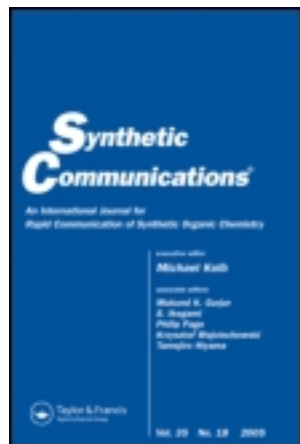


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## DEVELOPMENT OF AN IMPROVED METHOD FOR CONVERSION OF THIURAM DISULFIDES INTO N,N-DIALKYL CARBAMOYL HALIDES AND DERIVATIVES

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*A convenient procedure for preparing N,N-disubstituted carbamoyl halides is reported. It consists of two steps: (1) reaction of carbon disulfide and a secondary amine in the presence of a polar organic solvent and oxygen to produce the corresponding tetraalkyl thiuram disulfides and (2) reaction of tetraalkyl thiuram disulfide with a halide in the presence of an aprotic organic solvent to produce the corresponding N,N-disubstituted carbamoyl halide.*

**Keywords:** Carbon disulfide; N,N-disubstituted carbamoyl halide; secondary amine; tetraalkyl thiuram disulfide

### INTRODUCTION

Carbamoyl halides<sup>[1]</sup> are an important class of commercially available chemicals. These are useful intermediates in the preparation of thiocarbamate herbicides via their reaction with thiols (e.g., sodium alkylmercaptides). Carbamoyl halides, particularly chlorides, are useful in the preparation of 1,4-disubstituted-5(4H)-tetrazolinones,<sup>[2]</sup> imidazole derivatives,<sup>[3]</sup> Reissert analogs,<sup>[4]</sup> phenyl carbamates,<sup>[5]</sup> unsymmetrical ureas, pyrrole-N-carbonyl compounds,<sup>[6]</sup> O-β-oxoalkylcarbamates,<sup>[7]</sup> O-allylic urethanes and carbonates,<sup>[8]</sup> synthesis of carbamates,<sup>[9]</sup> phthalides,<sup>[10]</sup> preparation of arylisocyanates,<sup>[11]</sup> N,N-dimethylcarbamoyloxy-3-thiadiazoles-1,2,4,<sup>[12]</sup> and N,N-dialkyl carbamate esters. Carbamoyl chlorides are also used for Friedel–Crafts acylation<sup>[13]</sup> followed with treatment of ammonia or amines to produce aromatic amides or substituted amides, which on hydrolysis yield corresponding acids. Triphosgene<sup>[14]</sup> is also being used in the synthesis of carbamoyl chloride. In this communication, we describe a novel method of N,N-disubstituted carbamoyl chloride by reaction of tetraalkyl thiuramdisulfide and chlorine gas.

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## RESULTS AND DISCUSSION

The tetraalkyl thiuramdisulfides were prepared by reacting secondary amines with carbon disulfide in the presence of manganese acetate. The yields of thiurams were more than 98%. The tetrasubstituted thiuramdisulfides were fully characterized and are summarized in Table 1. The next step was chlorination of thiurams. For this purpose, chlorine gas was passed in the solution of tetraalkylthiuram in dichloromethane. Subsequent hydrolysis of the intermediate with saturated sodium bicarbonate solution gave carbamoyl chloride.

## EXPERIMENTAL

All chemicals (dimethylamine, diethylamine, di-n-propylamine, diisopropyl amine, N,N-ethyl, methylamine, di-n-butylamine, piperidine, isopropyl alcohol, and dichloromethane) were purchased from Merck, India. All the products gave satisfactory, melting and boiling points. Gas chromatographic (GC) analysis was performed on a Thermo Fisher model 1000 gas chromatograph.


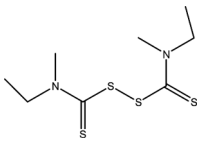

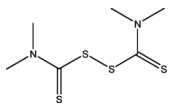
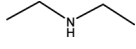
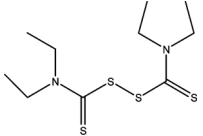
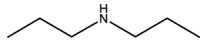
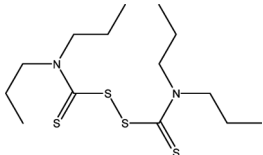
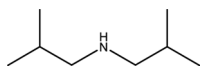
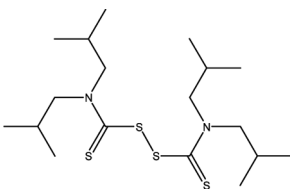
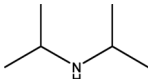
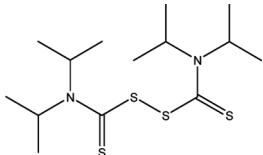

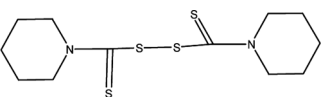
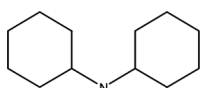
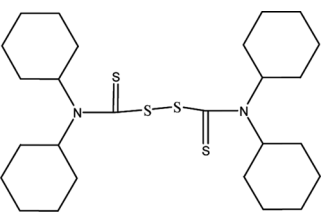
### Preparation of Tetraalkyl Thiuram Disulfide

In a 500-ml autoclave-type reaction flask equipped with a double jacket for the circulation of heating liquid, thermometer, pressure gauge, reflux condenser, and stirrer, a solution of secondary amine (300 mmol) and 24.4 mg manganese acetate was dissolved in isopropanol (250 ml), and carbondisulfide (19 ml) was added to the solution. The reflux condenser was replaced with a stopper. The reaction mixture was heated at 50 °C and stirred vigorously, and oxygen gas was introduced up to a pressure of 1.7 bar. Under these conditions, the reaction was complete after 1–3 h. Tetraalkyl thiuram disulfide was obtained in 98–99% yield.

### Preparation of N,N'-Dialkylcarbamoylchloride

In a 1-L reaction flask equipped with a reflux condenser and stirrer, a solution of tetraalkyl thiuram disulfide (0.47 mol) in dichloromethane (800 ml) and chlorine gas (130 g) were bubbled into the resulting suspension over a period of 6–8 h, maintaining the reaction mass at a temperature of 24–26 °C in an ice bath. After half of the chlorine had been added, the tetraalkyl thiuram disulfide dissolved to a clear reddish brown solution. After three quarters of the chlorine had been added, the solution became cloudy because of the formation of free sulfur. At the completion of chlorination, the reaction mass became a thick slurry because of the formation of phosgenimonium salt (N,N-dialkyldichloro methanium chloride). After stirring for 20 min more, saturated sodium bicarbonate solution (2 g in 15 ml water) was added during a period of 2–3 h. At the completion of addition of sodium bicarbonate, the precipitate disappeared and sulfur was separated from the mass as a sticky paste. The dichloromethane layer was separated and distilled at atmospheric pressure. The residual material was transferred to a 100-ml distillation flask and distilled under reduced pressure (10 mm Hg). The total yield of N,N'-dialkylcarbamoylchlorides varied from 85 to 90%.

**Table 1.** Reaction conditions for step 1, conversion of secondary amines to tetraalkyl thiuram disulfides by reaction with carbon disulfide

No.	Starting amine	Tetraalkyl thiuramdisulfide	Reaction time	Yield (%)	Mp (°C) observed	Mp (°C) lit.
1			2 h	98.6	66–68	67–69 <sup>[15]</sup>
2			1 h, 50 min	98.2	150–151	151 <sup>[15]</sup>
3			1 h, 30 min	98.5	68–70	70 <sup>[15]</sup>
4			1 h, 25 min	99.2	47.5–48.0	48 <sup>[16]</sup>
5			1 h	98.3	68–69	69 <sup>[17]</sup>
6			3 h	95.5	115–117	117 <sup>[18]</sup>
7			30 min	94.2	115–116	115 <sup>[19]</sup>
8			2 h, 30 min	93.8	88–89	87 <sup>[20]</sup>

**Table 2.** Reaction conditions for step 2, conversion of tetraalkyl thiuram disulfides to *N,N*-disubstituted carbamoyl chlorides

No.	Starting tetraalkyl thiuram disulfide	<i>N,N</i> -disubstituted carbamoyl chloride	Reaction time	Yield (%)	Boiling point (°C) at mm Hg
1			6 h	92.00	bp <sub>40</sub> : 88–89
2			6 h	86.20	bp <sub>775</sub> : 167–168
3			6 h, 40 min	90.30	bp <sub>15</sub> : 60–62
4			6 h, 30 min	92.65	bp <sub>10</sub> : 115–116
5			7 h, 15 min	87.00	bp <sub>10</sub> : 110–112
6			6 h, 50 min	88.65	
7			7 h, 30 min	85.60	bp <sub>10</sub> : 108–109
8			7 h, 15 min	88.10	bp <sub>0.2</sub> : 165–167

## CONCLUSION

The present method describes a simple and efficient method for the synthesis of commercially important N,N'-substituted carbamoylchlorides from the corresponding tetraalkyl thiuram disulfides, prepared from secondary alkyl amines and carbon disulfide. The notable feature of this two-step preparation is that the process is economically viable (i.e., enhanced rate of reaction and negligible by-products), with a cleaner reaction profile, which makes it a useful and attractive process for synthesis. The generality and simple experimental and product isolation procedures are expected to play an important role in the development of this new method. It is an important step in the development of a greener and more efficient commercial synthesis. This will certainly prove to be an important improvement over the phosgenation method being used at present.

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## REFERENCES

1. Lide, D. R. Properties of dimethylcarbamoyl chloride. *CRC Handbook of Chemistry and Physics*, 87th ed.; CRC Press: Boca Raton, FL, 2006–2007.
2. Yanagi, A.; Watanabe, Y.; Narabu, S.-I. Process for the preparation of 1-4-disubstituted-5 (4H)-tetrazolinones. U.S. Patent 5,767,286, June 16 1998.
3. Ngochindo, R. I. 2-Protecting groups for 5-lithiation in the syntheses of imidazoles. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1645–1648.
4. El-Sayed, A. M.; Badawey, T. K. Benzimidazole condensed ring systems, 7: An entry to substituted 1*h*,6*h*-2,6*a*,10*b*-triazafuoranthene-1,3,6-(2*h*)-triones and related systems as possible chemotherapeutic. *J. Heterocycl. Chem.* **1991**, 28, 995–998.
5. Enz, A. Process for the preparation of phenyl carbamate. U.S. Patent 5,602,176, Feb. 11, 1997.
6. Boger, D. L.; Patel, M. Activation and coupling of pyrrole-1-carboxylic acid in the formation of pyrrole N-carbonyl compounds: Pyrrole-1-carboxylic acid anhydride. *J. Org. Chem.* **1987**, 52(11), 2319–2323.
7. Bruneau, C.; Dixneuf, P. H. Catalytic synthesis of O- $\beta$ -oxoalkylcarbamates. *Tetrahedron Lett.* **1987**, 28(18), 2005–2008.
8. McGhee, W. D.; Riley, D. P.; Christ, M. E.; Christ, K. M. Palladium-catalyzed generation of O-allylic urethanes and carbonates from amines/alcohols, carbon dioxide, and allylic chlorides. *Organometallics* **1993**, 12(4), 1429–1433.
9. Shim, S. C.; Baeg, J. O.; Doh, C. H.; Youn, Y. Z.; Kim, T. J. Synthesis of carbamates from amine, acetylenic alcohol, and CO<sub>2</sub> using lanthanide as catalyst. *Bull. Korean Chem. Soc.* **1990**, 11(5), 467–468.
10. Paleo, M. R.; Lamas, C.; Castedo, L. A new synthesis of phthalides by internal trapping in ortho-lithiated carbamates derived from benzylic alcohol. *J. Org. Chem.* **1992**, 57(7), 2029–2033.

11. Bacaloglu, R.; Bunton, C. A. Reactions of arylcarbamoyl chlorides, II: Reaction with aromatic amines. *Tetrahedron* **1973**, *29*, 2725–2730.
12. Taliani, L.; Perronnet, J. Electrophilic reagents may react either with the hydroxyl group in position 3, or with the 2-nitrogen atom of 3-hydroxy-1,2,4-thiadiazoles (1). *J. Heterocycl. Chem.* **1979**, *16*, 961–971.
13. Friedel–Crafts reactions. *Kirk–Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1982; vol. 11, p. 286.
14. Gumaste, V. K.; Dshmkh, A. R. A. S. One-pot preparation of dialkylcarbamoyl azides from tertiary amines using triphosgene and sodium azide. *Tetrahedron Lett.* **2004**, *45*(35), 6571–6573.
15. Rothstein, R.; Binpovic, K. A comparative study oxidants thiols. *Rec. Trav. Chem. Pays-Bas.* **1954**, 73561.
16. Bergomi, A.; Tazuma, J. J. Method of preparing tetraalkyl thiuram disulfides. U.S. Patent 4,144,272, March 13, 1979.
17. *MSDS*; Westco TiBTD; Wrchem.com.
18. Kumar, V.; Aravamudan, G.; Seshasayee, M. A centric thiuram disulfide: Structure of tetraisopropylthiuram disulfide. *Acta Cryst.* **1990**, *C46*, 674–676.
19. Hong, S. W.; Wheeler, E. L. Tire compounds containing an elastomer and a resin cured with 1-aza-5-methylol-3,7-dioxabicyclo (3,3,0) octane are disclosed, as well as methods for the preparation of such compounds. U.S. Patent 5,023,292, June 11, 1991.
20. Fischer, W. F.; Neu, R. F.; Zapp, R. C. *Ind. Eng. Chem.* **1959**, *51*, 205.