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SHORT COMMUNICATIONS

*Dedicated to the Memory of Y.G. Yatluk*

# Synthesis of Alkylene Carbonates in Ionic Liquid

**V. A. Kuznetsov, M. G. Pervova, and A. V. Pestov**

*Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences,*
*ul. S. Kovalevskoi/Akademicheskaya 22/20, Yekaterinburg, 620990 Russia*
*e-mail: kuznetsov@ios.uran.ru*

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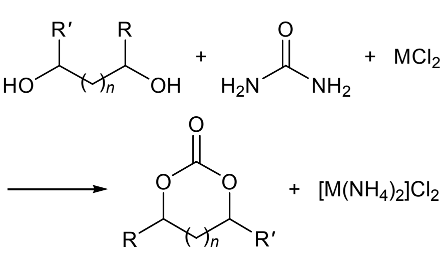
Alkylene carbonates are widely used in industry as solvents, heat carriers, plasticizers, monomers, and intermediate products in organic synthesis. Traditional methods of synthesis of alkylene carbonates (as well as of starting compounds) utilize toxic compounds (phosgene, alkylene oxides) and often require elevated pressure, which involves high operational risks.

At present, much attention is given to phosgene-free syntheses of organic carbonates. For this purpose, new catalytic systems promoting reactions of alkylene oxides with carbon dioxide have been proposed, e.g., ionic liquids [1, 2], alkali metal chlorides in combination with macrocyclic chelating compounds [3], dibutyltin oxide and methoxide [4]. However, all these reactions occur under elevated pressure. Alternative procedures are based on reactions of diols with urea on heating to 170°C [5] in the presence of a mixture of metal acetates and alkoxides [6] and oxide catalysts [7] under excess pressure. Alkylene carbonates can also be prepared by transesterification with the corresponding diols of dialkyl carbonates synthesized by a phosgene-free procedure [8].

We now propose a new synthesis of alkylene carbonates from urea and alkylene glycols, which requires neither elevated pressure nor high temperature. The reactions are carried out in a two-phase system consisting of a ionic liquid and a chlorinated organic solvent. As ionic liquid we used a mixture of equimolar amounts of a metal chloride, urea, and glycol [9], which formed a colorless transparent solution on heating above 50°C. The yields attained 80%. The reactions were carried out with a number of glycols and metal chlorides.



**I–V**

**I**, *n* = 0: R = R′ = H; **II**; R = H, R′ = Me; **III**, R = R′ = Me; **IV**, *n* = 1: R = R′ = H; **V**, R = H, R′ = Me; M = Zn, Sn, $Bu_2Sn$.

A mixture of 3.71 g (22.7 mmol) of zinc(II) chloride sesquihydrate $ZnCl_2 \cdot 1.5H_2O$, 1.36 g (22.7 mmol)

Synthesis of alkylene carbonates from glycols and urea in the system chlorinated organic solvent–ionic liquid ($ZnCl_2$–urea–glycol); reaction time 24 h.

| Comp. no. | Solvent | Temperature, °C | Yield, % |
|---|---|---|---|
| **I** | 1,2-Dichloroethane | 84 | 62 |
| | | | 75[a] |
| | | | 30[b] |
| | | | 22[c] |
| | 1,1,2,2-Tetrachloroethane | 146 | 39 |
| **II** | 1,2-Dichloroethane | 84 | 70 |
| **III** | 1,2-Dichloroethane | 84 | 80 |
| **IV** | 1,2-Dichloroethane | 84 | 6[d] |
| | 1,1,2,2-Tetrachloroethane | 146 | 12[d] |
| **V** | 1,1,2,2-Tetrachloroethane | 146 | 19[e] |

[a] Reaction time 60 h.
[b] 0.5 mol of $ZnCl_2$.
[c] 2 mol of ethylene glycol.
[d] According to the GLC data.
[e] In a mixture of oligomers.

of urea, 1.41 g (22.7 mmol) of ethylene glycol, and 10 mL of 1,2-dichloroethane or 1,1,2,2-tetrachloroethane was heated for 24 h under reflux with stirring. When the reaction was complete, the solvent was removed by decanting. The remaining viscous material was a mixture of zinc(II) chloride ammonium complex and unreacted initial compounds. It was washed with the corresponding solvent (3 × 3 mL), and the washings were combined with the decanted solution and evaporated on a rotary evaporator at 50°C under reduced pressure. Yield of ethylene carbonate 0.62 g (31%), purity 100% (GLC). Found, %: C 40.90; H 4.59. *m/z* 88 $[M]^+$. $C_3H_4O_3$. Calculated, %: C 40.92; H 4.58. *M* 88.06.

Repeated experiment with addition of 1.52 mL of water (to obtain homogeneous polar phase at room temperature) gave no ethylene carbonate. Therefore, further syntheses were carried out using anhydrous reactants with protection from atmospheric moisture. The yield of ethylene carbonate in the reaction with anhydrous zinc(II) chloride was 1.24 g (62%), purity 100% (GLC). Found, %: C 40.91; H 4.58. *m/z* 88 $[M]^+$. $C_3H_4O_3$. Calculated, %: C 40.92; H 4.58. *M* 88.06. In the reaction with anhydrous $CaCl_2$, $SnCl_2$, and $Bu_2SnCl_2$, the yields of ethylene carbonate were 2, 26, and 25%, respectively. Analogous reactions were carried out with propane-1,2-diol, propane-1,3-diol, butane-1,3-diol, and butane-2,3-diol (see table).

Alkylene carbonates were formed most readily from vicinal glycols, and the yield increased in parallel with the number of substituents, which suggests an essential role of steric factor in the cyclization process.

The products were identified by GC/MS using an Agilent GC 7890A–MSD 5975C inert XL EI/CI instrument (quadrupole mass analyzer; electron impact, 70 eV). The elemental compositions were determined on a Perkin Elmer 2400 CHN analyzer.

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