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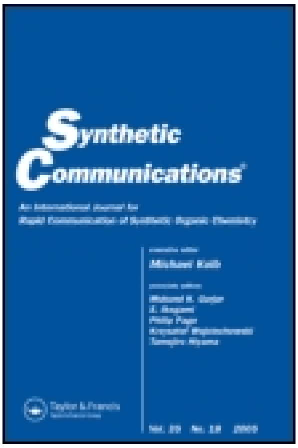

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New Effective Synthetic Method for Preparation of N,N-Dichlorocarbamates

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NEW EFFECTIVE SYNTHETIC METHOD FOR PREPARATION OF N,N-DICHLOROCARBAMATES

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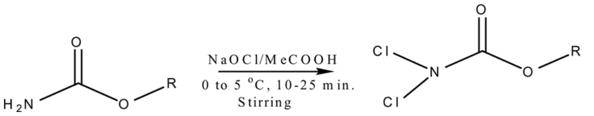
GRAPHICAL ABSTRACT



Abstract *A rapid, efficient, economical, and easy-to-scale method for the effective conversion of carbamates to corresponding N,N-dichlorocarbamates by using sodium hypochlorite in acidic medium has been described. N,N-Dichlorocarbamates were obtained in quantitative yield through a simple workup in reduced reaction time.*

Keywords Acidic medium; sodium hypochlorite; substituted N,N-dichlorocarbamates

INTRODUCTION

N-Chloro compounds have been extensively exploited, for both fundamental research and a wide range of industrial applications, owing to their easy handling, commercial availability, and high stability. As a result, intensive research and studies have been carried out over a long period of time on their chlorination, oxidation, water disinfection, and other applications[1–3] in synthetic organic chemistry. N-Chloro compounds have also been reported for decontamination of chemical warfare agents.[4,5] N,N-Dichlorocarbamate was prepared by Dutta and Gupta[6] and subsequently by Houben[7] and Chabrier,[8] but explicit details concerning yield, method of isolation, purity, and physical characteristics of products were not reported. One of the major drawbacks of Foglia and Swern's method[9] was passing chlorine gas for long time at room temperature, which creates inhalation toxicity. White and Kovaic[10] have also reported poor yield and a time-consuming process for the synthesis of N,N-dichlorocarbamates, and also isolation of pure N,N-dichlorocarbamate was very difficult.

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These limitations prompted us to develop a rapid and efficient synthetic procedure for N,N-dichlorocarbamates that involves easy workup and quantitative yields in shorter reaction times by making use of sodium hypochlorite. In this paper, we report an improved method, which gives greater yield in less time of pure N,N-dichlorocarbamates in an acidic medium without any volatile solvents for extraction.

RESULTS AND DISCUSSION

Sodium hypochlorite is a commercially available compound that produce positive chlorine for N-chlorination of carbamate. For chlorination of carbamate, an acidic medium is required to avoid the formation of sodium salt of monochlorocarbamates. In this procedure, the carbamate was first suspended in acetic acid, and the reaction mixture cooled to 5 °C with stirring until the starting material was completely dissolved. Sodium hypochlorite was added to this slowly within 15 min with stirring. Acetic acid was added in portions to turn the pH of the mixture acidic. After 15 min, a translucent yellow organic layer was separated in the aqueous medium.

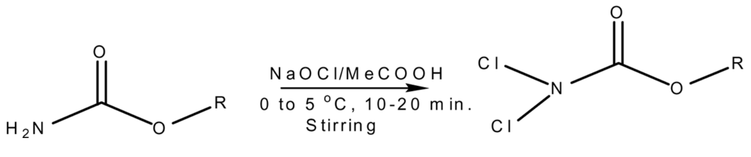
The reaction of various substituted carbamates with sodium hypochlorite afforded corresponding N,N-dichlorocarbamates in 15–20 min with excellent yields. The reaction scheme and yield of N,N-dichlorocarbamates are depicted in Scheme 1 and Table 1. This method has allowed us to obtain the quantitative yields of the products in reduced reaction time. The important advantage of this reaction is no inhalation of chlorine at 5 °C, and completion of the reaction is indicated by separation of the pure product in the organic phase in the bottom of the flask within 15–20 min.

NaOCl solution is basic, and by adding acetic acid the pH of the reaction mixture was changed to acidic (from pH 9 to pH 6). It is necessary to avoid the formation of sodium salt during N-chlorination, so an acidic medium is mandatory for N-chlorination. The products formed were characterized by Fourier transform–infrared (FT-IR) and NMR. Yields of all compounds were quantitative. The positive chlorine content of these compounds was determined by standard iodometric titration.[11]

EXPERIMENTAL

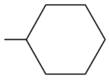
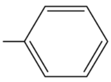
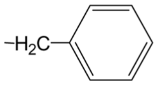
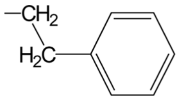
General Procedure

A mixture of ethyl carbamate (8.9 g, 0.1 mol) and acetic acid (30 mL) were taken in a two-necked round-bottom flask equipped with condenser and dropping



Scheme 1. Synthesis of N,N-dichlorocarbamates.

Table 1. Synthesis of N,N-dichlorocarabamates

					Active chlorine[b] (%)	
Entry	R	Time (min)	Yield[a] (%)	Bp(°C)/(mm Hg)	Observed	Calculated
1	-CH_3	15	94	49–50/7.5	49.27	49.31
2	-C_2H_5	15	95	44–45/6.0	44.46	44.90
3	-$CH_2CH_2CH_2CH_3$	15	81	46.0/0.3	37.79	38.17
4	-$C(CH_3)_3$	16	86	44–45/2.6	38.25	38.17
5	-$CH_2(CH_2)_6CH_3$	16	82	51–52/2.5	29.55	29.34
6		16	87	122/3.0	33.12	33.49
7		20	89	120/1.0	34.31	34.46
8		20	88	124/1.5	32.11	32.27
9		20	78	126/5.0	29.41	30.34

[a] Isolated yield.

[b] Active chlorine of products was determined by iodometric titration.

funnel and mounted on a magnetic stirrer. The reaction mixture was cooled to 5 °C in an ice bath, and sodium hypochlorite (25–30 mL, 12–15%) was added slowly with the help of dropping funnel within 15 min with stirring. Acetic acid (5–10 mL) was added in portions to bring down the pH of the mixture to acidic. After 15 min, a translucent yellow layer of the product was separated from the aqueous layer. The organic phase was washed with water and dried with anhydrous sodium sulfate. Yield was 95% as a yellow oil, bp 44–45 °C at 6.0 mm Hg. The positive chlorine of N,N-dichloro ethyl carbamates were checked by standard iodometric titration, and results are given in Table 1.

Spectral Data for Selected Compounds

N,N-Dichloro ethyl carbamate (2). ^1H NMR ($CDCl_3$/TMS 400 MHz): δ 1.39 (t, 3H, CH_3), 4.37 (q, 2H, CH_2). IR (KBr) 1753 (C=O), 1230, 1100, 1047, 993, 900, 827, 803, 766, 735 cm^{-1}. Analysis (iodometric titration) calcd. for $C_3H_5Cl_2NO_2$: Cl, 44.9. Found: Cl, 44.5.

N,N-Dichloro t-butyl carbamate (4). ^1H NMR ($CDCl_3$/TMS 400 MHz): δ 1.53 (s, CH_3). IR (KBr) 1765 (C=O), 1400, 1373, 1274, 1240, 1143, 1045, 994, 882, 820, 785, 753 cm^{-1}. Analysis (iodometric titration) calcd. for $C_5H_9Cl_2NO_2$: Cl, 38.25. Found: Cl, 38.17.

CONCLUSION

In conclusion we have reported an efficient, convenient, and rapid one-pot conversion of carbamates to N,N-dichlorocarbamates in excellent yield by making use of sodium hypochlorite in an acidic medium.

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