Tetrahedron Vol. 49, No. 12, pp. 2403-2412, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

REACTIONS OF UNSTABLE DIALKYLCARBAMOYL LITHIUMS WITH SULFUR COMPOUNDS

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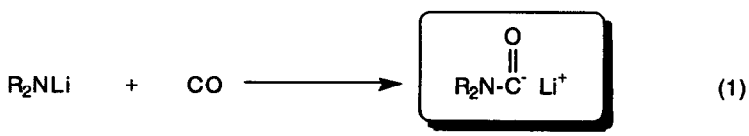
(*Received in Japan* 15 *December* 1992)

Abstract : Unstable dialkylcarbamoyl lithiums, generated from the reaction of lithium dialkylamides with carbon monoxide, were successfully trapped by sulfur compounds (elemental sulfur, disulfides, carbon disulfide, and carbonyl sulfide) at low temperature, through their potent affinity with a sulfur atom. These efficient reactions were also applied to development of a facile synthetic method for thiocarbamates, useful herbicides, and thiooxamates.

INTRODUCTION

The formation of carbamoyl anions (**1**) from the reaction of lithium dialkylamides with carbon monoxide has been well-established (Eq. 1). However, until recently control of **1** generated *in situ*, has been generally difficult and use of **1** as active reaction intermediates for organic syntheses has been considerably limited because of much difficulty in treating and least stability under ordinary reaction conditions.



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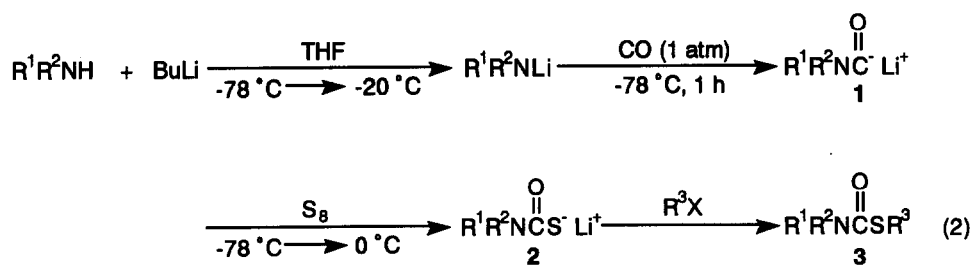
About ten years ago, Rautenstrauch *et al.* reported the practical synthesis of amide derivatives using a suitable trapping method of carbamoyl anions (**1**) as intermediates.[1,2] Thus, effective trapping of carbamoyl anions was performed at low temperature (*ca.* -78 °C) using water, alkyl halides, aldehydes, or ketones as electrophiles. Though the reaction of **1** with a variety of electrophiles has been known, the reactivities of **1** with sulfur compounds were hitherto

unexplored.[3] Very recently, by our extensive studies on the reactions of carbamoyl anions (**1**) with elemental sulfur and disulfides, we found that these sulfur compounds could play an important role as new desirable trapping reagents for **1** through potent affinity of carbamoyl lithiums (**1**) with sulfur atom as reported preliminary results.[4,5] In this paper, we wish to describe full details of this first and successful trapping of carbamoyl lithium (**1**) using a variety of sulfur compounds[6] which include elemental sulfur, disulfides, carbon disulfide, and carbonyl sulfide, and also revealed a new useful synthesis of thiocarbamates (**3**), useful herbicides, and thiooxamates (**5**).

RESULTS AND DISCUSSION

At the outset, elemental sulfur was chosen as the first target to examine the reactivity with carbamoyl lithiums (**1**), because elemental sulfur readily causes cleavage of the S-S bond in its S_8 ring through the reaction with nucleophiles such as alkyl lithiums to form thiolate anions.[7] The reaction of **1** with elemental sulfur was performed as follows (Eq. 2). *N,N*-Diethylcarbamoyl lithium (**1 a**) was synthesized from the reaction of carbon monoxide and lithium diethylamide, prepared from diethylamine and butyl lithium, at -78 °C for 1 h. Then, elemental sulfur was added into the solution of **1 a** under low temperature (-78 °C) and the reaction mixture was gradually warmed up with stirring from -78 °C to 0 °C. After alkylation with benzyl bromide of lithium *N,N*-diethylthiocarbamate (**2 a**) at 0 °C, *S*-benzyl *N,N*-diethylthiocarbamate (**3 a**) was given in 99% yield. This result showed that carbamoyl lithiums (**1**) readily give rise to efficient fission of the S-S bond of elemental sulfur to form lithium thiocarbamates (**2**) under very mild reaction conditions (-78 ~ 0 °C).

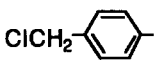
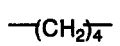
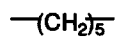
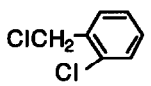


(2)

The synthesis of a variety of S-alkyl thiocarbamates (**3 a-j**) by a similar procedure was summarized in Table 1. Most of **3 a-j** prepared from secondary amines were obtained in good to excellent yields. Thus, the present method may be characterized by facile one-pot synthesis of **3** from secondary amines, butyl lithium, carbon monoxide, sulfur, and alkyl halides.[8] However, synthesis of **3 k** from a primary amine, hexylamine, did not proceeded smoothly, and only a complex mixture was obtained. A series of *S*-alkyl thiocarbamates are well known as useful herbicides. For instance, *S*-ethyl *N,N*-dipropylthiocarbamate (EPTC, **3 f**) was used for control of annual grasses and many broadleave weeds,[9,12] and *S*-4-chlorobenzyl *N,N*-diethylthiocarbamate (benthiocarb,

3d) has been produced for rice crop in a large-scale as an important herbicide.[13,14] These herbicides (**3d-g**) were also prepared in good yields by this method.

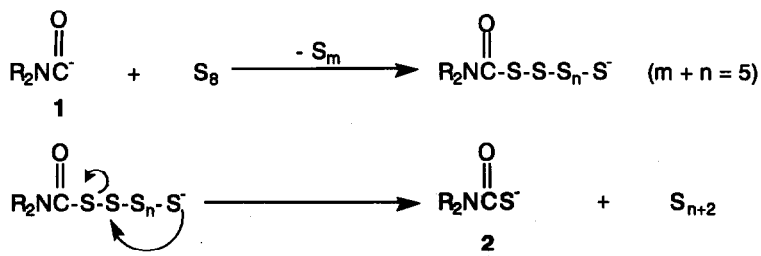
Table 1. Synthesis of S-Alkyl Thiocarbamates (**3a-k**)

R^1	R^2	R^3X		Yield, %[a]	R^1	R^2	R^3X		Yield, %[a]
Et	Et	$PhCH_2Br$	**3a**	99	Pr	Pr	EtI	**3f**	55[e]
		MeI	**3b**	88			PrI	**3g**	57[f]
		BuI	**3c**	75			$PhCH_2Br$	**3h**	73
			**3d**	85[b]			$PhCH_2Br$	**3i**	43
							$PhCH_2Br$	**3j**	65
			**3e**	83[d]	Hex	H	$PhCH_2Br$	**3k**	—[g]

a) Isolated yields. b) Benthiocarb (Saturn®).[c] C) General names were shown. Tradenames were in parentheses. d) Orthobencarb.[c] e) EPTC (Eptam®).[c] f) Vernolate (Vernam®).[c] g) A complex mixture was obtained.

According to a reaction pathway proposed in the case of the reaction of carbamoyl lithiums (**1**) with elemental sulfur, nucleophilic attack of **1** to the sulfur atom brings about efficient opening of the S_8 ring followed by fission of some of these S-S bonds to form a lithium thiolate, and subsequent elimination of sulfur molecule gives lithium thiocarbamate (**2**) (Scheme 1).

Scheme 1



Next attempt was the reaction of carbamoyl anions (**1**) with disulfides which have S-S bond similar to elemental sulfur, and we found that disulfides readily reacted with **1** to give thiocarbamates (**3**) (Eq. 3). For example, *N,N*-diethylcarbamoyl lithium (**1a**) reacted at -78 °C with diphenyldisulfide followed by warming up of the mixture to room temperature to form *S*-phenyl *N,N*-diethylthiocarbamate (**3l**) in 65% yield. Nucleophilic attack of carbamoyl lithiums (**1**) to sulfur atom brought about the fission of the S-S bond of disulfides to yield thiocarbamates (**3**). The result of the reaction of **1** with disulfides is shown in Table 2. Thiocarbamates (**3**) were afforded in moderate to good yields, except for **3s** from primary carbamoyl lithium. In the case of this reaction of carbamoyl lithiums (**1**) with diaryldisulfides, *S*-aryl thiocarbamates (**3**) which is almost impossible to prepare from lithium thiocarbamates (**2**) with aryl halides were obtained without difficulty. Furthermore, the reaction of *N,N*-diethylcarbamoyl lithium (**1a**) with diphenylsulfide did not occur at all as expected, because monosulfides have no S-S bond.

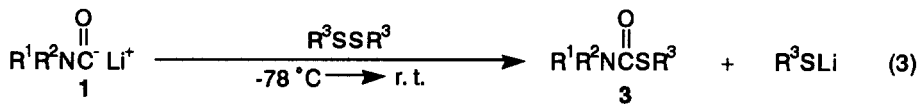


Table 2. Synthesis of Thiocarbamates Using Disulfides

R^1	R^2	R^3		Yield, %[a]	R^1	R^2	R^3		Yield, %[a]
Et	Et	Ph	**3l**	65	Pr	Pr	Ph	**3o**	47
		Bu	**3c**	66			Et	**3f**	44[b]
		Me	**3b**	54	i-Pr	i-Pr	Ph	**3p**	43
		Et	**3m**	45	$-(CH_2)_4-$		Ph	**3q**	35
		CH_2=$CHCH_2$	**3n**	68	$-(CH_2)_5-$		Ph	**3r**	36
					Hex	H	Ph	**3s**	0

a) Isolated yields. b) EPTC (Eptam®).

Then, we also tried the reaction of carbamoyl lithiums (**1**) with carbon disulfide or carbonyl sulfide. Because these compounds have two reaction points which are the carbonyl carbons and the sulfur atoms, these reactions are suitable models for the examination of relative nucleophilicity of **1** for carbonyl carbon against affinity of **1** for sulfur atom.

Thus, the reaction of *N,N*-diethylcarbamoyl lithium (**1 a**) with carbon disulfide was carried out at -78 to 0 °C to give lithium *N,N*-diethylthiocarbamate (**2 a**) accompanying with formation of CS polymers. By alkylation of **2 a** with benzyl bromide, *S*-Benzyl *N,N*-diethylthiocarbamate (**3 a**) was given in 61% yield (Eq. 4).[15] All cases of the reaction of carbamoyl lithium (**1**) with carbon disulfide followed by S-alkylation with alkyl halides gave the corresponding thiocarbamates (**3**) in good yields, as shown in Table 3. This result showed that the affinity of **1** to sulfur atom was apparently preferential to nucleophilicity of **1** for the carbonyl carbon in the reaction with carbon disulfide.[16]

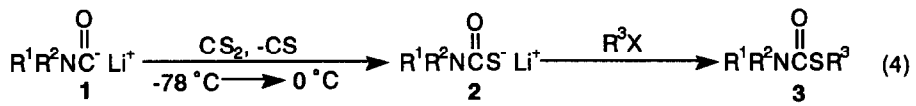


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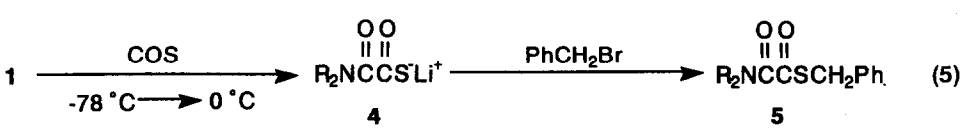
Table 3. Reaction with Carbon Disulfide

R^1	R^2	R^3X		Yield, %[a]	R^1	R^2	R^3X		Yield, %[a]
Et	Et	$PhCH_2Br$	**3 a**	61	Pr	Pr	$PhCH_2Br$	**3 h**	57
		MeI	**3 b**	53			MeI	**3 u**	40
		EtI	**3 m**	51			$CH_2=CHCH_2Br$	**3 v**	38
		BuI	**3 e**	55	$-(CH_2)_4-$		$PhCH_2Br$	**3 i**	51
Bu	Bu	$PhCH_2Br$	**3 t**	37	$-(CH_2)_5-$		$PhCH_2Br$	**3 j**	72

a) Isolated yields.

In contrast to the reaction with carbon disulfide, carbamoyl lithium (**1 a**) easily reacted with carbonyl sulfide to afford lithium *N,N*-diethylthiooxamates (**4 a**) in 56% yield (Eq. 5).[17] In this case, the reaction of **1** with carbonyl sulfide dominantly involved nucleophilic attack of **1** to the carbonyl carbon. The present sharp contrast between the reaction of carbamoyl lithium (**1**) with carbon disulfide and that with carbonyl sulfide may depend on the dual characters of **1**, the affinity for a



(5)

R=Et : **5 a**, 56% R=n-Pr : **5 b**, 37%

sulfur atom and nucleophilicity for a carbonyl carbon, which may be noteworthy as an example similar to those characters of acyl anions.[18]

In summary,utilizing the strong affinity of unstable carbamoyl lithiums (**1**) for a sulfur atom, the corresponding thiocarbamates (**3**) were efficiently prepared in good yields by the facile reaction of **1** with sulfur compounds such as elemental sulfur, disulfides, and carbon disulfide. These reactions were also successfully developed to a new synthetic method for thiocarbamates (**3**) as herbicides. However, in the reaction of **1** with carbonyl sulfide, nucleophilicity of **1** for a carbonyl carbon play the most important role to provide thiooxamates (**5**). These results showed the dual characters of carbamoyl lithiums (**1**), the affinity for sulfur atom and nucleophilicity for carbonyl carbon.

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 04217105 from the Ministry of Education, Science and Culture, Japan.

EXPERIMENTAL SECTION

General Comments : Melting points were determined on a Mettler FP 5 and were uncorrected. Gas chromatography (GC) was measured on Shimadzu GC-7A. ^{1}H-NMR spectra were obtained on JEOL JNM-EX270 or JEOL JNM-FX90Q spectrometers. Chemical shifts were reported in ppm relative to tetramethylsilane (δ-units). Infrared (IR) spectra were recorded on a JASCO A-3 or Shimadzu IR-435 spectrometers. Mass spectra were recorded on JEOL JMS-DX303HF spectrometer. THF used was dried over sodium wire and purified by distillation.

Typical Procedure for Synthesis of S-Alkyl Thiocarbamates through Reaction of Carbamoyl Lithiums and Elemental Sulfur : To a THF solution (20 mL) of diethylamine (1.03 mL, 10 mmol) was added slowly 10 %w/v hexane solution of butyl lithium (6.4 mL, 10 mmol) at -78 °C, and the solution was gradually warmed to -20 °C with stirring. Then, the resulting colorless solution of lithium diethylamide was cooled to -78 °C and was vigorously stirred under carbon monoxide (1 atm) for 1 h at -78 °C. After the absorption of carbon monoxide was completed, elemental sulfur (0.32 g, 10 mmol) was added at -78 °C to the orange solution of *N,N*-diethylcarbamoyl lithium (**1 a**). This solution was gradually warming-up to 0 °C and was quenched with benzyl bromide (1.43 mL, 12 mmol). The reaction mixture was then poured into aq. 1*N* HCl (100 mL), and extracted by Et_2O (100 mL, 2 X 50 mL). The extract was dried over $MgSO_4$ and the solvent was evaporated. Purification by short-column chromatography (silica gel, benzene) gave 2.20 g (99%) of *S*-benzyl *N,N*-diethylthiocarbamate (**3 a**).

General Procedure for Thiocarbamate Synthesis Using Disulfides : To the solution of *N,N*-diethylcarbamoyl lithium (**1 a**), which prepared in the same manner as before, diphenyl disulfide (2.62 g, 12 mmol) was added at -78 °C. Warming-up of the mixture slowly toroom temperature followed by similar work-up and purification through short-column chromatography (silica gel, benzene) gave 1.35 g (65%) of *S*-phenyl *N,N*-diethylthiocarbamate (**3 l**).

The Typical Procedure for the Reaction of Carbamoyl Lithiums with Carbon Disulfide : Carbon disulfide (0.60 mL, 10 mmol) was added at -78 °C to the solution of carbamoyl lithium (**1 a**). Immediately, color of the solution was changed to black, possibly caused by polymerization of CS. Gradual warming-up of the mixture to 0 °C followed by S-alkylation with benzyl bromide (1.43 mL, 12 mmol) gave 1.35 g (61%) of *S*-benzyl *N,N*-diethylthiocarbamate (**3 a**) after similar work-up and purification by short-column chromatography (silica gel, benzene).

Reaction of Carbamoyl Lithiums with Carbonyl Sulfide : Into the THF solution of *N,N*-diethylcarbamoyl lithium (**1 a**) prepared *in situ*, carbonyl sulfide was blown at -78 °C for 30 min. Gradual warming-up to 0 °C followed by S-alkylation with benzyl bromide (1.43 mL, 12 mmol) gave 1.41 g (56%) of *S*-benzyl *N,N*-diethylthiooxamate (**5 a**) after similar work-up and purification by short-column chromatography (silica gel, ethyl acetate).

***S*-Benzyl *N,N*-diethylthiocarbamate (3 a).** 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. 223.1031, found 223.1004.

***S*-Methyl *N,N*-diethylthiocarbamate (3 b).** Oil; 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. 147.0718, found 147.0735. Anal. Calcd for $C_6H_{13}NOS$: 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*-Butyl *N,N*-diethylthiocarbamate (3 c).** Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.92 (t, J=7 Hz, 3H), 1.16 (t, J=7 Hz, 6H), 1.28-1.80 (m, 4H), 2.89 (t, J=7 Hz, 2H), 3.38 (q, J=7 Hz, 4H); MS, m/z (%), 189 (M^+, 8), 100 (100), 72 (56); exact MS calcd. 189.1187, found 189.1221.

***S*-4-Chlorobenzyl *N,N*-diethylthiocarbamate (3 d).** 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. 257.0641, found 257.0639.

***S*-2-Chlorobenzyl *N,N*-diethylthiocarbamate (3 e).** 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. 257.0641, found 257.0638.

***S*-Ethyl *N,N*-dipropylthiocarbamate (3 f).** Oil; IR (neat) 1655 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.91 (t, J=7 Hz, 6H), 1.27 (t, J=7 Hz, 3H), 1.40-1.84 (m, 4H), 2.90 (q, J=7 Hz, 2H), 3.29 (t, J=7 Hz, 4H); MS, m/z (%), 189 (M^+, 29), 160 (10), 128 (100), 86 (71); exact MS calcd. 189.1187, found 189.1204.

***S*-Propyl *N,N*-dipropylthiocarbamate (3 g).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ

0.90 (t, J=7 Hz, 6H), 0.98 (t, J=7 Hz, 3H), 1.41-1.84 (m, 4H), 2.88 (t, J=7 Hz, 2H), 3.29 (t, J=7 Hz, 4H); MS, m/z (%), 203 (M^+, 16), 128 (100), 86 (67); exact MS calcd. 203.1344, found 203.1311.

***S*-Benzyl *N,N*-dipropylthiocarbamate (3h).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, J=7 Hz, 6H), 1.39-1.81 (m, 4H), 3.28 (t, J=7 Hz, 4H), 4.13 (s, 2H), 7.22-7.32 (m, 5H); MS, m/z (%), 251 (M^+, 52), 128 (100), 91 (79), 86 (58); exact MS calcd. 251.1344, found 251.1300.

***S*-Benzyl pyrrolidinecarbothioate (3i).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.89 (brs, 4H), 3.34 (brs, 2H), 3.53 (brs, 2H), 4.17 (s, 2H), 7.18-7.37 (m, 5H); MS, m/z (%), 221 (M^+, 43), 188 (18), 98 (100), 91 (35), 55 (51); exact MS calcd. 221.0874, found 221.0859.

***S*-Benzyl piperidinecarbothioate (3j).** Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.51-1.68 (m, 6H), 3.48 (brs, 4H), 4.16 (s, 2H), 7.18-7.36 (m, 5H); MS, m/z (%), 235 (M^+, 40), 202 (12), 112 (100), 91 (35), 69 (56); exact MS calcd. 235.1031, found 235.1078.

***S*-Phenyl *N,N*-diethylthiocarbamate (3l).** Oil; IR (neat) 1660 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.22 (t, J=7 Hz, 6H), 3.44 (q, J=7 Hz, 4H), 7.32-7.57 (m, 5H); MS, m/z (%) 209 (M^+, 12), 109 (11), 100 (100), 72 (41); exact MS calcd. 209.0874, found 209.0900.

***S*-Ethyl *N,N*-diethylthiocarbamate (3m).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.19 (t, J=7 Hz, 6H), 1.30 (t, J=7 Hz, 3H), 2.95 (q, J=8 Hz, 2H), 3.43 (q, J=6 Hz, 4H); MS, m/z (%), 161 (M^+, 48), 100 (100), 72 (60); exact MS calcd. 161.0874, found 161.0896.

***S*-Allyl *N,N*-diethylthiocarbamate (3n).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.18 (t, J=7 Hz, 6H), 3.43 (q, J=7 Hz, 4H), 3.60 (d, J=6 Hz, 2H), 4.95-5.48 (m, 2H), 5.61-6.24 (m, 1H); MS, m/z (%) 173 (M^+, 11), 100 (100), 72 (62); exact MS calcd. 173.0874, found 173.0891.

***S*-Phenyl *N,N*-dipropylthiocarbamate (3o).** Oil; IR (neat) 1660 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.91 (t, J=6 Hz, 6H), 1.39-1.92 (m, 4H), 3.31 (t, J=7 Hz, 4H), 7.20-7.56 (m, 5H); MS, m/z (%) 237 (M^+, 7), 128 (100), 86 (46); exact MS calcd. 237.1187, found 237.1215.

***S*-Phenyl *N,N*-di-isopropylthiocarbamate (3p).** Oil; IR (neat) 1660 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.31 (d, J=7 Hz, 12H), 3.23-4.36 (brs, 2H), 7.19-7.55 (m, 5H); MS, m/z (%) 237 (M^+, 2), 128 (100), 110 (40), 86 (96); exact MS calcd. 237.1187, found 237.1203.

***S*-Phenyl pyrrolidinecarbothioate (3q).** Oil; IR (neat) 1665 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.92 (brs, 4H), 3.40-3.64 (m, 4H), 7.22-7.61 (m, 5H); MS, m/z (%), 207 (M^+, 20), 109 (12), 98 (100), 55 (43); exact MS calcd. 207.0718, found 207.0679.

***S*-Phenyl piperidinecarbothioate (3r).** mp 53.1 °C; IR (neat) 1660 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.59 (brs, 6H), 3.50 (brs, 4H), 7.22-7.57 (m, 5H); MS, m/z (%), 221 (M^+, 12), 112 (100), 69 (46); exact MS calcd. 221.0874, found 221.0870.

***S*-Benzyl *N,N*-dibutylthiocarbamate (3t).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.92 (t, J=7 Hz, 6H), 1.24-1.38 (m, 4H), 1.50-1.61 (m, 4H), 3.30 (brs, 4H), 4.15 (s, 2H), 7.21-7.36 (m, 5H); MS, m/z (%), 279 (M^+, 40), 156 (82), 100 (39), 91 (62), 57 (100); exact MS calcd. 279.1657, found 279.1712.

***S*-Methyl *N,N*-dipropylthiocarbamate (3u).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, J=7 Hz, 6H), 1.40-1.84 (m, 4H), 2.31 (s, 3H), 3.29 (t, J=8 Hz, 4H); MS, m/z (%), 175 (M^+, 35), 128 (100), 86 (55), 75 (41); exact MS calcd. 175.1031, found 175.1034. Anal. Calcd for $C_8H_{17}NOS$: 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*-Allyl *N,N*-dipropylthiocarbamate (3v).** Oil; IR (neat) 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, J=7 Hz, 6H), 1.37-1.88 (m, 4H), 3.29 (t, J=6 Hz, 4H), 3.57 (d, J=7 Hz, 2H), 5.00-5.42 (m, 2H), 5.65-6.16 (m, 1H); MS, m/z (%) 201 (M^+, 19), 128 (100), 112 (13), 86 (47); exact MS calcd. 201.1187, found 201.1185.

***S*-Benzyl *N,N*-diethylthiooxamate (5a).** Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.17 (t, J=7 Hz, 3H), 1.18 (t, J=7 Hz, 3H), 3.41 (q, J=7 Hz, 2H), 3.42 (q, J=7 Hz, 2H), 4.17 (s, 2H), 7.21-7.34 (m, 5H); MS, m/z (%), 251 (M^+, 6), 223 (14), 100 (100), 91 (20), 72 (53); exact MS calcd. 251.0980, found 251.0942.

***S*-Benzyl *N,N*-dipropylthiooxamate (5b).** Oil; IR (neat) 1645 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 0.83 (t, J=7 Hz, 3H), 0.91 (t, J=7 Hz, 3H), 1.50-1.67 (m, 4H), 3.28-3.34 (m, 4H), 4.16 (s, 2H), 7.20-7.34 (m, 5H); MS, m/z (%), 279 (M^+, 8), 251 (16), 128 (100), 91 (31), 86 (52); exact MS calcd. 279.1293, found 279.1292.

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15. *S*-Benzyl *N,N*-diethyldithiocarbamate (0.36 g, 15%) was also formed.
16. In this reaction with carbon disulfide, an another route which the carbophilic attack of **1** initially occurs followed by migration of the dithiocarbolate sulfur anion, can be considered.[6b]
17. *S*-Benzyl *N,N*-diethylthiocarbamate (0.37 g, 17%) was also obtained. It might be formed by the reaction of lithium *N,N*-diethylamide with carbonyl sulfide, or by thiophilic attack of *N,N*-diethylcarbamoyl lithium (**1 a**) to carbonyl sulfide.
18. The reactions of acyl anion with carbon disulfide or carbonyl sulfide showed the similar dual reactivities.[6b]