



CADMIUM IODIDE AS A CATALYST FOR THE ADDITION OF CARBON DIOXIDE TO OXIRANES

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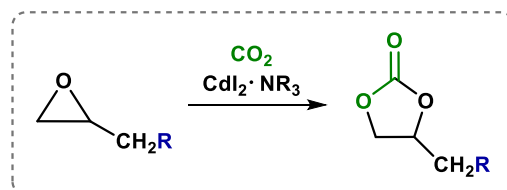
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Abstract

The CdI₂-catalyzed addition of CO₂ to oxiranes is presented. The catalysts are obtained by mixing amines with CdI₂. It is found that amines with a large number of aliphatic groups provide the higher conversion; the presence of additional OH and NH groups negatively affects the conversion.

Key words: cadmium iodide, amines, epoxides, CO₂ fixation, organic carbonates.



Introduction

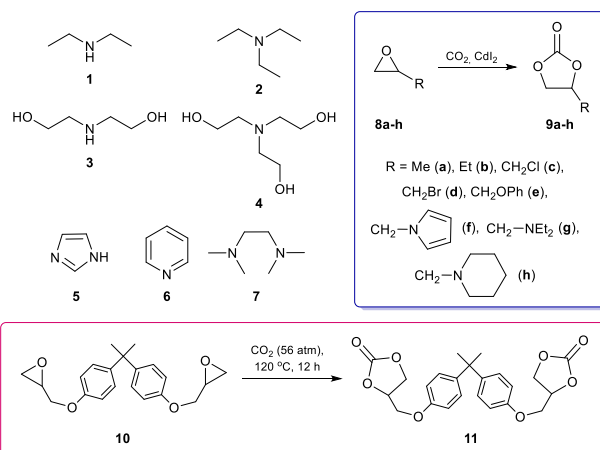
Carbon dioxide is the main anthropogenic greenhouse gas produced by the chemical, thermoelectric and steel industries, as well as the transport sector. Worldwide CO₂ emissions have caused many environmental problems, such as climate change and global warming, which makes the recycling of carbon dioxide into different compounds for application purposes an urgent task, despite the sufficient inertness of the molecule. One popular group of chemicals that can be produced from CO₂ is comprised by organic carbonates. The latter are used as fuel additives, electrolytes for lithium-ion batteries, polar solvents, monomers for the production of polycarbonates and non-isocyanate polyurethanes [1, 2]. 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 substrates, are used as catalysts for this process [3, 4]. One of the appealing approaches to reduce the cost of this process is the use of inorganic salts as catalysts owing to their widespread availability. However, due to the low solubility of inorganic halides in organic media, the reactions involving them require high temperatures and a long time [5].

Herein, we report on the use of cadmium iodide as a catalyst for the addition of CO₂ to oxiranes, leading to organic carbonates, and the methods for the catalyst activation.

Results and discussion

Cadmium iodide is an inorganic compound that features high solubility in water, alcohols and diethyl ether, suggesting its compatibility with organic compounds. However, its application (1 mol %) in the addition of CO₂ to propylene oxide (**8a**, Scheme 1) afforded only low conversion (Table 1, entry 1).

In order to increase the conversion, we decided to add amines (2 mol %) as the ligands for CdI₂. It was found that



Scheme 1. Addition of CO₂ to oxiranes.

the higher conversions are provided by amines with a large number of aliphatic groups (Table 1, entries 2, 3 and 4, 5). The presence of additional OH and NH groups negatively affects the conversion (Table 1, entries 2–8), which is most likely associated with the competitive coordination with the oxirane oxygen atom. Triethylamine provides the highest performance. For the optimization of the reaction conditions, the temperature was increased from 110 to 120 °C, which led to the quantitative conversion in the case of triethylamine used as an additive (Table 1, entry 9). The reaction of epoxide **8b** bearing an ethyl substituent (Scheme 1) required a longer time (Table 1, entries 10, 11). In the case of more polar oxiranes **8c–h**, the complete conversion was achieved in 2 h (Table 1, entries 13–18).

The catalytic system based on triethylamine and CdI₂ was also tested for the addition of CO₂ to bis-oxirane **10**. The quantitative conversion of the substrate was achieved in 12 h. It is noteworthy that bicarbonate **11** is used in the production of high-temperature and mechanically stable adhesives and hydrophilizing coatings [6, 7].

Table 1. CdI₂-catalyzed (1 mol %) addition of CO₂ to oxiranes (56 atm)

Entry	Additive	Oxirane	T, °C	Time, h	Conversion, %	Yield, %
1	–	8a	110	2	26	–
2	1	8a	110	2	81	–
3	2	8a	110	2	90	–
4	3	8a	110	2	60	–
5	4	8a	110	2	72	–
6	5	8a	110	2	65	–
7	6	8a	110	2	88	–
8	7	8a	110	2	80	–
9	2	8a	120	2	100	95
10	2	8b	120	2	88	–
11	2	8b	120	2.5	100	97
12	2	8c	120	2	100	96
13	2	8d	120	2	100	96
14	2	8e	120	2	100	92
15	2	8f	120	2	100	93
16	2	8g	120	2	100	95
17	2	8h	120	2	100	94
18	2	10	120	12	100	96

Experimental section

The ¹H NMR spectra (400.13 MHz) were recorded on a Bruker Avance 400 spectrometer in CDCl₃. Amines **1–7** and epoxides **8a–e**, **10** were purchased from commercial sources. Epoxides **8f–h** were synthesized according to the published procedures [8–10]. The work was performed with CO₂ of 99.99% purity using HIP equipment for its handling.

Synthesis of carbonates 9a–h, 11 from epoxides. CdI₂ (0.06 mmol) and amine (0.06 or 0.12 mmol) were placed in a 10 mL autoclave. Then the corresponding oxirane (6.00 mmol) was added. CO₂ was introduced into the autoclave at room temperature and heated to the required temperature in a thermostat. After the specified time, the autoclave was cooled to 5 °C, CO₂ was released, and CDCl₃ (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 carbonates were in good agreement with the literature data [8, 10–13].

Conclusions

Hence, we tested a series of amines in combination with CdI₂ in the addition of CO₂ to oxiranes. It was found that amines with a large number of aliphatic groups provide the higher conversion, while the presence of additional OH and NH groups negatively affects the conversion. In addition, this report is the first example of the cadmium-catalyzed addition of CO₂ to oxiranes [14].

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References

- Y. Fan, M. Tiffner, J. Schörghenheimer, R. Robiette, M. Waser, S. R. Kass, *J. Org. Chem.* **2018**, *83*, 9991–10000. DOI: 10.1021/acs.joc.8b01374
- B. Song, A. Qin, B. Z. Tang, *Cell Rep. Phys. Sci.*, **2022**, *3*, 100719. DOI: 10.1016/j.xcrp.2021.100719
- T. Weidlich, B. Kamenická, *Catalysts*, **2022**, *12*, 298. DOI: 10.3390/catal12030298
- T. Lv, B. Wang, R. Wang, *Aerosol Air Qual. Res.*, **2022**, *22*, 220227. DOI: 10.4209/aaqr.220227
- S. E. Lyubimov, A. A. Zvinchuk, B. Chowdhury, *Russ. Chem. Bull.*, **2021**, *70*, 1324–1327. DOI: 10.1007/s11172-021-3218-z
- A. S. Nair, S. Cherian, N. Balachandran, U. G. Panicker, S. K. K. Sankaranarayanan, *ACS Omega*, **2019**, *4*, 13042–13051. DOI: 10.1021/acsomega.9b00789
- J. Nanclares, Z. S. Petrović, I. Javni, M. Ionescu, F. Jaramillo, *J. Appl. Polym. Sci.*, **2015**, *132*, 42492. DOI: 10.1002/app.42492
- S. E. Lyubimov, P. V. Cherkasova, R. R. Aysin, *INEOS OPEN*, **2022**, *5*, 38–41. DOI: 10.32931/iao2208a
- V. S. Reuss, M. Werre, H. Frey, *Macromol. Rapid Commun.*, **2012**, *33*, 1556–1561. DOI: 10.1002/marc.201200307
- T. Tsuda, K. Kondo, T. Tomioka, Y. Takahashi, H. Matsumoto, S. Kuwabata, C. L. Hussey, *Angew. Chem., Int. Ed.*, **2011**, *50*, 1310–1313. DOI: 10.1002/anie.201005208
- H. Zhou, G.-X. Wang, W.-Z. Zhang, X.-B. Lu, *ACS Catal.*, **2015**, *5*, 6773–6779. DOI: 10.1021/acscatal.5b01409
- V. Legros, G. Taing, P. Buisson, M. Schuler, S. Bostyn, J. Rousseau, C. Sinturel, A. Tatibouët, *Eur. J. Org. Chem.*, **2017**, 5032–5043. DOI: 10.1002/ejoc.201700646
- J.-Z. Hwang, S.-C. Wang, P.-C. Chen, C.-Y. Huang, J.-T. Yeh, K.-N. Chen, *J. Polym. Res.*, **2012**, *19*, 9900. DOI: 10.1007/s10965-012-9900-y
- F. Della Monica, C. Capacchione, *Asian J. Org. Chem.*, **2022**, *11*, e202200300. DOI: 10.1002/ajoc.202200300

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