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Solvent-assisted thiocarboxylation of amines and alcohols with carbon monoxide and sulfur under mild conditions

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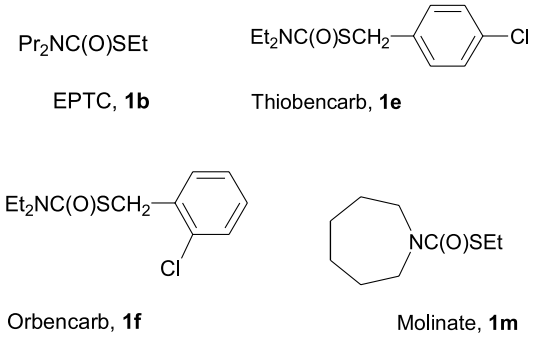
Abstract—DMSO or DMF as a solvent strongly accelerated the thiocarboxylation of amines and alcohols with carbon monoxide and sulfur. Under mild conditions (1 atm, 20 °C), this thiocarboxylation of amines assisted by DMSO with carbon monoxide and sulfur has been developed into a practical and convenient synthetic method for *S*-alkyl thiocarbamates in good to excellent yields, including EPTC, thiobencarb, orbencarb, and molinate (herbicides). DMF also showed the similar solvent effect. NMP slightly decreased the effect for the thiocarboxylation of amines, and the yield of *S*-alkyl thiocarbamate was lowered in DMAc. Surprisingly, no formation of *S*-alkyl thiocarbamate was observed at the use of the other solvents, such as THF, hexane, toluene, AcOEt, MeCN, MeOH, and H_2O. The present solvent-assisted thiocarboxylation with carbon monoxide and sulfur could be also applied to a new synthesis of *S*-alkyl *O*-alkyl carbonothioates from alcohols under mild conditions (1 atm, 20 °C) in DMF using DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).

1. Introduction

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



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 two steps 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]

Direct thiocarboxylation of primary amines with carbon monoxide and sulfur to form urea derivatives was introduced by Monsanto group in 1961.[8–10] Furthermore, Grisley and Stephens developed *S*-alkyl thiocarbamate **1** synthesis from secondary amines, carbon monoxide, sulfur, and alkyl halides in similar manners.[11] However, these reactions require high temperature and pressurized carbon monoxide.

Our research group has found that selenium exhibits an excellent catalytic activity toward the thiocarboxylation of amines with carbon monoxide and sulfur in 1989. This selenium-catalyzed thiocarboxylation of amines **2** smoothly proceeded under mild conditions (1 atm, 30 °C) to give thiocarbamate salts **3**. Then, the alkylation of **3** by alkyl halides, led to the formation of *S*-alkyl thiocarbamates **1** in excellent yields.[12,13] Owing to the toxicity of elemental selenium, however, use of this preparative method was 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

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monoxide (1 atm) at low temperature (−78 °C), with elemental sulfur and alkyl halides, or disulfides.[14–16] However, this synthetic method may not be suitable for industrial production of *S*-alkyl thiocarbamate herbicide, because of the production cost of **1**.

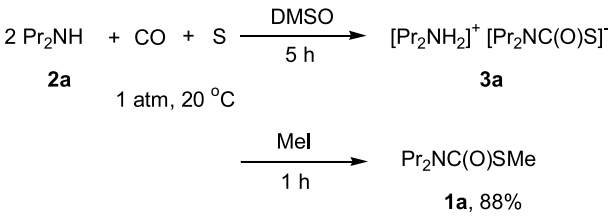
Recently, we reported the thiocarboxylation of amines **2** with carbon monoxide and sulfur, assisted by DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to provide *S*-alkyl thiocarbamates **1** in excellent yields in THF under mild conditions (1 atm, 20 °C).[17] But, this method also seemed to be not attractive for industrial production of *S*-alkyl thiocarbamate herbicides **1**, because of the price of DBU compared with inorganic bases, such as K_2CO_3. Furthermore, a more useful synthetic method for *S*-alkyl thiocarbamate herbicides **1** has been developed in 2004.[18] Under mild conditions (1 atm, 20 °C), in which the thiocarboxylation of amines **2** with carbon monoxide and sulfur was powerfully assisted by K_2CO_3 and DMSO as a solvent. However, still weak point of this procedure was the need of an excess amount of K_2CO_3 as a base.

Then, thiocarboxylation of alcohols **5** with carbon monoxide and sulfur to give *S*-alkyl carbonothioates **4** was also established by us, using base such as DBU[19–21] and triethylamine,[22,23] and selenium-catalyst.[24] However, these thiocarboxylation reactions from alcohols **5** proceeded under high temperature and pressurized carbon monoxide using an autoclave.

Therefore, in our strategy, we explored a new practical synthetic method to the *S*-alkyl thiocarbamates **1** including herbicides under mild conditions (1 atm, 20 °C) without using additional base, and useful route of *S*-alkyl *O*-alkyl carbonothioates (**4**) under similar mild conditions.

2. Results and discussion

Our trial employing DMSO or DMF as a solvent, which is cheap and commercially available, led to a successful thiocarboxylation of dipropylamine (**2a**) with carbon monoxide and sulfur without other base. Dipropylamine (**2a**) smoothly reacted with carbon monoxide (1 atm) and sulfur (1.0 equiv) at 20 °C for 5 h in DMSO solvent. Then, color of solution was changed from reddish black to green, the resulting thiocarbamate salt (**3a**) in DMSO solution was esterified by methyl iodide (1.2 equiv) under an ambient pressure at 20 °C for 1 h. Finally, *S*-methyl *N*,*N*-dipropylthiocarbamate (**1a**) was obtained in 88% yield (Eq. 1) (Table 1, entry 1).



(1)

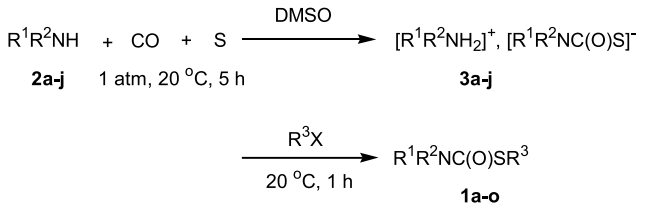
To examine the influence of solvent on this thiocarboxylation of dipropylamine (**2a**) with carbon monoxide and sulfur, various solvents were screened (Table 1). When DMF was employed as a solvent for this thiocarboxylation, DMF also showed the similar solvent effect to afford *S*-methyl *N*,*N*-dipropylthiocarbamate (**1a**) in good yields (82%) (entry 2). NMP used as solvent somewhat weakly accelerated the carboxylation of **2a** to give *S*-methyl *N*,*N*-dipropylthiocarbamate (**1a**) in moderate yield (67%) (entry 3). In DMAc, the yield of **1a** was lowered (entry 4). In contrast, we surprisingly observed that the use of other solvents (THF, hexane, toluene, AcOEt, MeCN, MeOH, and H_2O) resulted in no formation of the desired **1a** at all (entries 5–11). Therefore, we believe that solvents are a predominant factor for reactivity of the present thiocarboxylation of amines with carbon monoxide and sulfur.

Table 1. Influence of solvent on the synthesis of *S*-methyl *N*,*N*-dipropylthiocarbamate (**1a**)

Entry	Solvent	Isolated yield[a]
1	DMSO	88
2	DMF	82
3	NMP	67
4	DMAc	30
5	THF	0
6	Hexane	0
7	Toluene	0
8	AcOEt	0
9	MeCN	0
10	MeOH	0
11	H_2O	0

[a] Reaction conditions: dipropylamine (2.74 mL, 20 mmol), sulfur (321 mg, 10 mmol), methyl iodide (0.75 mL, 12 mmol), solvent (20 mL), CO (1 atm), 20 °C, 5 h for carbonylation and 1 h for alkylation.

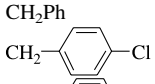
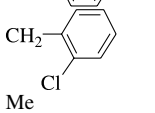
To demonstrate the efficiency and scope of the present method, a variety of *S*-alkyl thiocarbamates **1a–o** were synthesized from the corresponding amines **2a–j** and alkyl halides (Eq. 2, Table 2). Under 1 atm of carbon monoxide at 20 °C for 5 h in DMSO, ammonium salts of thiocarbamates **3a–j** were formed from amines **2a–j** with carbon monoxide and sulfur, followed by quenching by alkyl halides to afford the corresponding *S*-alkyl thiocarbamates **1a–o** in good to excellent yields.



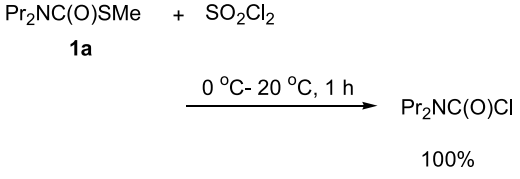
(2)

Secondary amines **2a–c**, **2e–h** were suitable for this thiocarboxylation to provide *S*-alkyl thiocarbamates **1a–g**, **1i–m** in good to excellent yields under mild conditions (1 atm, 20 °C) (entries 1–8 and 10–14). Even in 10 times large scale, *S*-methyl *N*,*N*-dipropylthiocarbamate (**1a**) was obtained in excellent yield (91%) for longer reaction time (entry 2). Furthermore, the chlorination of *S*-alkyl *N*,*N*-dialkylthiocarbamates **1** from secondary amines was successfully performed using sulfuryl chloride, to afford the corresponding carbamoyl chlorides in good yields (Eq. 3).[17]

Table 2. Synthesis of *S*-alkyl thiocarbamates (**1a–o**)

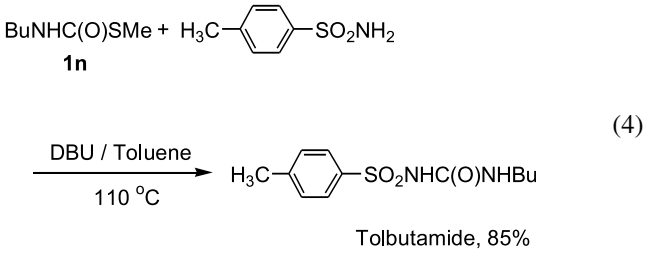
Entry	R^1	R^2		R^3	X		Yield%[a]
1	Pr	Pr	**2a**	Me	I	**1a**	88
2	Pr	Pr	**2a**	Me	I	**1a**	91[b]
3	Pr	Pr	**2a**	Et	I	**1b**[c]	82
4	Pr	Pr	**2a**	CH_2Ph	Cl	**1c**	95[d]
5	Et	Et	**2b**	CH_2Ph	Cl	**1d**	94[d,e]
6	Et	Et	**2b**		Cl	**1e**[f]	83[d,e], 39[g], 99[g,h], 80[d,i]
7	Et	Et	**2b**		Cl	**1f**[j]	86[d,e]
8	Bu	Bu	**2c**	Me	I	**1g**	68
9	*i*-Pr	*i*-Pr	**2d**	Me	I	**1h**	42, 45[i]
10	$-(CH_2)_4-$		**2e**	Me	I	**1i**	83
11	$-(CH_2)_5-$		**2f**	Me	I	**1j**	84
12	$-(CH_2)_2O(CH_2)_2-$		**2g**	Me	I	**1k**	76
13	$-(CH_2)_6-$		**2h**	Me	I	**1l**	88
14	$-(CH_2)_6-$		**2h**	Et	I	**1m**[k]	86
15	Bu	H	**2i**	Me	I	**1n**	73 (10)[l]
16	Ph	H	**2j**	Me	I	**1o**	0, 82[i]

[a] Reaction conditions: amine (20 mmol), sulfur (321 mg, 10 mmol), alkyl halide (12 mmol), DMSO (20 mL), CO (1 atm), 20 °C, 5 h for thiocarboxylation and 1 h for alkylation.
[b] Reaction conditions: dipropylamine (27.4 mL, 200 mmol), sulfur (3.21 g, 100 mmol), methyl iodide (7.5 mL, 120 mmol), DMSO (50 mL), CO (1 atm), 20 °C, 20 h for carbonylation and 1 h for alkylation.
[c] EPTC.
[d] Alkyl halides (10 mmol) was used.
[e] Reaction time: 8 h for thiocarboxylation and 1 h for alkylation.
[f] Thiobencarb.
[g] 4-Chlorobenzyl chloride (1.39 mL, 11 mmol) was used.
[h] K_2CO_3 (2.07 g, 15 mmol) was added.
[i] Amine (10 mmol) and DBU (1.50 mL, 10 mmol) were used.
[j] Orbencarb.
[k] Molinate.
[l] Yield of *N*,*N*′-dibutylurea.



(3)

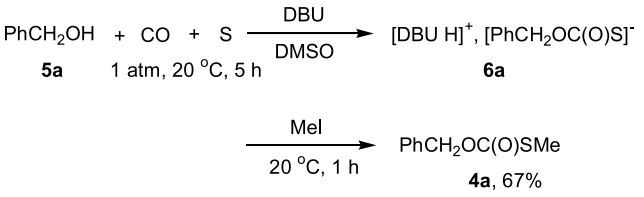
S-Alkyl diethylthiocarbamates **1d–f** synthesis from diethylamine (**2b**) occurred in considerably good yields, but this thiocarboxylation for **2b** needed slightly longer reaction time (8 h for thiocarboxylation). Without using other base, thiocarboxylation of **2b** did not finished perfectly to give **1e** in diminished yield (39%) in shorter reaction time (5 h for thiocarboxylation).[18] Addition of K_2CO_3 or DBU for this reaction system was also effective, **1e** was obtained in better yields for shorter reaction time (99[18] and 80%, respectively) (entry 6). Then, di-*i*-propylamine (**2d**) gave *S*-methyl *N*,*N*-di-*i*-propylthiocarbamate (**1h**) in low yield (42%), because of steric hindrance of di-*i*-propylamine (**2d**). Furthermore, in the presence of DBU, **1h** was given in similar yield (45%) (entry 9). Using this procedure, herbicides, such as EPTC (**1b**),[1,3] thiobencarb (**1e**),[1–3] orbencarb (**1f**),[1–3] and molinate (**1m**)[1,3] could be successfully synthesized in good yields (82–86%) (entries 3, 6, 7, and 14). The yield of *S*-methyl *N*-butylthiocarbamate (**1n**) from the primary amine (butylamine, **2i**) was somewhat diminished, accompanied with the formation of the corresponding urea derivative (entry 15).[25] Recently, we showed a methodology for useful medicine synthesis that these *N*-alkylthiocarbamates smoothly reacted with bezenesulfonamides in the presence of DBU, to afford the corresponding sulfonylurea derivatives in good yields, in which are used as oral antidiabetics (tolbutamide and chlorpropamide) (Eq. 4).[27]



(4)

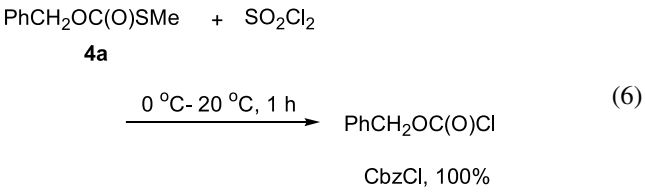
Furthermore, in spite of the low basicity of aniline (**2j**), *S*-methyl *N*-phenylthiocarbamate (**1o**) was obtained in good yield, in the case of using DBU (entry 16).[17]

Extension of this thiocarboxylation has yielded promising results. Then, we tested the effect of solvent DMSO on the thiocarboxylation of benzyl alcohol (**5a**) by carbon monoxide and sulfur under mild conditions (1 atm, 20 °C). This trial was easily performed for the thiocarboxylation of benzyl alcohol (**5a**) in the presence of DBU under 1 atm at 20 °C, followed by esterification using methyl iodide to afford the corresponding *S*-methyl *O*-benzyl carbonothioate (**4a**) in good yield (67%) (Eq. 5).



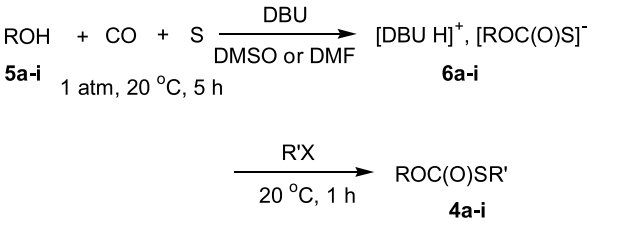
(5)

Also, we described *S*-methyl *O*-benzyl carbonothioate (**4a**) was a useful materials for further synthetic manipulation. *S*-Methyl *O*-benzyl carbonothioate (**4a**) was easily converted with sulfuryl chloride into the corresponding *O*-benzyl chloroformate (CbzCl) used as an *N*-protective reagent for amino group in peptide synthesis (Eq. 6).[20,21]



(6)

A variety of *S*-alkyl *O*-alkyl carbonothioates **4a–i** were synthesized from the corresponding alcohols and phenol **5a–i** and alkyl halides (Eq. 7, Table 3).

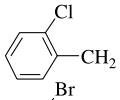
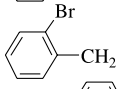
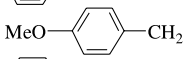
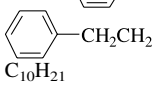


(7)

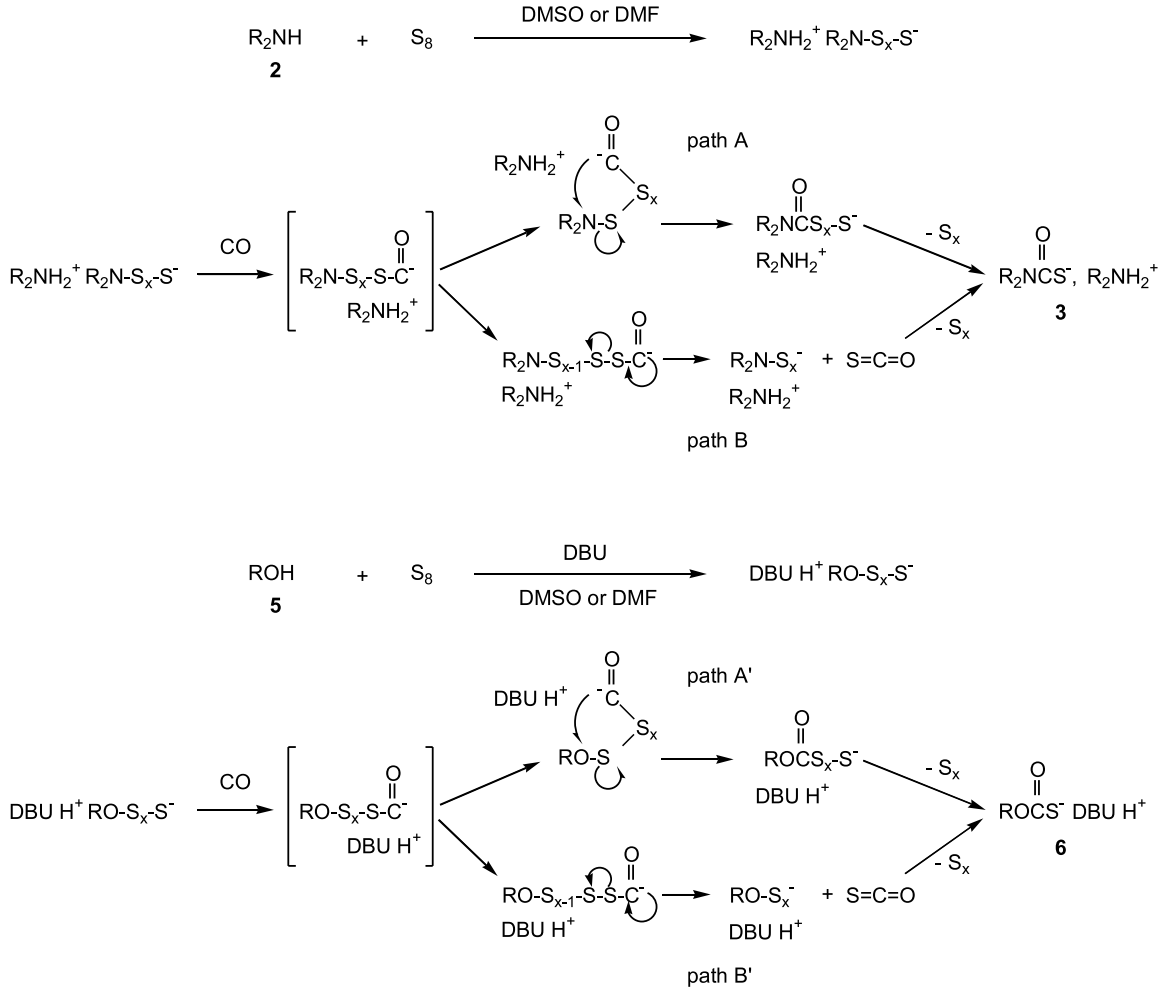
DMF using as a solvent, thiocarboxylation of benzyl alcohol (**5a**) with carbon monoxide and sulfur in the presence of DBU smoothly proceeded to give *S*-methyl *O*-benzyl carbonothioate (**4a**) in almost similar yield (65%) (entry 2), compared with that of **4a** using DMSO and DBU (entry 1). K_2CO_3 was weakly affected for this thiocarboxylation of benzyl alcohol (**5a**) to afford **4a** in poor yield (entry 3). DBN (1,5-diazabicyclo[4.3.0]non-5-ene) and triethylamine were not effective for this thiocarboxylation of **5a** in DMSO (entries 4 and 5). In the absence of base, no formation of salts of *O*-benzyl carbonothioate (**6a**) was observed (entry 6). Nevertheless, *S*-methyl *O*-benzyl carbonothioate (**4a**) was obtained successfully from benzyl alcohol (**5a**) in DBU/DMSO system (entry 1), the trials of synthesis of *S*-methyl *O*-(2-chloro)benzyl carbonothioate (**4b**), *S*-methyl *O*-(2-bromo)benzyl carbonothioate (**4c**), and *S*-methyl *O*-(4-methoxy)benzyl carbonothioate (**4d**) using DBU/DMSO system gave poor results (entries 7–9). It seemed that the products **4b–d** were easily decomposed into alcohols and thiol under very strong basic conditions (DBU/DMSO). However, using DMF as a solvent, **4b–d** were fortunately given in moderate to good yields (52–63%) in the presence of DBU (entries 7–9). According to these results, thiocarboxylation of various alcohols **5a–i** was performed with carbon monoxide and sulfur using 1 equiv of DBU under 1 atm at 20 °C for 5 h in DMF. Quenching by alkyl halides (1 h), the corresponding *S*-alkyl *O*-alkyl carbonothioates **4a–h** were afforded in good yields (52–68%) (entries 2, 7–13). However, the yield of *S*-methyl *O*-phenyl carbonothioate (**4i**) lowered (29%), because of very low basicity of phenol (**5i**) (entry 14).

Scheme 1 shows a plausible pathway for this thiocarboxylation. Based on our finding of the ready reaction for salts of thiolates with carbon monoxide to convert into salts of thiocarbamates **3**,[28] we suggest a plausible pathway via thiolate anions for this solvent-assisted thiocarboxylation of amines or alcohols with carbon monoxide and sulfur. In the case of thiocarboxylation on amines **2**, elemental sulfur is readily subject to S–S bond fission by the reaction with amines strongly assisted by DMSO[29] or DMF, to form ammonium salts of thiolate anions. The reaction of thiolate

Table 3. Synthesis of *S*-alkyl *O*-alkyl carbonothioates (**4a–i**)

Entry	R		Base	R′X		Yield%[a]
1	$PhCH_2$	**5a**	DBU	MeI	**4a**	67
2	$PhCH_2$	**5a**	DBU	MeI	**4a**	65[b]
3	$PhCH_2$	**5a**	K_2CO_3	MeI	**4a**	35
4	$PhCH_2$	**5a**	DBN	MeI	**4a**	5
5	$PhCH_2$	**5a**	Et_3N	MeI	**4a**	0
6	$PhCH_2$	**5a**	None	MeI	**4a**	0[c]
7		**5b**	DBU	MeI	**4b**	0, 61[b]
8		**5c**	DBU	MeI	**4c**	0, 63[b]
9		**5d**	DBU	MeI	**4d**	9, 52[b]
10		**5e**	DBU	MeI	**4e**	58[b]
11	$C_{10}H_{21}$	**5f**	DBU	EtI	**4f**	68[b]
12	$C_{18}H_{37}$	**5g**	DBU	EtI	**4g**	66[b]
13	$C_4H_9CHEtCH_2$	**5h**	DBU	EtI	**4h**	62[b]
14	Ph	**5i**	DBU	MeI	**4i**	29[b]

[a] Reaction conditions: alcohol (10 mmol), sulfur (321 mg, 10 mmol), base (10 mmol), alkyl halide (12 mmol), DMSO (20 mL), CO (1 atm), 20 °C, 5 h for thiocarboxylation and 1 h for alkylation.
[b] DMF (20 mL) was used as a solvent, instead of DMSO.
[c] Benzyl alcohol (20 mmol) was used.



Scheme 1.

anions with carbon monoxide gives the carbonylated species. Through an intramolecular rearrangement of the carbonylated species (path A) or elimination of carbonyl sulfide from the carbonylated species (path B), thiocarbamate salts **3** are generated. A plausible pathway for thiocarboxylation of alcohols **5** is the similar to that of amines **2**. But, in this case of alcohols **5**, solvents and DBU assist the thiocarboxylation of **5** to form DBU salts of thiolates and carbonothioates **6** as intermediates.

3. Conclusion

A useful synthetic method for *S*-alkyl thiocarbamates **1** has been developed under mild conditions (1 atm, 20 °C) without using additional base, in which the carboxylation of amines with carbon monoxide and sulfur was powerfully assisted by solvent DMSO or DMF. This thiocarboxylation was employed successfully for the synthesis of EPTC (**1b**), thiobencarb (**1e**), orbencarb (**1f**), and molinate (**1m**) used as herbicides. Also, synthesis of *S*-alkyl *O*-alkyl carbonothioates **4a–h** from alcohols **5a–h** and alkyl halides with carbon monoxide and sulfur, assisted by DMF have been explored in the presence of DBU under mild condition (1 atm, 20 °C). From the viewpoint of application to actual industrial production of *S*-alkyl thiocarbamates **1** such as herbicides, the present reaction is very significant, in terms of the use of easily available and cheap carbon monoxide, sulfur, and DMSO (or DMF), and mild reaction conditions.

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 JASCO FT/IR-4100 instrument. ^{1}H 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–j**, alcohols **5a–i**, alkyl halides, DMSO, other solvent, DBU, other bases, sulfur (99.5%), and carbon monoxide (99.9%) were used as purchased.

4.2. Typical procedure for the synthesis of *S*-methyl *N*,*N*-dipropylthiocarbamate (1a) from dipropylamine (2a), carbon monoxide, sulfur, and methyl iodide

A DMSO (20 mL) solution containing dipropylamine (**2a**) (2.74 mL, 20 mmol), and powdered sulfur (321 mg,

10 mmol) was vigorously stirred under carbon monoxide (1 atm) at 20 °C for 5 h. Into the DMSO solution of thiocarbamate salt (**3a**), methyl iodide (0.75 mL, 12 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 mL, 50 mL×2). After evaporation of solvents and purification by short-column chromatography (silica gel, toluene/AcOEt=1:1), *S*-methyl *N*,*N*-dipropylthiocarbamate (**1a**) was afforded in 88% yield (1.54 g).

4.2.1. *S*-Methyl *N*,*N*-dipropylthiocarbamate (1a).[4,12,13,17] Oil; IR (neat) 2965, 1655, 1405, 1225, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J=7 Hz, 6H), 1.60 (br s, 4H), 2.32 (s, 3H), 3.28 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 12.8, 21.4, 49.3, 168.2; MS (*m*/*z*, %) 175 (M^+, 100), 128 (89), 86 (79), 75 (65). Exact MS calcd for $C_8H_{17}NOS$: 175.1031. Found: 175.1012.

4.2.2. *S*-Methyl perhydroazepin-1-carbothioate (1l). Oil; IR (neat) 2925, 1650, 1405, 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.54–1.58 (m, 4H), 1.74 (br s, 4H), 2.33 (s, 3H), 3.45 (q, J=6 Hz, 2H), 3.57 (t, J=6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.9, 26.9, 27.2, 27.9, 28.4, 47.4, 47.6, 168.2; MS (*m*/*z*, %) 173 (M^+, 41), 126 (100), 83 (18), 55 (48). Exact MS calcd for $C_8H_{15}NOS$: 173.0874. Found: 173.0861.

Identification of the other *S*-alkyl thiocarbamates **1b–k**, **1m–o** was performed by comparison of the IR, NMR, MS spectra, and mp of **1b–k**, **1m–o** with those of authentic samples, which were prepared according to the literatures, **1b**, **1g–k**, **1n**, **1o**,[17] **1c**, **1e**, **1f**, **1m**,[18] and **1d**.[13]

4.3. General synthetic method of *S*-methyl *O*-benzyl carbonothioate (4a) under mild conditions

Into DMSO (20 mL), benzyl alcohol (**5a**) (1.03 mL, 10 mmol), powdered sulfur (321 mg, 10 mmol) and DBU (1.50 mL, 10 mmol) were added. The solution was very vigorously stirred under carbon monoxide (1 atm) at 20 °C for 5 h. Then, methyl iodide (0.75 mL, 12 mmol) was added carefully at 0 °C under argon atmosphere in the DMSO solution of carbonothioate salt (**6a**). The solution was stirred for additional 1 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 mL, 50 mL×2). After evaporation of solvents and purification by short-column chromatography (silica gel, toluene), *S*-methyl *O*-benzyl-carbonothioate (**4a**) was obtained in 67% yield (1.23 g).

4.3.1. *S*-Methyl *O*-benzyl carbonothioate (4a).[20,21] Oil; IR (neat) 1710, 1135 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 5.24 (s, 2H), 7.36 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 68.9, 128.4, 128.5, 135.5, 171.6; MS (*m*/*z*, %) 182 (M^+, 69), 92 (48), 91 (100), 77 (27), 65 (36). Exact MS calcd for $C_9H_{10}O_2S$: 182.0402. Found: 182.0368.

4.3.2. *S*-Methyl *O*-2-phenylethyl carbonothioate (4e). Oil; IR (neat) 1710, 1145 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.98 (t, J=7 Hz, 2H), 4.42 (t, J=7 Hz, 2H), 7.20–7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 35.2, 67.8, 126.7, 128.6, 128.9, 137.3, 171.6; MS (*m*/*z*, %) 196 (M^+, 0.2), 105 (100), 104 (100), 91 (99), 77 (68). Exact MS calcd for $C_{10}H_{12}O_2S$: 196.0558. Found: 196.0547.

4.3.3. *S*-Ethyl *O*-decyl carbonothioate (4f). Oil; IR (neat) 2925, 2855, 1715, 1145 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J=7 Hz, 3H), 1.26–1.34 (m, 17H), 1.61–1.68 (m, 2H), 2.86 (q, J=7 Hz, 2H), 4.20 (t, J=7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 15.0, 22.7, 25.3, 25.8, 28.7, 29.2, 29.3, 29.5, 29.5, 31.9, 67.5, 171.2; MS (*m*/*z*, %) 246 (M^+, 7), 185 (28), 85 (59), 71 (80), 57 (100). Exact MS calcd for $C_{13}H_{26}O_2S$: 246.1654. Found: 246.1637.

4.3.4. *S*-Ethyl *O*-stearyl carbonothioate (4g). Oil; IR (neat) 2925, 2850, 1715, 1145 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J=7 Hz, 3H), 1.26–1.34 (m, 33H), 1.63–1.68 (m, 2H), 2.86 (q, J=7 Hz, 2H), 4.20 (t, J=7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 15.0, 22.7, 25.3, 25.8, 28.7, 29.2, 29.4, 29.5, 29.5, 29.6, 29.7, 29.7, 31.9, 67.4, 171.1; MS (*m*/*z*, %) 358 (M^+, 14), 297 (43), 85 (74), 71 (83), 57 (100). Exact MS calcd for $C_{21}H_{42}O_2S$: 358.2906. Found: 358.2909.

4.3.5. *S*-Ethyl *O*-2-ethylhexyl carbonothioate (4h). Oil; IR (neat) 2960, 2930, 1710, 1150 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J=7 Hz, 6H), 1.29–1.41 (m, 11H), 1.53–1.62 (m, 1H), 2.86 (q, J=7 Hz, 2H), 4.13 (d, J=6 Hz, 1H), 4.14 (d, J=6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.9, 14.0, 15.0, 22.9, 23.7, 25.3, 28.9, 30.2, 38.9, 69.7, 171.2; MS (*m*/*z*, %) 218 (M^+, 4), 157 (8), 112 (24), 71 (92), 57 (100). Exact MS calcd for $C_{11}H_{22}O_2S$: 218.1341. Found: 218.1341.

Identification of the other *S*-methyl *O*-alkyl carbonothioates **4b–d** and *S*-methyl *O*-phenyl carbonothioate (**4i**) was performed by comparison of the IR, NMR, and MS spectra of **4b–d** and **4i** with those of authentic samples, which were prepared according to the literatures.[20,21]

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