, J=7 Hz, 3H), 2.90 (q, J=7 Hz, 2H), 3.38 (q, J=7 Hz, 4H); MS, m/z (%), 161 (M$^+$, 48), 100 (100), 72 (60); exact MS calcd. for $C_7H_{15}NOS$ 161.0874, found 161.0896.

***S*-Benzyl *N,N*-diethylthiocarbamate** (**4c**). Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 1.16 (t, J=7 Hz, 6H), 3.37 (q, J=7 Hz, 4H), 4.15 (s, 2H), 7.14-7.48 (m, 5H); MS, m/z (%), 223 (M$^+$, 50), 100 (100), 91 (33), 72 (49); exact MS calcd. for $C_{12}H_{17}NOS$ 223.1031, found 223.1004.

***S*-Methyl *N,N*-dipropylthiocarbamate** (**4d**). Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 0.90 (t, J=7 Hz, 6H), 1.36-1.84 (m, 4H), 2.32 (s, 3H), 3.28 (t, J=7 Hz, 4H); MS, m/z (%), 175 (M$^+$, 35), 128 (100), 86 (55), 75 (41); exact MS calcd. for $C_8H_{17}NOS$ 175.1031, found 175.1034. Anal. Calcd : C, 54.82; H, 9.77; N, 7.99; S, 18.29%. Found : C, 54.72; H, 9.99; N, 7.93; S, 18.22%.

***S*-Ethyl *N,N*-dipropylthiocarbamate** (**Eptam®**) (**4e**). Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 0.89 (t, J=7 Hz, 6H), 1.27 (t, J=7 Hz, 3H), 1.36-1.80 (m, 4H), 2.90 (q, J=7 Hz, 2H), 3.27 (t, J=8 Hz, 4H); MS, m/z (%), 189 (M$^+$, 29), 160 (10), 128 (100), 86 (71); exact MS calcd. for $C_9H_{19}NOS$ 189.1187, found 189.1204.

***S*-Methyl *N,N*-dibutylthiocarbamate** (**4f**). Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 0.93 (t, J=7 Hz, 6H), 1.10-1.76 (m, 8H), 2.31 (s, 3H), 3.30 (t, J=7 Hz, 4H); MS, m/z, 203 (M$^+$).

***S*-Methyl piperidinecarbothioate** (**4g**). Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 1.40-1.76 (m, 6H), 2.32 (s, 3H), 3.32-3.64 (m, 4H); MS, m/z, 159 (M$^+$). Anal. Calcd for $C_7H_{13}NOS$: C, 52.80; H, 8.23; N, 8.80; S, 20.13%. Found : C, 52.45; H, 8.33; N, 8.50; S, 19.89%.

***S*-Methyl pyrrolidinecarbothioate** (**4h**). Mp 30-31.5 °C (lit.,[24] 32.5-34 °C); IR (neat) 1655 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 1.76-2.12 (m, 4H), 2.34 (s, 3H), 3.20-3.64 (m, 4H); MS, m/z, 145 (M$^+$).

***S*-Methyl *N*-butylthiocarbamate** (**4i**). Mp 33-33.5 °C (lit.,[24] 34 °C); IR (KBr) 3330 (N-H), 1640 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 0.92 (t, J=7 Hz, 3H), 1.10-1.72 (m, 4H), 2.33 (s, 3H), 3.28 (q, J=6 Hz, 2H), 5.72 (brs, 1H); MS, m/z, 147 (M$^+$).

***S*-Methyl *N*-phenylthiocarbamate** (**4j**). Mp 78-78.5 °C (lit.,[25] 80 °C); IR (KBr) 3290 (N-H), 1655 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 2.19 (s, 3H), 6.96-7.52 (m, 5H), 7.60 (brs, 1H); MS, m/z, 167 (M$^+$).

***S*-4-Chlorobenzyl *N,N*-diethylthiocarbamate (Benthiocarb®) (4k)**. Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.16 (t, J=7 Hz, 6H), 3.36 (q, J=7 Hz, 4H), 4.08 (s, 2H), 7.25 (s, 4H); MS, m/z (%), 257 (M$^+$, 26), 125 (23), 100 (100), 72 (49); exact MS calcd. for $C_{12}H_{16}ClNOS$ 257.0641, found 257.0639.

***S*-2-Chlorobenzyl *N,N*-diethylthiocarbamate (Orthobencarb®) (4l)**. Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.16 (t, J=7 Hz, 6H), 3.36 (q, J=7 Hz, 4H), 4.26 (s, 2H), 7.10-7.54 (m, 4H); MS, m/z (%), 257 (M$^+$, 4), 222 (36), 125 (26), 100 (100), 72 (58); exact MS calcd. for $C_{12}H_{16}ClNOS$ 257.0641, found 257.0638.

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15. Direct reaction of amines with carbon monoxide and elemental sulfur requires severe conditions (90-120 °C, 200-400 psi, 60-62%).[9]
16. Two mole equivalents of elemental sulfur are needed for selective synthesis of *S*-methyl *N,N*-diethylthiocarbamate (**4 a**). Diethylammonium *N,N*-diethylselenocarbamate (**2 a**) was completely decomposed and elemental selenium was recovered quantitatively. GLC analysis showed that **4 a** was entirely pure, and *Se*-methyl *N,N*-diethylselenocarbamate (**6 a**) was not detected (<0.01%). Microanalysis of **4 a** gave a satisfactory result.
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22. Additional elemental sulfur (1 mmol) was effective in the decomposition of diethylammonium *N,N*-diethylselenocarbamate (**2 a**). **2 a** was completely decomposed and elemental selenium was recovered quantitatively. GLC analysis showed that **4 a** was entirely pure, and *Se*-methyl *N,N*-diethylselenocarbamate (**6 a**) was not detected (<0.01%). Microanalysis of **4 a** gave a satisfactory result.
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