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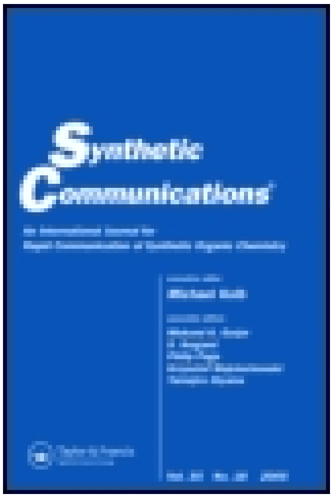

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Mild and Convenient Synthesis of Organic Carbamates from Amines and Carbon Dioxide using Tetraethylammonium Superoxide

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Published online: 14 Aug 2007.

To cite this article: Krishna Nand Singh (2007) Mild and Convenient Synthesis of Organic Carbamates from Amines and Carbon Dioxide using Tetraethylammonium Superoxide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:16, 2651-2654, DOI: 10.1080/00397910701465149

To link to this article: http://dx.doi.org/10.1080/00397910701465149

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Synthetic Communications®, 37: 2651–2654, 2007
Copyright © Taylor & Francis Group, LLC
ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910701465149

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Mild and Convenient Synthesis of Organic Carbamates from Amines and Carbon Dioxide using Tetraethylammonium Superoxide

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Abstract: A safe and simple method of preparing organic carbamates has been achieved from amines and carbon dioxide using tetraethylammonium superoxide generated in situ.

Keywords: amines, carbamates, carbon dioxide, tetraethylammonium superoxide

Organic carbamates represent an important class of compounds that have unique applications in the field of pharmaceutics (drugs), agriculture (pesticides, herbicides, and fungicides), and chemical industries (polyurethane-based polymers and novel protecting groups).[1–3] Recently, because of rapid development of combinatorial techniques in the field of drug discovery and owing to their medicinal and biological properties, carbamates have gained immense importance in the preparation of small molecule libraries.[4] The common methodologies for carbamate synthesis are based on specialized reagents and operational complexity due to the use of highly corrosive and toxic reagents such as phosgene and its derivatives or isocyanates or chloroformates.[3,5–7] Nevertheless, none of these methods are environmentally benign. To avoid the use of such toxic and harmful

Received in India January 8, 2007

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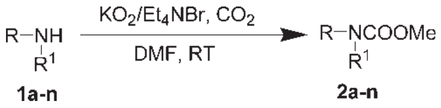


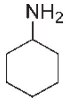
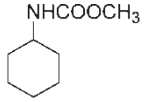
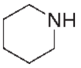
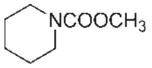
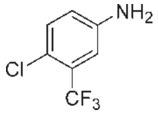
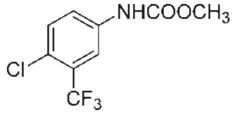
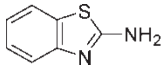
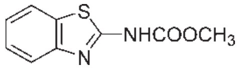
Scheme 1. R = Alkyl, aryl, heteroaryl; R_1 = alkyl, H.

reagents, several efforts have been made to develop environmentally benign, phosgene-free routes.[8–13]

As part of our research on the superoxide ion,[14–16] we report herein a milder and convenient method to achieve organic carbamates from amines in the presence of gaseous carbon dioxide using tetraethylammonium superoxide (Et_4NO_2) generated in situ, obtained by the phase-transfer reaction of KO_2 and Et_4NBr in dry DMF (Scheme 1).

The reactions were accomplished using a 2.0-fold molar excess of KO_2 and the same molar ratio of Et_4NBr with respect to substrate **1** in dry DMF.

Table 1. Synthesis of carbamates from amines and carbon dioxide activated by tetraethylammonium superoxide

1/2	Substrate (1)	Product (2)	Yield (%)
a	$CH_3(CH_2)_3NH_2$	$CH_3(CH_2)_3NHCOOCH_3$	80
b	$CH_3(CH_2)_5NH_2$	$CH_3(CH_2)_5NHCOOCH_3$	82
c			85
d			90
e	$C_6H_5NH_2$	$C_6H_5NHCOOMe$	79
f	p-$ClC_6H_4NH_2$	p-$ClC_6H_4NHCOOMe$	66
g	p-$NO_2C_6H_4NH_2$	p-$NO_2C_6H_4NHCOOMe$	54
h	p-$CH_3OC_6H_4NH_2$	p-$CH_3OC_6H_4NHCOOMe$	76
i			67
j			61
k	Ph_2NH	$Ph_2NCOOCH_3$	38
l	p-$MeC_6H_4(Et)NH$	p-$MeC_6H_4(Et)NCOOMe$	55
m	$C_6H_5(Me)CHNH_2$	$C_6H_5(Me)CHNHCOOMe$	86
n	$C_6H_5CH_2NH_2$	$C_6H_5CH_2NHCOOCH_3$	81

Generally, the reaction continued for 2–7 h at room temperature until the completion of the reaction was indicated by TLC. The reaction was then quenched with cold brine solution and worked up to afford the product **2** in reasonably good yields (Table 1). All the products **2** exhibited physical and spectral data consistent with their structures.

EXPERIMENTAL

General Experimental Procedure

Potassium superoxide (0.5688 g, 8 mmol) and tetraethylammonium bromide (0.8406 g, 4 mmol) were weighted under a nitrogen atmosphere using an atmosbag and were transferred to a two-necked, round-bottom flask containing dry dimethylformamide (15 ml) and fitted with an N_2/CO_2 inlet and a Leibig condenser protected by a drying tube. The mixture was agitated magnetically for 15 min while purging CO_2 and N_2 and then the amine **1** (4 mmol) was admitted. The stirring continued for 2–7 h at room temperature. A threefold molar excess of methyl iodide was added, and the mixture was maintained under stirring. The mixture was then treated with brine solution (10 ml) and extracted with diethyl ether/dichloromethane (3 × 20 ml). The combined organic extract was washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to give the product **2**.

ACKNOWLEDGMENT

The authors are thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial support (Ref. No. 01(1875)/03/EMR-II).

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