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A Facile Method for the Synthesis of Thiocarbamates: Palladium-Catalyzed Reaction of Disulfide, Amine, and Carbon Monoxide

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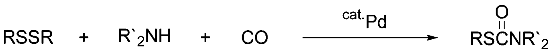

$$\mathrm{RSSR} + \mathrm{R'_2NH} + \mathrm{CO} \xrightarrow{\text{cat. Pd}} \mathrm{RS}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NR'_2}$$

A new method for the synthesis of thiocarbamates has been developed. When dialkyl or diaryl disulfides were allowed to react with secondary amines and carbon monoxide in the presence of a catalytic amount of a palladium complex, the thiocarbamates were obtained in moderate to good yields. In contrast to that of secondary amines, in the reaction of a primary amine, no formation of thiocarbamate was confirmed, but urea was formed in good yield.

The development of the process to replace the use of phosgene as a carbonylating reagent has received considerable attention in recent years due to environmental and industrial concerns. Carbon monoxide is one of the promising agents for the replacement of phosgene; the development of new methods for the carbonylation of various organic compounds with carbon monoxide could have a significant impact on organic and industrial chemistries.[1]

A series of thiocarbamates is known as useful herbicides, and many methods for the synthesis of thiocarbamates have already been reported.[2] Among them, the reaction of an amine with phosgene and a thiol or with carbonyl sulfide followed by alkylation with alkyl halides has been well-known as the general synthetic method.[3,4] As another approach, the development of carbonylation routes using carbon monoxide has attracted considerable attention, and various synthetic routes of thiocarbamates have been reported: (i) the reaction of a secondary amine, carbon monoxide, sulfur, and alkyl halides,[5] (ii) the selenium-catalyzed four-component coupling of an amine, sulfur, carbon monoxide, and alkyl halides,[6] (iii) the reaction of carbamoyllithium, which was prepared in situ by the reaction of lithium amide with carbon monoxide, with sulfur and alkyl halides or with disulfide,[7] (iv) nickel- and palladium-assisted or catalyzed coupling of an amine, thiol, and carbon monoxide,[8] and (v) palladium-catalyzed azathiolation of carbon monoxide using sulfeneamide.[9] However, there are several disadvantages of these methods: (i) the requirement of high reaction temperatures and highly pressurized carbon monoxide, (ii) the need for expensive lithium amide, (iii) the use of a thiol having a bad smell and unstable in air, (iv) low turn-over number of catalyst, (v) low or moderate yields of products, (vi) the use of unstable reagents, or (vii) multistep procedures. Therefore, there is increased interest in the development of convenient synthetic methods for thiocarbamate formation by using carbon monoxide. In this paper, we wish to report a facile method for the

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[1] For recent reviews of carbonylation, see: (a) Dugal, M.; Koch, D.; Naberfeld, G.; Six, C. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Wiley-VCH Verlag: Weinheim, Germany, 2002; Vol. 3. (b) Negishi, E., Ed. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; John Wiley & Sons: New York, 2002; pp 2691−2704. (c) Skoda-Foldes, R.; Kollar, L. *Corrent Org. Chem.* **2002**, *6*, 1097. (d) Bates, R. W. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, UK, 1995; Vol. 12, pp 349−386. (e) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. In *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.

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[4] *S*-Alkyl thiocarbamates were prepared by the reaction of trichloroacetyl chloride with amine and thiol. See: Wynne, J. H.; Jensen, S. D.; Snow, A. W. *J. Org. Chem.* **2003**, *68*, 3733.

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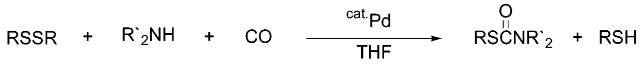
[8] (a) Jacob, J.; Reynolds, K. A.; Jones, W. D.; Goldleski, S. A.; Valente, R. R. *Organometallics* **2001**, *20*, 1028. (b) Jones, W. D.; Reynolds, K. A.; Sperry, C. K.; Lachicotte, R. J.; Godleski, S.; Valento, R. R. *Organometallics* **2000**, *19*, 1661.

[9] Kuniyasu, H.; Hiraike, H.; Morita, M.; Tanaka, A.; Sugoh, K.; Kurosawa, H. *J. Org. Chem.* **1999**, *64*, 7305.

10.1021/jo048350h CCC: $30.25

synthesis of *S*-aryl- and *S*-alkyl thiocarbamates by the palladium-catalyzed reaction of a disulfide, amine, and carbon monoxide (Scheme 1).

SCHEME 1

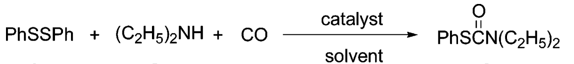


$$\mathrm{RSSR} + \mathrm{R'_2NH} + \mathrm{CO} \xrightarrow[\mathrm{THF}]{\mathrm{cat.\,Pd}} \mathrm{RS\overset{O}{\overset{\|}{C}}NR'_2} + \mathrm{RSH}$$

Results and Discussion

To determine the optimized reaction conditions, diphenyl disulfide (**1a**) was allowed to react with diethylamine (**2a**) and carbon monoxide in the presence of a catalytic amount of a transition metal complex under various reaction conditions and the results are shown in Table 1. When **1a** was treated with **2a** (15 equiv) in the presence of $Pd(PPh_3)_4$ (5 mol %) under a pressure of carbon monoxide (50 atm) at 70 °C for 5 h, *S*-phenyl-*N,N*-diethyl carbamate (**3a**) was obtained in 85% yield along with the formation of benzenethiol (75%) (entry 3). The yield of **3a** was decreased when the reaction was carried out with shorter reaction times, lower reaction temperatures, and lower carbon monoxide pressures (entries 3−6). The yield of **3a** was also affected by the amount of **2a** (entries 1−3). Although **1a** was coupled with **2a** and carbon monoxide, even using 1,4-dioxane, DMF, CH_3CN, $CHCl_3$, benzene, and toluene instead of THF as the solvent, the best yield was observed in the THF solvent (entries 3 and 7−12). The other zerovalent palladium catalyst, $Pd(dba)_2$, divalent palladium complexes, $Pd(OAc)_2$, $PdCl_2$, $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, and $PdCl_2(CH_3CN)_2$, and other metal complexes containing rhodium and platinum also functioned as a catalysts; however, the yield of **3a** distinctly decreased (entries 3 and 13−20). In this reaction, it is possible to still further reduce the amount of the palladium complex (1 mol %) with a longer reaction time (15 h) giving **3a** in 76% yield (Scheme 2).

TABLE 1. The Reaction of Diphenyl Disulfide (1a), Diethylamine (2a), and Carbon Monoxide[a]



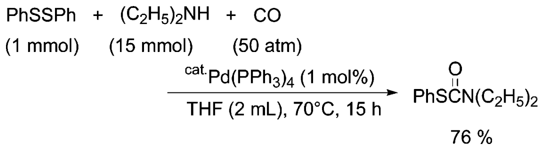
$$\mathrm{PhSSPh} + \mathrm{(C_2H_5)_2NH} + \mathrm{CO} \xrightarrow[\mathrm{solvent}]{\mathrm{catalyst}} \mathrm{PhS\overset{O}{\overset{\|}{C}}N(C_2H_5)_2}$$

1a **2a** **3a**

entry	catalyst	solvent	2a/ equiv	temp/ °C	CO/ atm	time/ h	yield/ %[b]
1	$Pd(PPh_3)_4$	THF	5	70	50	5	43
2	$Pd(PPh_3)_4$	THF	10	70	50	5	55
3	$Pd(PPh_3)_4$	THF	15	70	50	5	85 (82)
4	$Pd(PPh_3)_4$	THF	15	70	50	3	53
5	$Pd(PPh_3)_4$	THF	15	50	50	5	35
6	$Pd(PPh_3)_4$	THF	15	70	25	5	35
7	$Pd(PPh_3)_4$	1,4-dioxane	15	70	50	5	81
8	$Pd(PPh_3)_4$	DMF	15	70	50	5	84
9	$Pd(PPh_3)_4$	CH_3CN	15	70	50	5	63
10	$Pd(PPh_3)_4$	$CHCl_3$	15	70	50	5	83
11	$Pd(PPh_3)_4$	benzene	15	70	50	5	68
12	$Pd(PPh_3)_4$	toluene	15	70	50	5	62
13	$Pd(dba)_2$	THF	15	70	50	5	9
14	$Pd(OAc)_2$	THF	15	70	50	5	26
15	$PdCl_2$	THF	15	70	50	5	23
16	$PdCl_2(PPh_3)_2$	THF	15	70	50	5	47
17	$PdCl_2(PhCN)_2$	THF	15	70	50	5	23
18	$PdCl_2(CH_3CN)_2$	THF	15	70	50	5	26
19	$RhCl(PPh_3)_3$	THF	15	70	50	5	23
20	$Pt(PPh_3)_4$	THF	15	70	50	5	27

[a] Reaction conditions: **1a** (1 mmol), solvent (2 mL), and catalyst (5 mol %). [b] GC yield based on **1a**. The number in the parentheses shows the isolated yield.

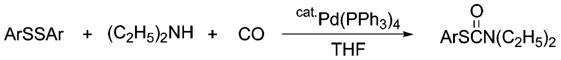
SCHEME 2



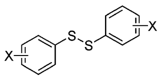
$$\underset{(1\ \mathrm{mmol})}{\mathrm{PhSSPh}} + \underset{(15\ \mathrm{mmol})}{\mathrm{(C_2H_5)_2NH}} + \underset{(50\ \mathrm{atm})}{\mathrm{CO}} \xrightarrow[\mathrm{THF\ (2\ mL),\ 70°C,\ 15\ h}]{\mathrm{cat.\,Pd(PPh_3)_4\ (1\ mol\%)}} \underset{76\ \%}{\mathrm{PhS\overset{O}{\overset{\|}{C}}N(C_2H_5)_2}}$$

To determine the scope and limitation of the palladium-catalyzed synthesis of *S*-aryl-*N,N*-diethylthiocarbamates, various diaryl disulfides were reacted with diethylamine and carbon monoxide in the presence of a catalytic amount of $Pd(PPh_3)_4$ and the results are shown in Table 2. In the case of di(3-methylphenyl), di(4-methylphenyl), and di(4-methoxyphenyl) disulfide, the reaction efficiently proceeded giving the corresponding *S*-aryl-*N,N*-diethylthiocarbamates in 83%, 98%, and 78% yields, respectively (entries 2−4). Similarly, the sterically hindered diaryl disulfide, such as di(2-methylphenyl) disulfide, was coupled with **2a** and carbon monoxide to form the *S*-(2-methylphenyl)-*N,N*-diethylcarbamate in 84% yield (entry 1). *S*-(4-Chlorophenyl)-*N,N*-diethylthiocarbamate was obtained in 70% yield for the reaction of di(4-chlorophenyl) disulfide (entry 5). In the case of the nitro-substituted diaryl disulfide, the product yield was low due to the preparation of complex byproducts (entry 6).

TABLE 2. Synthesis of Various *S*-Aryl Thiocarbamates[a]



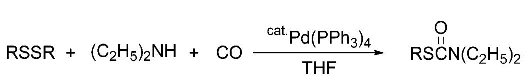
$$\mathrm{ArSSAr} + \mathrm{(C_2H_5)_2NH} + \mathrm{CO} \xrightarrow[\mathrm{THF}]{\mathrm{cat.\,Pd(PPh_3)_4}} \mathrm{ArS\overset{O}{\overset{\|}{C}}N(C_2H_5)_2}$$

entry	ArSSAr	yield/%[b]
		
1	X = 2-CH_3	84 (78) (**3b**)
2	X = 3-CH_3	83 (77) (**3c**)
3	X = 4-CH_3	98 (95) (**3d**)
4	X = 4-CH_3O	78 (76) (**3e**)
5	X = 4-Cl	70 (68) (**3f**)
6	X = 4-NO_2	25 (21) (**3g**)

[a] Reaction conditions: diaryl disulfide (1 mmol), diethylamine (15 mmol), $Pd(PPh_3)_4$ (5 mol %), THF (2 mL), and CO (50 atm) at 70 °C for 5 h. [b] GC yield based on diaryl disulfide. The numbers in parentheses show the isolated yield.

The synthesis of *S*-alkyl thiocarbamates by the treatment of dialkyl disulfide with diethylamine and carbon monoxide in the presence of a catalytic amount of $Pd(PPh_3)_4$ was next examined. These results, summarized in Table 3, showed that the reaction is amenable to the synthesis of various *S*-alkyl-*N,N*-diethylcarbamates. When dibutyl disulfide was allowed to react with **2a** and carbon monoxide under similar reaction conditions to that of the diaryl disulfide, the yield of *S*-butyl-*N,N*-diethylcarbamate was low (14%); however, the yield of the thiocarbamate was improved by elevating the reaction temperature and extending the reaction time (48 h) (entry 1). Similarly, the di(*sec*-butyl), di(*tert*-butyl), di(cyclohexyl), and di(benzyl) sulfides were coupled with **2a** and carbon monoxide to yield the corresponding thiocarbamates in 82−100% yields (entries 2−5).

TABLE 3. Synthesis of Various *S*-Alkyl Thiocarbamates[a]

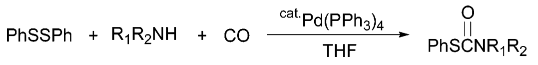


$$\mathrm{RSSR + (C_2H_5)_2NH + CO \xrightarrow[\text{THF}]{\text{cat. }Pd(PPh_3)_4} RS\overset{O}{\overset{\|}{C}}N(C_2H_5)_2}$$

entry	RSSR	yield/%[b]
1	R = n-C_4H_9	78 (72) (**3h**)
2	R = s-C_4H_9	89 (83) (**3i**)
3	R = t-C_4H_9	100 (94) (**3j**)
4	R = c-C_6H_{11}	100 (92) (**3k**)
5	R = $C_6H_5CH_2$	82 (78) (**3*l***)

[a] Reaction conditions: dialkyl disulfide (1 mmol), diethylamine (15 mmol), $Pd(PPh_3)_4$(5 mol %), THF (2 mL), and CO (50 atm) at 120 °C for 48 h. [b] GC yield based on dialkyl disulfide. The numbers in parentheses show the isolated yield.

TABLE 4. Synthesis of Various Thiocarbamates[a]



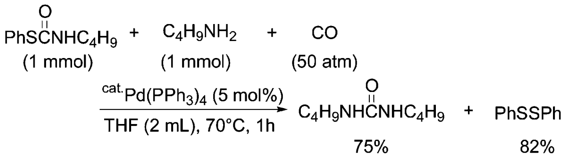
$$\mathrm{PhSSPh + R_1R_2NH + CO \xrightarrow[\text{THF}]{\text{cat. }Pd(PPh_3)_4} PhS\overset{O}{\overset{\|}{C}}NR_1R_2}$$

entry	R_1	R_2	yield/%[b]
1	C_2H_5	C_2H_5	85 (**3a**)
2	i-C_3H_7	C_2H_5	72 (**3m**)
3	i-C_3H_7	i-C_3H_7	trace (**3n**)
4	C_6H_5	CH_3	trace (**3o**)
5	$-(CH_2)_2O(CH_2)_2-$		74 (**3p**)
6	$-(CH_2)_4-$		56 (**3q**)
7	$-(CH_2)_5-$		62 (**3r**)
8	C_4H_9	H	0 (**3s**)

[a] Reaction conditions: PhSSPh (1 mmol), amine (15 mmol), $Pd(PPh_3)_4$ (5 mol %), THF (2 mL), and CO (50 atm) at 70 °C for 5 h. [b] GC yield based on amine.

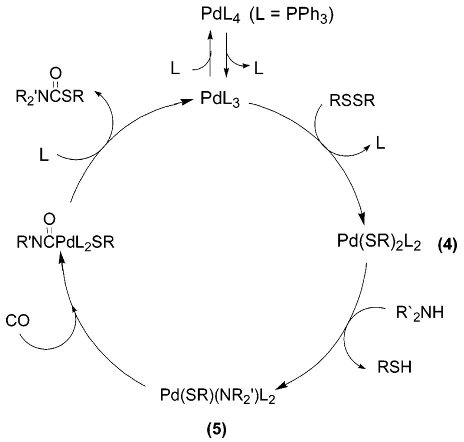
Next, diphenyl disulfide was allowed to react with various amines in the presence of a catalytic amount of $Pd(PPh_3)_4$ under pressurized carbon monoxide in order to determine the application of the synthetic method of thiocarbamates by the reaction of diphenyl disulfide with various amines and carbon monoxide (Table 4). In the reaction, the increase in the steric hindrance of the alkyl group of secondary amines led to a decrease in the thiocarbamate yield. Diethylamine and ethyl isopropylamine gave the corresponding *S*-phenyl-*N,N*-dialkylcarbamates in 85% and 72% yields (entries 1 and 2). However, for the more hindered diisopropylamine or aromatic amine, no thiocarbamate formation was observed even if the reaction was carried out under harsh reaction conditions (entries 3 and 4). *S*-Phenyl pyrrolidine, *S*-phenyl piperidine, and *S*-phenyl morpholine carbamate were synthesized in moderate yields by the same method (entries 5−7). On the other hand, in the case of the primary amines, the corresponding thiocarbamate was not obtained and the corresponding urea was formed (entry 8). *S*-Phenyl-*N*-butylcarbamate was not obtained, even if the reaction was stopped after 2 h. In addition, when *S*-phenyl-*N*-butylcarbamate was treated with butylamine and carbon monoxide at 70 °C for 1 h, a 75% yield of dibutyl urea and an 82% yield of diphenyl disulfide were formed (Scheme 3).[10] Based on these results, we suggested that thiocarbamate formed in situ was very susceptible to nucleophilic substitution by primary amines to produce urea.

SCHEME 3

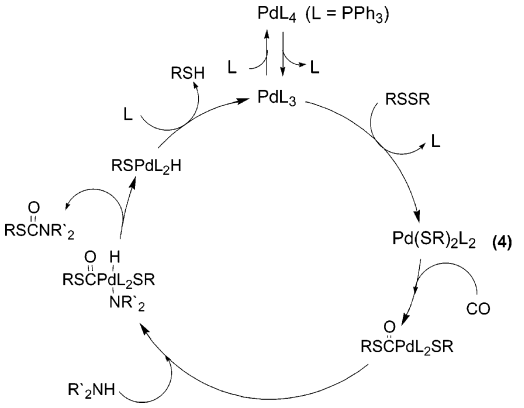


$$\mathrm{\underset{(1\ mmol)}{PhS\overset{O}{\overset{\|}{C}}NHC_4H_9} + \underset{(1\ mmol)}{C_4H_9NH_2} + \underset{(50\ atm)}{CO} \xrightarrow[\text{THF (2 mL), 70°C, 1h}]{\text{cat. }Pd(PPh_3)_4\text{ (5 mol\%)}} \underset{75\%}{C_4H_9NH\overset{O}{\overset{\|}{C}}NHC_4H_9} + \underset{82\%}{PhSSPh}}$$

SCHEME 4



SCHEME 5



Although we cannot clearly determine the catalytic reaction pathway for the synthesis of thiocarbamates, the catalytic cycles shown in Schemes 4 and 5 were suggested for the reaction. The oxidative addition of a disulfide into a low-valent palladium species generated in situ gave the thiopalladium species (**4**) as the first step in the reaction. Jones et al. have reported the palladium-catalyzed synthesis of thiocarbamates by the reaction of a thiol with an amine and carbon monoxide.[8] On the basis of the kinetic study and the isolation of intermediates, they disclosed the reaction mechanism including the insertion of CO into the Pd−N bond.[11,12] From the information provided, we proposed the reaction pathway including the

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(10) When the reaction was carried out in the absence of palladium complex or under an atmosphere of nitrogen, the yields of urea were decreased (37% in the absence of palladium complex; 65% under the nitrogen atmosphere).

(11) Alper et al. have reported the Co-catalyzed carbonylation of thiazolidines, in which insertion of CO into the Co−N bond has been proposed. See: Khumtaveeporn, K.; Alper, H. *J. Am. Chem. Soc.* **1994**, *116*, 5662.

(12) There are some reports on the insertion of CO into the metal−nitrogen bond. See: (a) Piotti, M. E.; Alper, H. *J. Am. Chem. Soc.* **1996**, *118*, 111. (b) Rahim, M.; Bushweller, C. H.; Ahmed, K. J. *Organometallics* **1994**, *13*, 4952. (c) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931. (d) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939.

ligand exchange with an amine, insertion of CO into the Pd−N bond, and subsequent reductive elimination (Scheme 4). On the other hand, Kuniyasu and Kurosawa et al. have shown the palladium complex catalyzed azathiolation of carbon monoxide using sulfeneamide.[9] For the reaction, they proposed that the insertion of CO into the Pd−S bond of $Pd(SPh)_2(PPh_3)_3$, which was generated in situ by the reaction of the palladium complex with a sulfeneamide, providing the short-lived $Pd[C(O)SPh](SPh)(PPh_3)_3$, was a key step in the reaction. From this information, an alternative reaction pathway involving the insertion of carbon monoxide into the palladium−sulfur bond of **4**, ligand exchange with the amine, and subsequent reductive elimination cannot be ruled out (Scheme 5).

In summary, from the viewpoint of a simple operation, mild reaction conditions, and good yields, the present reaction provides a useful method for the synthesis of thiocarbamates.

Experimental Section

General Procedure for the $Pd(PPh_3)_4$-Catalyzed Reaction of Diaryl Disulfide with Diethylamine and Carbon Monoxide. In a 50 mL stainless steel autoclave were placed diaryl disulfide (1.0 mmol), diethylamine (1.5 mL, 15.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and THF (2 mL). The autoclave was then flushed several times with carbon monoxide and finally charged with carbon monoxide at 50 atm at room temperature. The reaction was carried out at 70 °C for 5 h maintaining the pressure of carbon monoxide. After the reaction was complete, di(isopropyl) ether (ca. 30 mL) was added to the crude reaction mixture. The brown precipitate was removed through Celite. The residual filtrate was concentrated in vacuo, and the residual mixture was purified by column chromatography on silica gel using hexane/AcOEt (6/1) as eluent giving the corresponding *S*-aryl *N*,*N*-diethylthiocarbamates. The product was characterized by comparison of its spectra data with those of authentic samples (**3a**,[7c] **3b**,[13] **3c**,[14] **3d**[9], **3f**,[9] and **3g**[15]). The structure of product (**3e**) was assigned by its ^{1}H and ^{13}C NMR and IR spectra.

***S*-4-Methoxyphenyl-*N*,*N*-diethylthiocarbamate (3e).** ^{1}H NMR ($CDCl_3$) δ 1.15−1.26 (m, 6H), 3.40 (q, $J = 7.1$ Hz, 4H), 3.79 (s, 3H), 6.88−6.92 (m, 2H), 7.38−7.42 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 13.1, 13.6, 42.2, 55.1, 54.9, 114.3, 119.3, 137.1, 160.2, 166.1. IR (neat) 537, 661, 827, 854, 1018, 1030, 1095, 1115, 1173, 1218, 1246, 1290, 1404, 1461, 1495, 1593, 1661, 2935, 2974 cm^{-1}. Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.02; H, 7.16; N, 5.85. Found: C, 60.37; H, 7.53; N, 5.62.

General Procedure for the $Pd(PPh_3)_4$-Catalyzed Three-Component Coupling of Dialkyl Disulfides with Diethylamine and Carbon Monoxide. In a 50 mL stainless steel autoclave, dialkyl disulfide (1.0 mmol), diethylamine (1.5 mL, 15.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and THF (2 mL) were placed under a nitrogen atmosphere. The autoclave was then flushed several times with carbon monoxide and finally charged with carbon monoxide at 50 atm at room temperature. The reaction was carried out at 120 °C for 48 h maintaining the pressure of carbon monoxide. After the reaction was complete, the resulting solution was dried over $MgSO_4$. The organic solvent was removed under reduced pressure. Purification by column chromatography (hexane/AcOEt (6/1)) on silica gel gave the corresponding *S*-alkyl *N*,*N*-diethylthiocarbamates. The product was characterized by comparison of its spectra data with those of authentic samples (**3h**[7c] and **3*l***[7c]). The structures of the product (**3i**, **3j**, and **3k**) were assigned by their ^{1}H and ^{13}C NMR and IR spectra.

***S*-*sec*-Butyl-*N*,*N*-diethylthiocarbamate (3i).** ^{1}H NMR ($CDCl_3$) δ 0.98 (t, $J = 7.2$ Hz, 3H), 1.25 (m, 6H), 1.33 (d, $J = 6.8$ Hz, 3H), 1.56−1.71 (m, 4H), 3.38−3.51 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 11.6, 13.3, 21.3, 29.7, 29.9, 30.0, 41.6, 42.0, 167.1. IR (neat) 666, 860, 1115, 1250, 1380, 1405, 1461, 1650, 2933, 2969 cm^{-1}. Anal. Calcd for $C_9H_{19}NOS$: C, 57.10; H, 10.12; N, 7.40. Found: C, 56.83; H, 10.38; N, 7.45.

***S*-*tert*-Butyl-*N*,*N*-diethylthiocarbamate (3j).** ^{1}H NMR ($CDCl_3$) δ 1.15 (t, $J = 6.8$ Hz, 6H), 1.51 (s, 9H), 3.48 (q, $J = 6.8$ Hz, 4H). ^{13}C NMR ($CDCl_3$) δ 13.5, 30.6, 47.2, 167.2. IR (neat) 859, 1112, 1248, 1361, 1403, 1460, 1644, 1742, 2854, 2925 cm^{-1}. Anal. Calcd for $C_9H_{19}NOS$: C, 57.10; H, 10.12; N, 7.40. Found: C, 57.26; H, 10.45; N, 7.26.

***S*-Cyclohexyl-*N*,*N*-diethylthiocarbamate (3k).** ^{1}H NMR ($CDCl_3$) δ 1.16 (t, $J = 6.4$ Hz, 6H), 1.12−1.39 (m, 1H), 1.43 (q, $J = 6.4$ Hz, 4H), 1.57−1.61 (m, 1H), 1.69−1.77 (m, 2H), 1.98−2.02 (m, 2H), 3.36−3.45 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 13.4, 25.7, 26.2, 33.9, 42.1, 43.6, 166.9. IR (neat) 665, 755, 859, 1097, 1116, 1221, 1248, 1380, 1405, 1449, 1650, 2853, 2932, 2974 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NOS$: C, 61.35; H, 9.83; N, 6.50. Found: C, 61.74; H, 9.65; N, 6.71.

General Procedure for the $Pd(PPh_3)_4$-Catalyzed Three-Component Coupling of Diphenyl Disulfide with Secondary Amines and Carbon Monoxide. In a 50 mL stainless steel autoclave, diphenyl disulfide (0.218 g, 1.0 mmol), amines (15.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and THF (2 mL) were placed under a nitrogen atmosphere. The autoclave was then flushed several times with carbon monoxide and finally charged with carbon monoxide at 50 atm at room temperature. The reaction was carried out at 70 °C for 5 h maintaining the pressure of carbon monoxide. After the reaction was complete, the resulting solution was dried over $MgSO_4$. The organic solvent was removed under reduced pressure. Purification by column chromatography (hexane/AcOEt (6/1)) on silica gel gave the corresponding *S*-phenyl thiocarbamates. The product was characterized by comparison of its spectral data with those of authentic samples (**3p**,[16] **3q**,[7c] and **3r**[7c]). The structure of the product (**3m**) was assigned by its ^{1}H and ^{13}C NMR and IR spectra.

***S*-Phenyl-*N*,*N*-ethylisopropylthiocarbamate (3m).** ^{1}H NMR ($CDCl_3$) δ 1.10−1.25 (m, 9H), 3.24−3.34 (m, 2H), 4.20−4.45 (m, 1H), 7.36−7.41 (m, 3H), 7.44−7.53 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 15.9, 20.9, 35.5, 35.5, 49.0, 128.4, 128.7, 128.8, 131.9, 132.0, 135.6, 163.1. IR (neat) 689, 748, 810, 848, 1090, 1109, 1209, 1252, 1277, 1335, 1378, 1401, 1440, 1661, 2935, 2974 cm^{-1}. Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67; N, 6.27. Found: C, 67.71; H, 7.65; N, 6.37.

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Supporting Information Available: Characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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