



# USE OF CYCLOHEXANE- AND PHENYLENE-1,2-DIAMINES MIXED WITH IODINE AS CATALYSTS FOR THE FORMATION OF ORGANIC CARBONATES FROM EPOXIDES AND CO<sub>2</sub>

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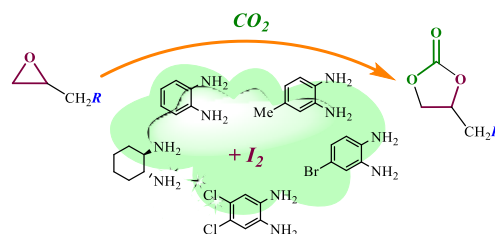
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## Abstract

Phenylene-1,2-diamines and (1*R*,2*R*)-cyclohexane-1,2-diamine were tested in the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>. It was found that the system based on aliphatic (1*R*,2*R*)-cyclohexane-1,2-diamine and iodine is the most effective one. An increase in the conversion was facilitated by an increase in the amount of iodine and the reaction temperature.

**Key words:** diamines, iodine, epoxides, CO<sub>2</sub> fixation, organic carbonates.



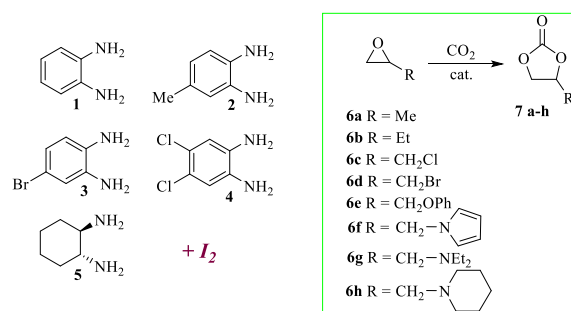
## Introduction

For many years, organic chemists had to use expensive, rare or toxic reagents and catalysts to obtain the target compounds. Reactions in organic synthesis often require a certain type of catalysts, indispensable reagents and solvents, which are extremely difficult to dismiss due to finely tuned parameters that affect the process conversion and selectivity. The use of carbon dioxide as a solvent and raw material is a practical way to address at least the cost and environmental issues. Nevertheless, the widespread application of carbon dioxide has a number of serious limitations due to its low solubilizing ability which is associated with a zero dipole moment and a dielectric constant ranging from 1.1 to 1.5 depending on the pressure and temperature [1]. One of the convenient approaches for the utilization of CO<sub>2</sub> in the synthesis of fuel additives, polar solvents, including those used in lithium-ion batteries, monomers for the production of polycarbonates and non-isocyanate polyurethanes is the reaction with oxiranes [2–5]. Nowadays, transition metal complexes, ionic liquids, as well as non-metallic catalysts, such as organic ammonium, imidazolium and phosphonium salts, including those covalently or weakly bound to solid supports, are used as catalysts for this process [6]. Each group of the catalysts has its own advantages and disadvantages. Thus, metal complexes are active at low loadings, pressures and temperatures, but their use is limited by the availability of starting compounds and complex synthesis [7]. Heterogeneous high molecular weight catalysts offer the advantages such as easy separation from the reaction products and recyclability, but there are also limitations related to the starting compounds and multistep synthesis of these catalysts [8]. Organocatalysts, as a rule, have lower activity, but an important feature of this type of catalysts is their availability [9]. In order to simplify and reduce the cost of catalysts, an approach has been suggested that is based on simple mixing of primary, secondary and tertiary amines, including high molecular weight

derivatives, with iodine. In this case, the systems of the [NR<sub>3</sub>]I composition are formed, the efficiency of which appears to be comparable to those of the catalysts that require significant synthetic efforts [10–17]. At the same time, we found that amines bearing additional hydroxy and amino groups are more effective. In order to search for new effective systems for the addition of CO<sub>2</sub> to oxiranes, in this work, we studied the performance of accessible cyclohexane- and phenylene-1,2-diamines with various substituents in combination with iodine.

## Results and discussion

A series of phenylene-1,2-diamines (compounds **1–4**, Scheme 1) and (1*R*,2*R*)-cyclohexane-1,2-diamine (**5**) in combination with iodine (1 mol %) were tested in the reaction of CO<sub>2</sub> with propylene oxide (**6a**) at 110 °C for 2 h.



**Scheme 1.** Addition of CO<sub>2</sub> to epoxides.

It was found that among the aryl-containing diamines, the most effective compound was diamine **1**. The introduction of additional substituents, especially halogen atoms, significantly reduced the conversion (Table 1, entries 1–4). The most effective system appeared to be a mixture of iodine and cyclohexane-1,2-diamine (Table 1, entry 5). This is likely to be associated with the higher solubility of this aliphatic catalyst in

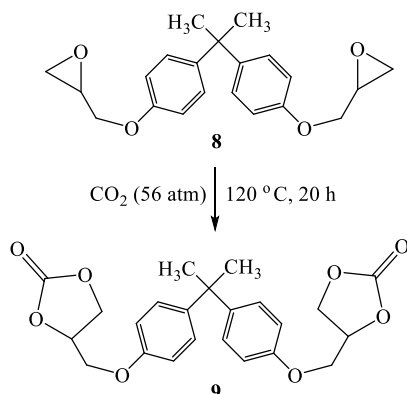
**Table 1.** Addition of CO<sub>2</sub> to oxiranes (56 atm)

Entry	Amine (1 mol %)	Oxirane	Additive	T, °C	t, h	Conversion (product yield), %
1	1	6a	I <sub>2</sub> (1 mol %)	110	2	72
2	2	6a	I <sub>2</sub> (1 mol %)	110	2	61
3	3	6a	I <sub>2</sub> (1 mol %)	110	2	42
4	4	6a	I <sub>2</sub> (1 mol %)	110	2	37
5	5	6a	I <sub>2</sub> (1 mol %)	110	2	79
6	5	6a	I <sub>2</sub> (1 mol %)	100	2	34
7	5	6a	I <sub>2</sub> (1 mol %) H <sub>2</sub> O (10 mol %)	110	2	88
8	5	6a	I <sub>2</sub> (1 mol %), CF <sub>3</sub> CH <sub>2</sub> OH (10 mol %)	110	2	84
9	5	6a	I <sub>2</sub> (1.5 mol %)	110	2	100
10	5	6a	I <sub>2</sub> (1 mol %)	120	2	100 (95)
11	5	6b	I <sub>2</sub> (1 mol %)	120	2	74
12	5	6b	I <sub>2</sub> (1 mol %)	120	4	100 (97)
13	5	6c	I <sub>2</sub> (1 mol %)	120	2	100 (96)
14	5	6d	I <sub>2</sub> (1 mol %)	120	2	100 (95)
15	5	6e	I <sub>2</sub> (1 mol %)	120	2	100 (92)
16	5	6f	I <sub>2</sub> (1 mol %)	120	2	100 (92)
17	5	6g	I <sub>2</sub> (1 mol %)	120	2	100 (95)
18	5	6h	I <sub>2</sub> (1 mol %)	120	2	100 (94)

low-polar propylene oxide compared to those obtained on the basis of aromatic diamines 1–4. It should be noted that a temperature decrease led to a drastic decrease in the catalyst efficiency (Table 1, entry 6).

In order to optimize the results, water and 2,2,2-trifluoroethanol were added to the reaction system as co-solvents, but the conversion increased only slightly (Table 1, entries 7 and 8). The quantitative conversion was achieved by increasing the amount of iodine from 1 to 1.5 mol % or by increasing the reaction temperature from 110 to 120 °C (Table 1, entries 9 and 10). The use of epoxide 6b (Scheme 1) bearing an ethyl substituent required a longer reaction time (Table 1, entries 11, 12). The latter can be explained by the limited solubility of the catalyst in nonpolar aliphatic oxirane 6b. In the case of more polar oxiranes 6c–h, the complete conversion was achieved in 2 h (Table 1, entries 13–18).

The catalyst based on diamine 5 and iodine was also tested in the addition of CO<sub>2</sub> to bis(epoxide) 8 (Scheme 2). At the iodine concentration of 1 mol %, the conversion in 20 h was 27%. An increase in the amount of iodine from 1 to 1.5 mol % led to the quantitative conversion under the same conditions. It is noteworthy that bicarbonate 9 is used to obtain high-temperature and mechanically stable adhesives and hydrophilizing coatings [18, 19].

**Scheme 2.** Addition of CO<sub>2</sub> to bis(epoxide) 8.

## Experimental section

### General remarks

The <sup>1</sup>H (400.13 MHz) and <sup>13</sup>C NMR spectra (100.61 MHz) were registered on a Bruker Avance 400 spectrometer in CDCl<sub>3</sub>. Diamines 1–5 and epoxides 6a–e are commercially available compounds. Epoxides 6f–h were synthesized according to the published procedures [15, 20, 21]. The work was performed with CO<sub>2</sub> of 99.99% purity using HIP equipment for its handling.

### Syntheses

#### Synthesis of carbonates 7a–h and 9 from the epoxides.

The corresponding diamine (0.06 mmol) and iodine (0.06 or 0.09 mmol) were placed in a 10 mL autoclave. Then the epoxide (6.00 mmol) was added. CO<sub>2</sub> was introduced into the autoclave at room temperature and heated to the required temperature in a thermostat. After the process completion, the autoclave was cooled to 5 °C, CO<sub>2</sub> was released, and CDCl<sub>3</sub> (2 mL) was added. The resulting mixture was filtered through a thin layer of silica gel to remove the catalyst residues, and the solution obtained was analyzed by NMR spectroscopy. The spectral characteristics of the resulting carbonates were in good agreement with the previously published data [15, 21–24].

## Conclusions

Thus, we tested different phenylene-1,2-diamines and (1*R*,2*R*)-cyclohexane-1,2-diamine in the production of cyclic carbonates from epoxides and CO<sub>2</sub>. It was shown that the system based on aliphatic (1*R*,2*R*)-cyclohexane-1,2-diamine and iodine is the most effective one. An increase in the conversion was facilitated by an increase in the amount of iodine and the reaction temperature.

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