



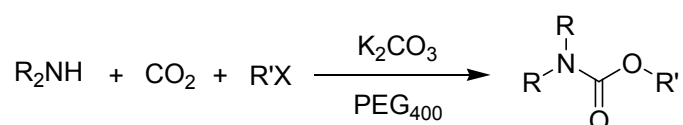
NOVEL METHODOLOGY TO FORMATION OF CARBAMATES FROM CARBON DIOXIDE

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The carbamation of amines has frequently been utilized in the synthesis of organic carbamates, which hold unique applications in the field of pharmaceuticals and agriculture. And also, Organic carbamates have played an important role in the area of synthetic organic chemistry, primarily as key intermediates or as novel protecting groups.^[1]

Recently, our group has found that polyethylene glycol could play the role both as the solvent and phase-transfer catalyst in synthesis of carbamates from amines, alkyl halides, and carbon dioxide in the presence of the inexpensive base (K₂CO₃) at mild and convenient conditions (Scheme 1).



Scheme 1. Carbamate formation from CO₂ promoted by PEG₄₀₀/K₂CO₃

In presence of PEG₄₀₀, the yield of carbamate could reach 95.6 % together with 98.3 % selectivity at room temperature and 1 atm of CO₂. The parallel experiments show PEG is much better than the traditional solvents, such as DMF and acetonitrile. The reaction no longer needs additional phase-transfer catalyst, such as ammonium salts and crown ethers.

We propose R₂NH₂⁺ ions, formation of complexation with PEG molecules, lowers the interaction with the carbamate anion oxygen atoms, which promotes the nucleophilicity towards alkyl halides. In addition, the PEG possibly also influences the thermodynamic properties of alkylammonium cations, which may repress the formation of N-alkylation products.^[2]

References

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- 2 (a) M. Aresta *et al. Dalton Trans.* **2007**, 2975-2992; (b) M. Aresta *et al. Tetrahedron* **1992**, 48, 1515-1530.