



MIXTURES OF HETEROCYCLES AND IODINE AS THE CATALYSTS FOR THE FORMATION OF ORGANIC CARBONATES FROM EPOXIDES AND CO₂

Cite this: *INEOS OPEN*, 2022, 5 (6), 158–160
DOI: 10.32931/io2227a

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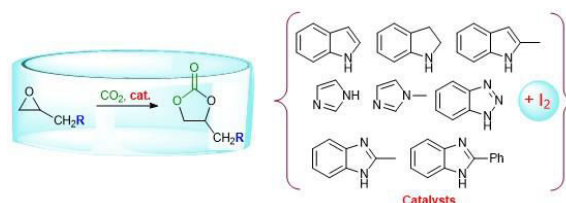
Received 31 July 2023,
Accepted 16 August 2023

<http://ineosopen.org>

Abstract

Combinations of a series of nitrogen-containing heterocycles with iodine were tested as the catalysts for the synthesis of cyclic carbonates from epoxides and CO₂. It is shown that the systems containing aliphatic substituents are more efficient, the presence of a free NH group has a beneficial effect on the conversion, and the systems with two or more nitrogen atoms are more active.

Key words: heterocycles, iodine, epoxides, CO₂ fixation, organic carbonates.



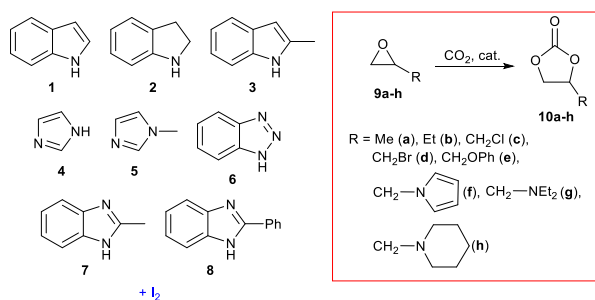
Introduction

Organic carbonates are widely used as fuel additives, polar solvents, including those used in lithium-ion batteries, as well as monomers for the production of polycarbonates and non-isocyanate polyurethanes [1]. One of the convenient approaches to the preparation of organic carbonates is the addition of CO₂ to epoxides [2–4]. Nowadays, the following catalysts are used to promote this reaction: transition metal complexes, ionic liquids, and nonmetallic catalysts such as organic ammonium, imidazolium, and phosphonium salts, in particular those covalently or weakly bound to solid supports [5, 6]. Recently, it has been shown that the catalysts for this process can be drastically simplified to the mixtures of iodine with amines, which give [NR₃]I systems [7–12]. The efficiency of these catalysts increases when the amine component contains donor aliphatic substituents. The presence of additional hydroxy or amino groups, which can facilitate both the opening of an epoxide ring and the subsequent insertion of CO₂ into the molecule, has an additional cocatalytic effect. Of particular interest for the production of highly efficient catalysts for the addition of CO₂ to epoxides are heterocyclic amines. In this communication, we report on the results of investigation of the catalytic performance of a series of nitrogen-containing heterocycles in combination with iodine in the addition of CO₂ to epoxides.

Results and discussion

Combinations of a series of heterocyclic amines (1–8) with iodine (1 mol %) were tested in the addition of CO₂ to propylene oxide (9a) for 2 h (Scheme 1).

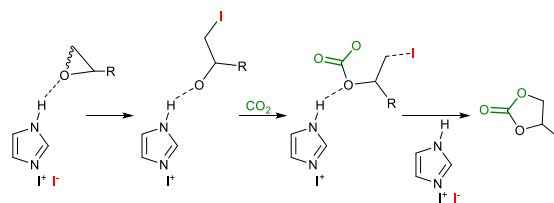
It was found that indole (1) provides a low conversion (Table 1, entry 1). In the case of indoline (2) and 2-methylindole (3) bearing aliphatic substituents in their structures, the conversion slightly increases (entries 2, 3). The use of imidazole



Scheme 1. Addition of CO₂ to epoxides.

(4) leads to a much higher conversion compared to the indole derivatives (entry 4). Note that 1-methylimidazole affords a lower result (entry 5). Most likely, the acidic NH group of imidazole exerts a cocatalytic effect by promoting the opening of an epoxide ring through hydrogen bonding (Scheme 2).

1*H*-Benzo[d][1,2,3]triazole (6) demonstrates the same efficiency as imidazole, which can be explained by the structural similarity of these compounds (entry 6). The highest conversion (entry 7) among this series of heterocycles was provided by 2-methyl-1*H*-benzo[d]imidazole (7). However, on passing to 2-phenyl-1*H*-benzo[d]imidazole (8), the conversion sharply decreases, which is likely to be connected with the lower solubility of this catalytic system in the epoxide (entry 8). It should be noted that the heterocycles or iodine on their own do not catalyze the process.



Scheme 2. Proposed mechanism of the process.

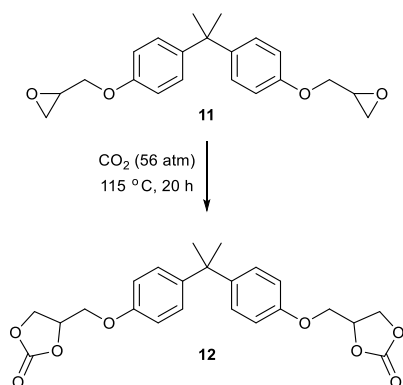
Table 1. Addition of CO₂ to epoxides

Entry	Heterocycle	Epoxide	P, atm	T, °C	t, h	Substrate conversion (product yield), %
1	1	9a	56	105	2	19
2	2	9a	56	105	2	21
3	3	9a	56	105	2	29
4	4	9a	56	105	2	72
5	5	9a	56	105	2	47
6	6	9a	56	105	2	73
7	7	9a	56	105	2	81
8	8	9a	56	105	2	38
9	7	9a	56	115	2	100 (95)
10	7	9a	10	115	2	95
11	7	9b	56	115	2	78
12	7	9b	56	115	4	100 (96)
13	7	9c	56	115	2	100 (96)
14	7	9d	56	115	2	100 (95)
15	7	9e	56	115	2	100 (91)
16	7	9f	56	115	2	100 (92)
17	7	9g	56	115	2	100 (95)
18	7	9h	56	115	2	100 (94)

In order to achieve a quantitative conversion in the reaction of propylene oxide with CO₂, the temperature was increased to 115 °C. The desired result was provided by the catalytic system based on compound **7** and iodine (entry 9). The reaction at the CO₂ pressure of 10 atm and the same temperature led to a slightly lower conversion (entry 10).

The use of epoxide **9b** (Scheme 2), which contains a more electron-donating ethyl substituent compared to the methyl one in **9a**, required a longer reaction time (entries 11, 12). In the case of epoxides **9c–h**, the complete conversion can be achieved in 2 h (entries 13–18).

Furthermore, the catalyst based on compound **7** and iodine proved to be effective in the addition of CO₂ to bis(epoxide) **11**, where the complete conversion was achieved in 20 h (Scheme 3). It should be noted that bis(carbonate) **5** is used in the production of high-temperature and mechanically stable adhesives and hydrophilizing coatings [13, 14].

**Scheme 3.** Addition of CO₂ to bis(epoxide) **11**.

Experimental section

General remarks

The ¹H (400.13 MHz) and ¹³C NMR (100.61 MHz) NMR spectra were recorded on a Bruker Avance 400 instrument in CDCl₃. Heterocycles **1–8** and epoxides **9a–e** are commercially

available compounds. Epoxides **9f–h** were obtained according to the published procedures [12, 15, 16]. The experiments were performed with CO₂ of 99.99% purity using HIP handling equipment.

Syntheses

Preparation of carbonates 4a–g from epoxides. The corresponding heterocycle (0.06 mmol) and iodine (0.06 mmol) were placed into a 10 mL autoclave. Then 6 mmol of the epoxide was added. The autoclave was loaded with CO₂ at room temperature and heated to the required temperature in a thermostat. After the reaction completion, the autoclave was cooled to 5 °C, CO₂ was released, and 2 mL of CDCl₃ 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 carbonates corresponded to the literature data [12, 16–19].

Conclusions

Thus, a series of heterocyclic amines in combination with iodine were tested in the synthesis of cyclic carbonates from epoxides and CO₂. It was found that the systems containing aliphatic substituents are more efficient. The presence of a free NH group has a beneficial effect on the substrate conversion, whereas the systems with two or more nitrogen atoms are more active.

Acknowledgements

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-03-2023-642).

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