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Practical synthesis of *S*-alkyl thiocarbamate herbicides by carbonylation of amines with carbon monoxide and sulfur

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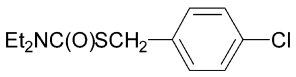
Dedicated to Professor Noboru Sonoda on the occasion of his 70th birthday

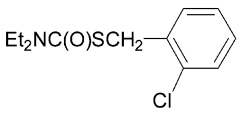
Abstract—An industrial and economic carbonylation of amines with carbon monoxide and sulfur has been developed for the synthesis of *S*-alkyl thiocarbamate herbicides. In the presence of potassium carbonate and solvent DMSO, *S*-alkyl thiocarbamates, such as thiobencarb and orbencarb (herbicides) are synthesized in excellent yields from amines, carbon monoxide, sulfur, and alkyl halides under mild conditions (1 atm, 20 °C).

1. Introduction

A series of *S*-alkyl thiocarbamates (**1**) is well known as useful herbicides, and these herbicides (**1**) (e.g., thiobencarb (**1a**) and orbencarb (**1b**)) have been produced in an industrial large-scale.[1–3] Therefore, development of synthetic methods of *S*-alkyl thiocarbamates (**1**) is of an importance.



Thiobencarb, **1a**



Orbencarb, **1b**

Many methods for the synthesis of *S*-alkyl thiocarbamates (**1**) have been reported. Among them, the reaction of amines (**2**) with thiols and phosgene or with carbonyl sulfide, followed by alkylation with alkyl halides has been known as the general routes.[4–6] Indeed, *S*-alkyl thiocarbamate herbicides (**1**) are industrially produced by a two-step reaction, which includes the generation of carbonyl sulfide from carbon monoxide and sulfur under high temperature, and the reaction of carbonyl sulfide with amines (**2**) and alkyl halides.[2]

Also, direct carbonylation of amines (**2**) with carbon monoxide and sulfur for the synthesis of *S*-alkyl thiocarbamate herbicides (**1**) has been developed. It seems to be a straightforward and useful method of herbicide synthesis.

Grisley and Stephens reported *S*-alkyl thiocarbamate (**1**) synthesis from secondary amines (**2**), carbon monoxide, sulfur, and alkyl halides.[8] However, this reaction requires high temperature and pressurized carbon monoxide.

In 1989, our research group found that selenium exhibits excellent catalytic activity toward the carbonylation of amines (**2**) with carbon monoxide and sulfur. This selenium-catalyzed carbonylation of amines (**2**) with carbon monoxide and sulfur smoothly proceeds under mild conditions to give thiocarbamate salts (**3**), the alkylation of which leads to the formation of *S*-alkyl thiocarbamates (**1**) in excellent yields.[9,10] Owing to the toxicity of selenium, however, use of this preparative method is considerably limited for industrial production of herbicides.

Next, we also found a high-yield synthesis of *S*-alkyl thiocarbamate (**1**) by the reaction of carbamoyl lithiums which were prepared in situ from lithium amides and carbon monoxide (1 atm) at low temperature (−78 °C), with elemental sulfur and alkyl halides, or disulfides.[11–13] However, this synthetic method may be not suitable for industrial production of *S*-alkyl thiocarbamate herbicides (**1**), because of the need for expensive lithium amides and low temperature reaction conditions (−78 °C).

Furthermore, we very recently reported the carbonylation of amines (**2**) with carbon monoxide and sulfur, assisted by

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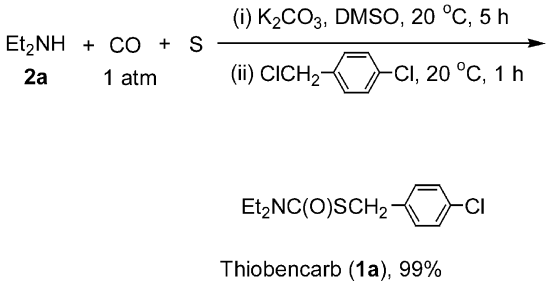
DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to provide *S*-alkyl thiocarbamates (**1**) in excellent yields under mild conditions (1 atm, 20 °C).[14] However, this method seems to be not attractive for industrial production of *S*-alkyl thiocarbamate herbicides (**1**), because of the price of DBU compared with inorganic bases.

Therefore, in our strategy, we explored an industrial and economic route to the *S*-alkyl thiocarbamates herbicides (**1**) under mild conditions (1 atm, 20 °C) using an inorganic base.

2. Results and discussion

Our trial employing K_2CO_3 as a base and DMSO as a solvent, which are cheap and commercially available, leads to successful carbonylation of diethylamine (**2a**) with carbon monoxide and sulfur. Diethylamine (2.07 mL, 20 mmol) (**2a**) easily reacted with carbon monoxide (1 atm) and sulfur (321 mg, 10 mmol) at 20 °C for 5 h in the presence of K_2CO_3 (2.07 g, 15 mmol) using DMSO (20 mL) as a solvent. The resulting thiocarbamate salt (**3a**) in DMSO was esterified by 4-chlorobenzyl chloride (1.39 mL, 11 mmol) under an ambient pressure, at 20 °C for 1 h to give *S*-4-chlorobenzyl *N*,*N*-diethylthiocarbamate (Thiobencarb,[3] **1a**) in quantitative yield (Eq. 1).



(1)

The influence of bases and solvents on the synthesis of **1a** from diethylamine, carbon monoxide, sulfur, and 4-chlorobenzyl chloride was examined (Table 1).

Table 1. Influence of bases (15 mmol) and solvents (20 mL) on the synthesis of Thiobencarb (**1a**)

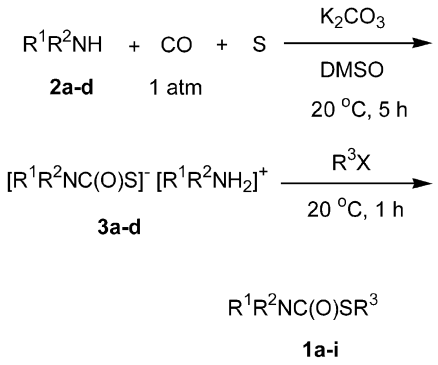
Entry	Base	Solvent	Yield (%)[a]
1	K_2CO_3	DMSO	99
2	K_2CO_3	DMSO	29[b]
3	K_2CO_3[c]	DMSO	69
4	K_2CO_3[d]	DMSO	66
5	K_2CO_3	DMF	68
6	K_2CO_3	NMP	48
7	K_2CO_3	Sulfolane	18
8	K_2CO_3	THF	10
9	Na_2CO_3	DMSO	60
10	$KHCO_3$	DMSO	50
11	$NaHCO_3$	DMSO	43
12	KOH	DMSO	54
13	NaOH	DMSO	47
14	AcONa	DMSO	70
15	none	DMSO	39

[a] Reaction conditions: diethylamine (2.07 mL, 20 mmol), sulfur (321 mg, 10 mmol), K_2CO_3 (2.07 g, 15 mmol), 4-chlorobenzyl chloride (1.39 mL, 11 mmol), DMSO (20 mL), CO (1 atm), 20 °C, 5 h for carbonylation and 1 h for alkylation.
[b] Et_2NH (10 mmol) was used.
[c] K_2CO_3 (10 mmol) was used.
[d] K_2CO_3 (5 mmol) was used.

S-4-Chlorobenzyl *N*,*N*-diethylthiocarbamate (Thiobencarb,[3] **1a**) are prepared in excellent yields in the presence of 1.5 equiv. of K_2CO_3 and DMSO as a solvent under 1 atm of carbon monoxide at 20 °C for 6 h (entry 1). When using 10 mmol of Et_2NH (**2a**), yield of **1a** was much lowered (29%) (entry 2). Thus, the need of 2 equiv. of diethylamine (**2a**) may be suggested for the formation of *N*,*N*-diethyl-ammonium salt of *N*,*N*-diethylthiocarbamate (**3a**) as an intermediate.

Use of 1.0 or 0.5 equiv. of K_2CO_3 lowered the yields of *S*-4-chlorobenzyl *N*,*N*-diethylthiocarbamate (Thiobencarb,[3] **1a**) (entries 3 and 4). Also, synthesis of **1a** in DMF resulted in moderate yield (entry 5). NMP, sulfolane, and THF as solvents were not effective for the preparation of **1a** (entries 6–8). The reaction in the presence of other bases (Na_2CO_3, $KHCO_3$, $NaHCO_3$, KOH, NaOH, AcONa) or in the absence of a base, resulted in the formation of the desired **1a** in moderate yields (43–70%) (entries 9–15).

In the presence of 1.5 equiv. of K_2CO_3 and DMSO as a solvent under 1 atm of carbon monoxide at 20 °C for 6 h, *S*-alkyl thiocarbamate herbicides (**1a-i**) were synthesized from the corresponding amines (**2a-d**) and alkyl halides (Eq. 2, Table 2).

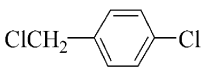
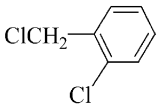
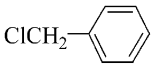
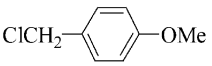
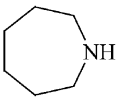
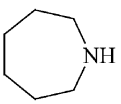
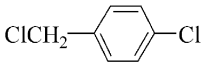


(2)

S-Alkyl thiocarbamates (**1a-i**) from secondary amines (**2a-d**) were prepared in excellent yields under mild conditions (1 atm, 20 °C) (entries 1–9). General names of herbicides are as follows: Thiobencarb: **1a**, Orbencarb: **1b**, Prosulfocarb: **1c**, Methiobencarb: **1d**, Molinate: **1e**, NTN-7072: **1f**, Ethiolate: **1g**, EPTC: **1h**, Cycloate: **1i**.[3] Even in considerably large scale, *S*-alkyl thiocarbamates (**1g**,**h**) were given in good yields (entries 7 and 8), although long reaction time was required (22 h for carbonylation and 2 h for alkylation).

Based on our finding on the smooth reaction of salts of thiolates **4** with carbon monoxide to convert into salts of thiocarbamates **3**,[15] we suggest a plausible pathway for this carbonylation of amines (**2**) with carbon monoxide and sulfur using K_2CO_3 and DMSO as follows (Scheme 1). Elemental sulfur is readily subjected to S–S bond fission by the reaction with secondary amines (**2**) strongly assisted by K_2CO_3 and DMSO as a solvent, to form ammonium salts of thiolate anions **4**.[16,17] The reaction of **4** with carbon

Table 2. Synthesis of *S*-alkyl thiocarbamate herbicides (**1a-i**)

Entry	R^1R^2NH		R^3X		Yield (%)[a]
1	Et_2NH	**2a**		**1a**[b]	99
2	Et_2NH	**2a**		**1b**[c]	98
3	*n*-Pr_2NH	**2b**		**1c**[d]	99
4	Et_2NH	**2a**		**1d**[e]	98
5		**2c**	EtI	**1e**[f]	94
6		**2c**		**1f**[g]	96
7	Et_2NH	**2a**	EtI	**1g**[h]	88(94)[i]
8	*n*-Pr_2NH	**2b**	EtI	**1h**[j]	94(85)[i]
9	*c*-HexEtNH	**2d**	EtI	**1i**[k]	98

[a] Reaction conditions: amine (20 mmol), sulfur (321 mg, 10 mmol), K_2CO_3 (2.07 g, 15 mmol), alkyl halide (11 mmol), DMSO (20 mL), CO (1 atm), 20 °C, 5 h for carbonylation and 1 h for alkylation.
[b] Thiobencarb.[3]
[c] Orbencarb.[3]
[d] Prosulfocarb.[3]
[e] Methiobencarb.[3]
[f] Molinate.[3]
[g] NTN-7072.[3]
[h] Ethiolate.
[i] Reaction conditions: amine (200 mmol), sulfur (3.21 g, 100 mmol), K_2CO_3 (20.7 g, 150 mmol), ethyl iodide (8.80 mL, 110 mmol), DMSO (50 mL), CO (1 atm), 20 °C, 22 h for carbonylation and 2 h for alkylation.
[j] EPTC.[3]
[k] Cycloate.[3]

monoxide gives the carbonylated species **5**. Through an elimination of carbonyl sulfide from **5**, ammonium salts of thiocarbamates **3** are generated.

It seems that the main role of K_2CO_3 and DMSO as a solvent in this carbonylation is the acceleration of the formation of thiolates **4**.

3. Conclusion

A practical synthetic method for *S*-alkyl thiocarbamate herbicides (**1**) has been developed under mild conditions (1 atm, 20 °C), in which the carbonylation of amines (**2**) with carbon monoxide and sulfur is powerfully assisted by K_2CO_3 and DMSO as a solvent.

From the viewpoint of application to actual industrial production of *S*-alkyl thiocarbamate herbicides (**1**), the present reaction is very significant, in terms of the use of easily available and cheap carbon monoxide, sulfur, K_2CO_3, and DMSO as a solvent, and mild reaction conditions (1 atm, 20 °C).

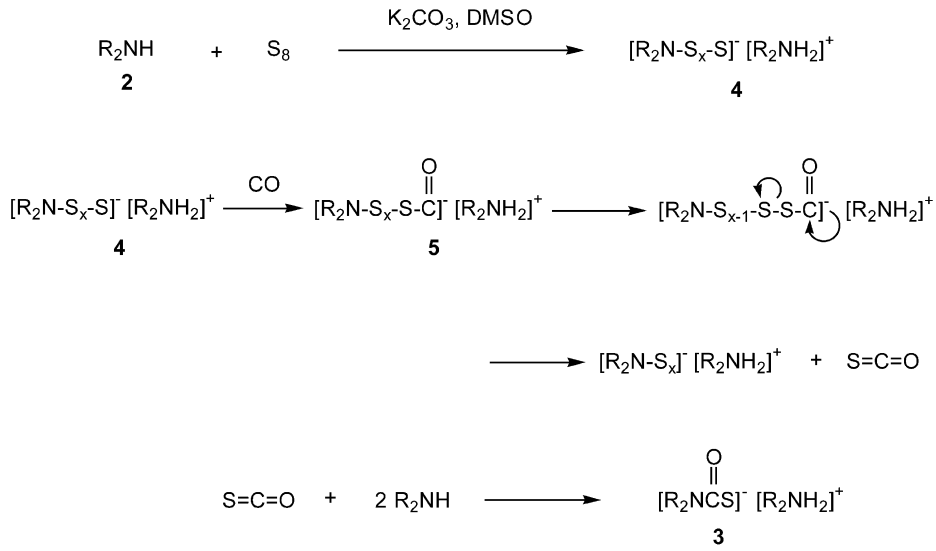
4. Experimental

4.1. General

Melting points were determined on a Mettler FP 5 instrument and were uncorrected. FT-IR spectra were recorded on a Nicolet Magna-IR 550 instrument. ^1H and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 (300, 75 MHz) instrument. Chemical shifts were reported in ppm relative to tetramethylsilane (δ-units). Mass and exact mass spectra were recorded on a JEOL JMS-600 spectrometer. Amines (**2a-d**), alkyl halides, solvents, inorganic bases, sulfur (99.5%), and carbon monoxide (99.9%) were used as purchased.

4.2. Typical procedure for the synthesis of *S*-4-chlorobenzyl *N*,*N*-diethylthiocarbamate (Thiobencarb,[3] 1a) from diethylamine (2a), 4-chlorobenzyl chloride, carbon monoxide, and sulfur

A DMSO (20 mL) solution containing diethylamine (**2a**) (2.07 mL, 20 mmol), powdered sulfur (321 mg, 10 mmol) and K_2CO_3 (2.07 g, 15 mmol) was vigorously stirred under carbon monoxide (1 atm) at 20 °C for 5 h. Into the DMSO



Scheme 1.

solution of thiocarbamate salt (**3a**), 4-chlorobenzyl chloride (1.39 mL, 11 mmol) was added slowly at 0 °C under argon atmosphere. The reaction mixture was stirred for additional 1 h at 20 °C. The resulting mixture was then poured into 1 N HCl (100 mL), and extracted with *t*-butyl methyl ether (100, 50 mL×2). After evaporation of solvents and purification by short-column chromatography (silica gel, toluene/AcOEt, 1:1), *S*-4-chlorobenzyl *N*,*N*-diethylthiocarbamate (Thiobencarb,[3] **1a**) was obtained in a 99% yield (2.54 g) as a pure form. *S*-4-Chlorobenzyl *N*,*N*-diethylthiocarbamate (Thiobencarb,[3] **1a**): oil; IR (neat) 2975, 1650, 1410, 1250, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J*=7 Hz, 6H), 3.37 (br s, 4H), 4.11 (s, 2H), 7.23–7.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 33.8, 42.1, 128.6, 130.3, 132.8, 137.2, 166.3; MS (*m*/*z*, %) 257 (M^+, 45), 125 (28), 100 (100), 72 (38). Exact MS calcd for $C_{12}H_{16}ClNOS$: 257.0641. Found: 257.0630.

4.2.1. *S*-2-Chlorobenzyl *N*,*N*-diethylthiocarbamate (Orbencarb,[3] 1b). Oil; IR (neat) 2975, 1650, 1410, 1250, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J*=7 Hz, 6H), 3.37 (br s, 4H), 4.28 (s, 2H), 7.15–7.22 (m, 2H), 7.33–7.36 (m, 1H), 7.49–7.52 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 32.3, 42.1, 126.9, 128.5, 129.4, 131.3, 134.2, 136.3, 166.5; MS (*m*/*z*, %) 257 (M^+, 16), 222 (55), 125 (31), 100 (100), 89 (10), 72 (35). Exact MS calcd for $C_{12}H_{16}ClNOS$: 257.0641. Found: 257.0633.

4.2.2. *S*-Benzyl *N*,*N*-di-*n*-propylthiocarbamate (Prosulfocarb,[3] 1c). Oil; IR (neat) 2965, 1650, 1405, 1220, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J*=7 Hz, 6H), 1.60 (q, *J*=7 Hz, 4H), 3.22 (br s, 2H), 3.32 (br s, 2H), 4.15 (s, 2H), 7.22–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 21.6, 34.7, 49.3, 127.0, 128.5, 128.9, 138.3, 167.2; MS (*m*/*z*, %) 251 (M^+, 50), 128 (100), 92 (21), 91 (97), 86 (51). Exact MS calcd for $C_{14}H_{21}NOS$: 251.1344. Found: 251.1328.

4.2.3. *S*-4-Methoxybenzyl *N*,*N*-diethylthiocarbamate (Methiobencarb,[3] 1d). Oil; IR (neat) 2975, 1650, 1515, 1405, 1250, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J*=7 Hz, 6H), 3.37 (br s, 4H), 3.78 (s, 3H), 4.11 (s, 2H), 6.83 (d, *J*=8 Hz, 2H), 7.27 (d, *J*=8 Hz, 2H); ^{13}C NMR (75 MHz $CDCl_3$) δ 13.3, 34.0, 41.9, 55.2, 113.9, 130.0, 130.2, 158.6, 166.8; MS (*m*/*z*, %) 253 (M^+, 98), 121 (100), 100 (60), 72 (29). Exact MS calcd for $C_{13}H_{19}NO_2S$: 253.1137. Found: 253.1141.

4.2.4. *S*-Ethyl perhydroazepin-1-carbothioate (Molinate,[3] 1e). Oil; IR (neat) 2930, 1650, 1405, 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, *J*=7 Hz, 3H), 1.54–1.60 (m, 4H), 1.73 (br s, 4H), 2.91 (q, *J*=7 Hz, 2H), 3.45 (t, *J*=6 Hz, 2H), 3.56 (t, *J*=6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 24.5, 26.9, 27.2, 27.9, 28.4, 47.3, 47.6, 167.8; MS (*m*/*z*, %) 187 (M^+, 73), 126 (100), 83 (24), 55 (36). Exact MS calcd for $C_9H_{17}NOS$: 187.1031. Found: 187.1021.

4.2.5. *S*-4-Chlorobenzyl perhydroazepin-1-carbothioate (NTN-7072,[3] 1f). Mp 58.0 °C (60–62 °C[4]); IR (melt) 2930, 1635, 1405, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.54–1.57 (m, 4H), 1.73 (br s, 4H), 3.42 (q, *J*=6 Hz, 2H), 3.56 (t, *J*=6 Hz, 2H), 4.11 (s, 2H), 7.23–7.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.9, 27.2, 27.8, 28.4, 33.9, 47.6, 47.7, 128.6, 130.3, 132.8, 137.2, 166.9; MS (*m*/*z*, %) 283 (M^+, 63), 126 (100), 125 (36), 55 (17). Exact MS calcd for $C_{14}H_{18}ClNOS$: 283.0798. Found: 283.0795.

4.2.6. *S*-Ethyl *N*,*N*-diethylthiocarbamate (Ethiolate,[3] 1g). Oil; IR (neat) 2975, 2935, 1650, 1405, 1250, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J*=7 Hz, 6H), 1.29 (t, *J*=7 Hz, 3H), 2.90 (q, *J*=7 Hz, 2H), 3.38 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 15.4, 24.5, 41.8, 167.2; MS (*m*/*z*, %) 161 (M^+, 26), 100 (100), 72 (83). Exact MS calcd for $C_7H_{15}NOS$: 161.0874. Found: 161.0859.

4.2.7. *S*-Ethyl *N*,*N*-di-*n*-propylthiocarbamate (EPTC,[3] 1h). Oil; IR (neat) 2965, 1650, 1405, 1220, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J*=7 Hz, 6H), 1.28 (t, *J*=7 Hz, 3H), 1.60 (br s, 4H), 2.90 (q, *J*=7 Hz, 2H), 3.27 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 15.3, 21.2, 24.6, 49.1, 167.7; MS (*m*/*z*, %) 189 (M^+, 28), 132 (24), 128 (100), 89 (20), 86 (80). Exact MS calcd for $C_9H_{19}NOS$: 189.1187. Found: 189.1185.

4.2.8. *S*-Ethyl *N*-cyclohexyl-*N*-ethylthiocarbamate (Cycloate,[3] 1i). Oil; IR (neat) 2935, 1650, 1405, 1230, 1095 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.03–1.80 (m, 16H), 2.90 (q, J=7 Hz, 2H), 3.31 (q, J=7 Hz, 2H), 3.65 (br s, 0.5H), 4.17 (br s, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 15.6, 24.3, 25.3, 25.7, 30.7, 38.2, 56.8, 167.1; MS (*m*/*z*, %) 215 (M^+, 38), 154 (100), 83 (98), 55 (31). Exact MS calcd for $C_{11}H_{21}NOS$: 215.1344. Found: 215.1331.

4.3. General procedure for the synthesis of ethyl *N*,*N*-diethylthiocarbamate (Ethiolate,[3] 1g) in large scale

A solution of diethylamine (**2a**) (20.7 mL, 200 mmol), powdered sulfur (3.21 g, 100 mmol) and K_2CO_3 (20.7 g, 150 mmol) in DMSO (50 mL) was very vigorously stirred under carbon monoxide (1 atm) at 20 °C for 22 h. Ethyl iodide (8.80 mL, 110 mmol) was added carefully at 0 °C under argon atmosphere into the DMSO solution of thiocarbamate salt (**3a**). The solution was stirred for additional 2 h at 20 °C. The resulting mixture was then poured slowly into 1 N HCl (100 mL), and extracted with *t*-butyl methyl ether (100, 50 mL×2). After evaporation of solvents and purification by vacuum distillation, *S*-ethyl *N*,*N*-diethylthiocarbamate (Ethiolate,[3] **1g**) was obtained in 94% yield (15.2 g).

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6. Very recently, *S*-alkyl thiocarbamtes (**1**) were synthesized by the reaction of trichloroacetyl chloride with amines (**2**) and thiols[7].
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