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A Facile Method for Generation of Carbon Oxide Sulfide

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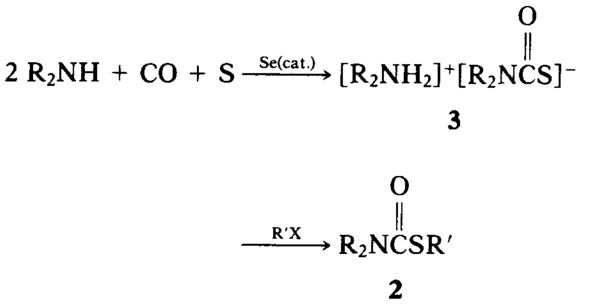
ABSTRACT

Carbon oxide sulfide was easily generated upon heating of amine salts of carbamothioic acids at 85°C which were produced in situ from amines, carbon monoxide, and elemental sulfur in the presence of a catalytic amount of selenium under mild conditions.

Carbon oxide sulfide (**1**) is a useful synthetic agent for the introduction of the thiocarboxy functionality into various organic molecules [1]. Many methods for the preparation of **1** have been explored [2]. Among them, the method employing the reaction of carbon monoxide with elemental sulfur at 250–450°C in the presence of transition metal sulfides as catalysts [3] has been widely used in industrial applications. However, these methods involve severe reaction conditions such as high temperatures, so that a more convenient method has been sought. Here we report a facile and efficient method that permits generation of carbon oxide sulfide (**1**) from carbon monoxide and elemental sulfur under mild conditions.

Recently, we have reported [4] a new method for the synthesis of an S-alkyl carbamothioate (**2**) via alkylation of an amine salt of a carbamothioic acid (**3**) produced by the reaction of an amine with carbon monoxide and sulfur using selenium as a catalyst at room temperature under atmospheric pressure (Equation 1).



$$2\,R_2NH + CO + S \xrightarrow{Se(cat.)} \underset{\mathbf{3}}{[R_2NH_2]^+[R_2N\overset{\overset{O}{\|}}{C}S]^-} \xrightarrow{R'X} \underset{\mathbf{2}}{R_2N\overset{\overset{O}{\|}}{C}SR'} \qquad (1)$$

On the other hand, it has been suggested in the patent literature that amine salts of dialkylcarbamothioic acids (**3**) can be pyrolyzed to carbon oxide sulfide (**1**) and secondary amines at elevated temperatures [5]. If both the formation of amine salts of dialkylcarbamothioic acids (**3**) and an efficient decomposition of the salts can be combined and made to occur successively, it may be possible to develop a new preparative method for **1**. A continuation of our study on this point led to the achievement of a facile and convenient one-pot method for the generation of carbon oxide sulfide (**1**) under extremely mild conditions; e.g., a solution of the amine salt of *N*,*N*-di-*n*-propylcarbamothioic acid **3b**, obtained by the reaction of di-*n*-propylamine with carbon monoxide (1 atm) and elemental sulfur containing 10 mol% of selenium as the catalyst in ethylene glycol dimethyl ether solution at room temperature, was refluxed to generate carbon oxide sulfide (**1**) in 87% yield, accompanied by the deposition of elemental selenium (Equation 2).

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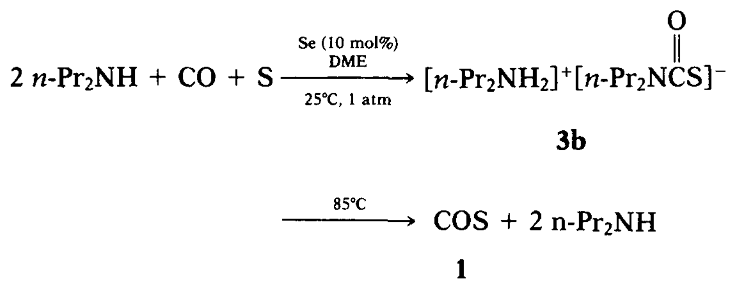


$$2\,n\text{-Pr}_2\text{NH} + \text{CO} + \text{S} \xrightarrow[25^\circ\text{C, 1 atm}]{\text{Se (10 mol\%)}\ \text{DME}} [n\text{-Pr}_2\text{NH}_2]^+[n\text{-Pr}_2\text{N}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{S}]^- \qquad (2)$$

3b

$$\xrightarrow{85^\circ\text{C}} \text{COS} + 2\ \text{n-Pr}_2\text{NH}$$

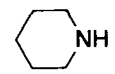
1

Various amines and solvents can be used for the generation of **1** and the results are shown in Table 1.

The effect of the selenium catalyst is obvious from the data of runs 1–6 in Table 1; good yields of 1 are attained when the ratio of Se/S is more than 0.05, and a polar aprotic solvent such as ethylene glycol dimethyl ether (DME) or tetrahydrofuran (THF) is used for these reactions (runs 1, 7–10). Generally, secondary amines provide good to moderate yields of carbon oxide sulfide (**1**); however, low boiling secondary amines such as diethylamine (bp = 55.5°C) were found to be inadequate (run 11), because they brought about the vaporization and the outflow of amines with **1** at the decomposition temperature of the salt [6]. Aliphatic primary amines gave generally low yields of **1** (runs 16, 17), because of a competitive formation of the corresponding urea derivatives, whereas aromatic amines afforded **1** in good yields when triethylamine was employed as a cocatalyst (runs 18, 19).

The present preparative method for carbon oxide sulfide can be characterized as follows: simple operation, extremely mild conditions (1 atm, 85°C), good yield, and complete recovery and repeated use of selenium-catalyst, amine, and solvent. This method should be useful and convenient for the production of carbon oxide sulfide (**1**).

TABLE 1 Preparation of Carbon Oxide Sulfide (**1**) from Sulfur, Carbon Monoxide, and Amines Using Selenium-Catalyst

Run	*Amine*	*Ratio of Se/S* (mol/mol)	*Solvent*	*Yield*[a] (%)
1	n-Pr$_2$NH	0.1	DME	87
2		0.1	DME	68[b]
3		0.05	DME	79
4		0.02	DME	42
5		0.01	DME	37
6		0	DME	14
7		0.1	THF	77
8		0.1	Dioxane	70
9		0.1	Benzene	28
10		0.1	n-Hexane	15
11	Et$_2$NH	0.1	DME	6[c]
12	i-Pr$_2$NH	0.1	DME	50
13	n-Bu$_2$NH	0.1	DME	84
14		0.1	DME	78
15		0.1	DME	76[b]
16	n-BuNH$_2$	0.1	THF	21[d]
17	Cyclo-HexNH$_2$	0.1	DME	49[e]
18	PhNH$_2$	0.1	THF[f]	74
19	PhNHMe	0.1	THF[f]	65

Reaction conditions: amine (120 mmol), S (50 mmol), CO (1 atm), solvent (100 mL).

[a] Yield based on sulfur used.

[b] Carbonylation was performed at 50°C for 1 h.

[c] Decomposed at 50°C.

[d] $(\text{n-BuNH})_2\text{CO}$ (73%) was also formed.

[e] $(\text{cyclo-HexNH})_2\text{CO}$ (35%) was also formed.

[f] Triethylamine (200 mmol) was added.

EXPERIMENTAL

Mass spectra (EI, 30 eV) were measured with a JEOL JMS-DX303-HF spectrometer. Infrared spectra were recorded on a JASCO A-3 spectrometer. DME, THF, dioxane, benzene, and n-hexane were dried over sodium wire and distilled before use. Amines (di-n-propylamine, diethylamine, di-isopropylamine, di-n-butylamine, piperidine, n-butylamine, cyclohexylamine, aniline, N-methylaniline, triethylamine) were all purchased from commercial sources and dried over potassium hydroxide, then purified by distillation. Metallic selenium (99.9%) from Nacalai Tesque Co., powdered sulfur (99.5%) from Yoneyama Chemical Co., and carbon monoxide (99.9%) from Seitetu Chemical Co. were used as purchased.

Carbon Oxide Sulfide (**1**)

Into a solution of distilled ethylene glycol dimethyl ether (100 mL) containing di-n-propylamine (16.5 mL, 120 mmol) were added 1.60 g (50 mmol) of powdered sulfur and 0.39 g (5 mmol) of metallic selenium, and the solution was stirred at 25°C for 20 h under carbon monoxide (1 atm). The resulting homogeneous, pale-orange solution of the amine salt of carbamothioic acid was allowed to reflux (85°C) for 2 h with gentle bubbling of nitrogen through the solution. Carbon oxide sulfide (**1**) which was generated was introduced with the stream of nitrogen into a cold trap cooled by a liquid *nitrogen-ethanol* bath (∼−100°C), and was characterized by its mass spectrum and comparison of its infrared (IR) spectrum with that of an authentic sample [7], and the amount was determined by titration with iodine [8]. The yield of **1** was 2.61 g (87% based on sulfur used), bp −50°C (lit. [2] −50.2°C). MS (30 eV), m/z (relative intensity) 60 (M^+; 40), 32 (33), 28 (100); IR (gas) 3090, 3080, 2910, 2890, 2310, 2150, 2100, 2020, 1980, 1900, 1880, 1720, 1700, 1060, 1040, 865, 845, 670, and 520 cm^{-1}. Metallic selenium and di-*n*-propylamine were recovered unchanged from the residual solution [9].

References and Notes

[1] K. Mori, S. Shimizu, T. Kanazawa, *J. Syn. Org. Chem. Jpn., 29,* 1971, 609.

[2] R. J. Ferm, *Chem. Rev.,* 1957, 621.

[3] Y. Nakayama, H. Sano, S. Okamura, K. Hirao, Japanese Patent, 131993 (1977), Ihara Chemical Co.; Ltd., *Chem. Abstr. 88,* 1978, 63801.

[4] For the selenium-catalyzed carbonylation of amines with carbon monoxide and sulfur to give amine salts of carbamothioic acids (**3**); see N. Sonoda, T. Mizuno, S. Murakami, K. Kondo, A. Ogawa, I. Ryu, N. Kambe, Angew. Chem. (in press).

[5] E. A. Swakon, U.S. Patent, 3382043 (1968), Standard Oil Co.; *Chem. Abstr. 68,* 1968, 116058.

[6] The decomposition temperatures of isolated amine salts of carbamothioic acids (**3a–c**) were determined by differential thermal analysis (measured with a Thermal Analyzer Shimadzu DT-2B). The results were as follows.

$[Et_2NH_2]^+[Et_2NC(O)S]^-$	**3a**	75–100°C
$[n\text{-}Pr_2NH_2]^+[n\text{-}Pr_2NC(O)S]^-$	**3b**	80–115°C
$[n\text{-}Bu_2NH_2]^+[n\text{-}Bu_2NC(O)S]^-$	**3c**	80–160°C

[7] An authentic sample of **1** was prepared by the reaction of potassium thiocyanate with sulfuric acid as described in the literature [2].

[8] R. E. Brewer, J. K. Ghosh, *Ind. Eng. Chem., 41,* 1949, 2044.

[9] The remaining mixture of selenium, amine, and solvent can be used repeatedly without any purification.