

## Method of synthesis of *O*-methyl-*N*-alkylcarbamate from amines and dialkylcarbonate

© Ratmir R. Dashkin,<sup>+</sup> Tatiana Yu. Vorobieva, Mary A. Seferyan,  
Daria V. Danilova, and Sergey N. Mantrov\*

Mendeleev University of Chemical Technology of Russia. Department of Chemistry and Organic Synthesis  
Technology. Miusskaya St., 9. Moscow, 125047. Russia.  
Phone: +7 (495) 944-32-73. E-mail: ratmir@engchem.ru

\*Supervising author; <sup>+</sup>Corresponding author

**Keywords:** carbamates, dialkylcarbonate, dimethylcarbonate, alkylamines.

### Abstract

A carbamates (urethanes) are an organic compounds with the general formula R'R"NCOOR are esters of carbamic acid and its derivatives. Due to their biological activity, carbamates are common as pesticides, insecticides, herbicides, and are used as drugs. Polyurethanes are widely used in industry. The main method of synthesis is the interaction of isocyanates with the corresponding alcohols or phenols, it is also possible to use urea, isocyanic acid or other methods, including the use of *in-situ* formed isocyanate.

In the literature, *N*-alkyl-*O*-methylcarbamate is synthesized by reacting amines with dimethylcarbonates with various catalysts. In view of the economic feasibility and difficulty of isolating the target product the overwhelming number of the described methods are hardly applicable for scaling and industrial synthesis.

A study was conducted to develop a method of synthesis of *O*-methyl-*N*-alkylcarbamate, which will be able to scale and be introduced into production. The most promising synthesis methods described in the literature have been tested, and a new method for producing various carbamates has been developed. The model amines for the experiment were selected industrially important – *n*-butylamine and cyclohexylamine. The structure of the product was confirmed by <sup>1</sup>H NMR spectra. A number of the described methods had a way out in practice several times below the literature data presented, and some target products could not be received. The best way to react with *n*-butylamine is to use water as a catalyst. The yield obtained according to this procedure for *O*-methyl-*N*-cyclohexylcarbamate was 53%, for *O*-methyl-*N*-*n*-butylcarbamate – 68%, so the method was expanded to obtain several *O*-methyl-*N*-alkylcarbamate.

### References

- [1] F. Villatte, V. Marcel, S. Estrada-Mondaca, & D. Fournier. Engineering sensitive acetylcholinesterase for detection of organophosphate and carbamate insecticides. *Biosensors and Bioelectronics*. **1998**. Vol.13. No.2. P.157-164.
- [2] T.A. Unger. Pesticide synthesis handbook. *William Andrew*. **1996**. P.55-60.
- [3] C. Franchi, B. Di Vico, A. Teggi. Long-term evaluation of patients with hydatidosis treated with benzimidazole carbamates. *Clinical Infectious Diseases*. **1999**. Vol.29. No.2. P.304-309.
- [4] C.L. Rose, H.R. Sullivan, A. Pohland. Local Anesthetic Agents: The Chemistry and Pharmacology of Twelve Carbamates. *J. Am. Pharm. Assoc. (Scientific ed.)*. **1955**. Vol.44. No.12. P.766-769.
- [5] M.R. Piazza. Composite building module *U.S. Patent* No. 3,984,957 Int. Cl. E04C2/288. **1976**.
- [6] N.J. Daly, F. Ziolkowski. The thermal decompositions of carbamates. II. Methyl *N*-methylcarbamate. *Aust. J. Chem.* **1972**. Vol.25. No.7. P.1453-1458.
- [7] J. Chambers, C.B. Reese. The thermal decomposition of some tolylene bis-carbamates. *Brit. Polym. J.* **1977**. Vol.9. No.1. P.41-46.
- [8] Y. Yamamoto, Y. Yoshida & M. Araki. Process for preparing a carbamate compound *U.S. Patent*. No. 13/520,999. **2012**.
- [9] B. Wang, J. He, R.C. Sun. Carbamate synthesis from amines and dialkyl carbonate over inexpensive and clean acidic catalyst – Sulfamic acid. *Chinese Chemical Letters*. **2010**. Vol.21. No.7. P.794-797.
- [10] Kumar Subodh, Jain, Suman L. L-Proline–TBAB-catalyzed phosgene free synthesis of methyl carbamates from amines and dimethyl carbonate. *New Journal of Chemistry*. **2013**. Vol.37. No.9. P.2935-2938.

- [11] M. Curini, F. Epifano, F. Maltese, & O. Rosati. Carbamate synthesis from amines and dimethyl carbonate under ytterbium triflate catalysis. *Tetrahedron letters*. **2002**. Vol.43. No.28. P.4895-4897.
- [12] R. Zeng, L. Bao, H. Sheng, L. Sun, M. Chen, Y. Feng, M. Zhu. Heterobimetallic Dinuclear Lanthanide Alkoxide Complexes as Acid–Base Bifunctional Catalysts for Synthesis of Carbamates under Solvent-Free Conditions *RSC Advances*. **2016**. Vol.6. No.82. P.78576-78584
- [13] Distaso Monica, and Eugenio Quaranta. Sc(OTf)<sub>3</sub>-catalyzed carbomethoxylation of aliphatic amines with dimethyl carbonate (DMC): DMC activation by η<sup>1</sup>-O (CO) coordination to Sc (III) and its relevance to catalysis." *Journal of Catalysis*. **2008**. Vol.253. No.2. P.278-288.
- [14] G.A. Hiegel, T.J. Hogenauer. Preparation of Methyl N-Substituted Carbamates from Amides through N-Chloroamides. *Synthetic communications*. **2005**. Vol.35. No.15. P.2091-2098.
- [15] T. Okawa. Mitsubishi Gas Chemical Company, Inc. Process for producing isocyanate compound *US Patent* No. 5166414. **1992**.
- [16] Tundo Pietro, Rossi, Laura, Loris Alessandro. Dimethyl Carbonate as an Ambident Electrophile *Journal of Organic Chemistry*. **2005**. Vol.70. No.6. P.2219-2224.
- [17] P. Wang, Y. Fei, Q. Li, & Y. Deng. Effective synthesis of dimethylhexane-1, 6-dicarbamate from 1, 6-hexanediamine and dimethyl carbonate using 3-amino-1, 2, 4-triazole potassium as a solid base catalyst at ambient temperature. *Green Chemistry*. **2016**. Vol.18. No.24. P.6681-6686.
- [18] M. Choi, X. Chen, J. Tang, X. Qiao, Zh. Fei. Nanjing University of Technology A synthetic isophorone method DICARBAMATE *Chinese Patent* No. CN103980160. **2016**.
- [19] D.W. Kim, E.S. Huh, S.D. Park, L.V. Nguyen, M.D. Nguyen, H.S. Kim, D.Q. Nguyen. Methoxycarbonylation of aliphatic diamines with dimethyl carbonate promoted by in situ generated hydroxide ion: a mechanistic consideration. *Advanced Synthesis & Catalysis*. **2010**. Vol.352. No.2-3. P.440-446.
- [20] D.A. Gordeev. Synthesis of aliphatic carbamates and isocyanates based on ethylene carbonate with out phosgene. *PhD thesis for the degree of candidate of chemical sciences*. **2017**. (russian)