Russian Journal of Applied Chemistry, Vol. 76, No. 5, 2003, pp. 842-843. Translated from Zhurnal Prikladnoi Khimii, Vol. 76, No. 5, 2003, pp. 870-871.

Original Russian Text Copyright © 2003 by Rybina, Srednev, Bobyleva.

BRIEF COMMUNICATIONS

Synthesis of Cyclic Organic Carbonates from C₃–C₁₆ Epoxides

G. V. Rybina, S. S. Srednev, and L. I. Bobyleva

Yaroslavl State Technical University, Yaroslavl, Russia

Received October 28, 2002; in final form, March 2003

Abstract-Cyclic organic carbonates were prepared from epoxides (derivatives of C3-C16 olefins, C4 and C8 dienes, styrene; epichlorohydrin) in the presence of a catalytic system consisting of $CoCl_2 \cdot 6H_2O$ and dimethylformamide.

Cyclic organic carbonates are used in oil refining as extractants of aromatic hydrocarbons, and also in synthesis of drugs and plant protection agents. Of particular interest for industrial organic synthesis is preparation of nitrogen-containing polymers from cyclic carbonates [1].

Cyclic organic carbonates are prepared in industry by reactions of epoxides with CO_2 in the presence of alkali metal halides:



This process, however, requires high pressures (3– 10 MPa) and temperatures (180-220°C) [2].

It was suggested previously [3] to perform this reaction in the presence of a Co(II) or Ni(II) halide and dimethylformamide (or dimethylacetamide). With this catalytic system, it appeared possible to decrease the reaction temperature (to $120-130^{\circ}$ C) and pressure (to 1.0–1.5 MPa), and also to prepare vinylethylene carbonate by carboxylation of divinyl oxide at a high rate and with a high selectivity with respect to the target product [4].

Our goal was to test the suggested catalytic system for synthesis of cyclic carbonates from epoxides of various structures, containing aliphatic (saturated and unsaturated), aromatic, and other substituents.

Carboxylation was performed at 130°C and CO₂ pressure of 1.5 MPa; the starting mixture contained 25.0 wt % epoxide and 2.50 wt % $CoCl_2 \cdot 6H_2O$. The reaction time was 120 min. The results are listed in the table.

The cyclic carbonates were isolated by vacuum

fractionation; their purity was no less than 98.5%. The purity, composition, and structure of the target products were confirmed by chromatography, chemical analysis, and ¹³C NMR spectroscopy.

EXPERIMENTAL

The starting epoxides were prepared by hydroperoxide oxidation of appropriate olefins and isolated by distillation. The main substance content was no less than 98.5%. The solvent, catalyst, and auxiliary substances met the requirements of the corresponding State Standards. Carboxylation of epoxides was performed in a temperature-controlled stirred metallic vessel.

The reaction products were analyzed by gas-liquid chromatography on an LKhM-8 MD device $(3000 \times$ 3-mm steel column, stationary phase 15% diisooctyl sebacate + 1.5% sebacic acid on Chromaton N AW-DMCS). 1-Propanol was used as internal reference. Chemical analysis was performed according to [5]. The ¹³C NMR spectra were recorded on a Tesla BS-576A spectrometer (25.142 MHz, internal reference HMDS).

CONCLUSION

A catalytic system consisting of $CoCl_2 \cdot 6H_2O$ and dimethylformamide is effective in synthesis of cyclic carbonates from various saturated and unsaturated epoxides.

ACKNOWLEDGMENTS

The study was financially supported by the program "Research at Higher Schools in Priority Fields of Science and Engineering," 2001.

SYNTHESIS OF CYCLIC ORGANIC CARBONATES

Epoxide	Conver- sion, %	Cyclic carbonate				
		selectivity, %	state of aggregation	T _b , °C	P, kPa	content, wt % [5]
Propylene oxide	97.4	95.7	Liquid*	_		_
1-Pentene oxide	95.0	91.1	"	127.0-127.5	0.93	98.81 ± 0.16
1-Heptene oxide	92.7	89.8	"	125.5-126.0	0.27	99.1 ± 0.13
1-Octene oxide	88.9	89.1	"	131.0-131.5	0.27	98.5 ± 0.14
1-Nonene oxide	84.8	84.5	"	148.0-149.0	0.27	98.68 ± 0.27
1-Undecene oxide	81.0	81.4	Amorphous	163.0-163.5	0.40	99.01 ± 0.11
1-Dodecene oxide	78.1	80.4	"	176.0-178.0	0.27	99.23 ± 0.08
1-Tetradecene oxide	67.2	85.1	"	181.5-182.0	0.27	98.96 ± 0.22
1-Hexadecene oxide	51.8	72.5	"	199.0-199.5	0.40	99.17 ± 0.09
1,3-Butadiene oxide	92.4	91.4	Liquid	121.0-121.5	1.33	99.41 ± 0.03
1,7-Octadiene oxide	96.9	94.2	"	156.0-156.6	1.33	98.78 ± 0.19
3-Methyl-1-butene oxide	86.1	91.1	"	96.0–96.5	0.27	99.06 ± 0.12
Epichlorohydrin	96.6	94.9	"	128.5-129.0	0.27	98.56 ± 0.22
Styrene oxide	85.2	80.0	Liquid*			

Synthesis of cyclic carbonates from epoxides in the presence of CoCl₂.6H₂O and dimethylformamide

* Not isolated from the reaction mixture.

REFERENCES

- 1. Koren'kova, O.P. and Kvasha, V.V., *Khim. Prom-st.*, 1961, no. 9, pp. 33-38.
- 2. Ufimtsev, A.V. and Kuzora, I.E., *Khim. Prom-st.*, 1993, no. 11, pp. 555–557.
- 3. RF Patent 2128658.
- Bobyleva, L.I., Rybina, G.V., and Srednev, S.S., *Khim. Prom-st.*, 2002, no. 7, pp. 1–5.
- Bobyleva, L.I., Kozlova, O.S., Rybina, G.V., and Moskvichev, Yu.A., *Zh. Anal. Khim.*, 2000, vol. 55, no. 10, pp. 1102–1104.