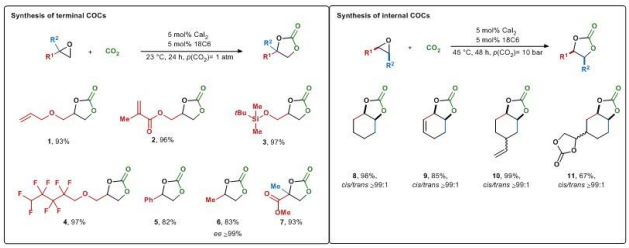
Technology Offer

Efficient synthesis of even challenging (i.e. silyl-functionalized, fluorinated or bicyclic) cyclic organic carbonates under mild conditions e.g. for improved coatings, electrolytes and/or non-isocyanate polyurethanes

Reference Number TO 28-00021(2)

Challenge

The synthesis of cyclic organic carbonates (COCs) from epoxides and CO_2 represents an exciting and vibrant area of research, which is particularly inspired by the COC's broad applicability, ranging from solvents and electrolytes, over raw materials for polymers, to functionalized coatings. Previous efforts yielded a multitude of catalytic systems, of which, however, only very few operate under ambient conditions ($T \leq 25$°C, $p(CO_2) \leq 1$ atm) and allow for the conversion of a broad range of (especially challenging and/or delicate) substrates. Moreover, the vast majority of known catalytic systems only work well for the synthesis of terminal COCs, whereas the corresponding conversion of internal epoxides is not efficiently catalyzed.



Selected examples for the synthesis of terminal and internal COCs (reaction conditions and isolated yields).

Technology

Scientists at the Leibniz Institute for Catalysis (LIKAT) have developed a rather simple catalytic system for the atom economical and efficient synthesis of even structurally challenging COCs, which is based on readily available calcium iodide and 18-crown-6 ether (18C6). ^{1}H NMR experiments revealed the selective *in situ* formation of a crown ether complex, which allows the conversion of various terminal epoxides under ambient conditions.

Remarkably, also a broad range of internal epoxides with various substitution patterns are smoothly converted to the corresponding COCs under mild conditions ($T = 45$°C, $p(CO_2) = 10$ bar), proving the catalytic system's high efficiency and capability. Notably, also most of the internal COCs were synthesized in exceptional high yields as well as diastereoselectivities of up to ≥ 99%. Moreover, the proprietary catalytic system operates under solvent-free conditions without any co-catalysts such as onium salts. However, if a solvent is necessary e.g. due to the solid nature of the epoxide, the catalyst system can also operate in various solvents.
In conclusion, the novel CaI_2/18C6-based catalyst system provides a powerful and versatile tool for the efficient and sustainable production of a wide range of terminal and internal COCs under ambient or mild conditions. Key features are (i) high selectivity, (ii) broad specificity, (iii) high efficiency, even under mild reaction conditions, (iv) high sustainability, (v) conversion of even delicate substrates, facilitating production of valuable, novel and/or rare COCs for multiple applications, (vi) low toxicity, as well as (vii) low costs.

Commercial Opportunity

The proprietary technology is offered for in-licensing and/or co-development.

Development Status

The practical applicability of CaI_2/18C6-based catalyst system has been broadly demonstrated in lab scale for a wide range of terminal and internal COCs. Figure 1 shows examples of selected COCs of particular interest, like e.g.:

- *Unsaturated terminal* COCs (**1**, **2**, **9** and **10**) as potential building blocks for homo- and co-polymerization,
- *Silyl-functionalized* COCs (**3**) with possible applications as electrolytes, for surface modifications and/or as precursors for the synthesis of non-isocyanate polyurethanes (NIPUs),
- *Highly fluorinated* COCs (**4**), which can be used as electrolytes in lithium batteries,
-

Licensing Contact
Dr. Torsten Stachelhaus
Technology Manager
T: +49 40 1888 43 48
stachelhaus@ascenion.de

Ascenion GmbH
Herzogstraße 64
D-80803 München
info@ascenion.de
www.ascenion.de

Efficient synthesis of even challenging (i.e. silyl-functionalized, fluorinated or bicyclic) cyclic organic carbonates under mild conditions e.g. for improved coatings, electrolytes and/or non-isocyanate polyurethanes -2-

- *Aliphatic substituted* COCs (**6**) like e.g. propylene carbonate, which is used as electrolyte and considered as one of the most sustainable alternative solvents in organic chemistry,
- *Disubstituted terminal* COCs (**7**), whose synthesis is considered to be particular challenging,
- *Bicyclic internal* COCs (**8**, **9**, **10**, **11**), which are of special interest as precursors for the diastereoselective synthesis of diols,
- *Biscarbonates* (**11**), which can be used as monomers for the synthesis of NIPUs.

Patent Situation
A German patent application has been filed in February 2017.

Further Reading
Steinbauer, Spannenberg & Werner (2017) An in situ formed Ca^{2+}–crown ether complex and its use in CO_2-fixation reactions with terminal and internal epoxides. Green Chemistry, DOI: 10.1039/c7gc01114h
Steinbauer & Werner (2017) Poly(ethylene glycol)s as Ligands in Calcium-Catalyzed Cyclic Carbonate Synthesis. ChemSusChem 10: 3025-3029
Büttner, Longwitz, Steinbauer, Wulf & Werner (2017) Recent developments in the synthesis of cylic carbonates from epoxides and CO_2.Top Curr Chem 375: 50. DOI: 10.1007/s41061-017-0136-5
Longwitz, Steinbauer, Spannenberg & Werner (2018) Calcium-based catalytic system for the synthesis of bio-derived cyclic carbonates under mild conditions. ACS Catalysis 8: 665-672

Catalysis LIKAT Leibniz-Institut für Katalyse e.V.

Licensing Contact
Dr. Torsten Stachelhaus
Technology Manager
T: +49 40 1888 43 48
stachelhaus@ascenion.de

Ascenion GmbH
Herzogstraße 64
D-80803 München
info@ascenion.de
www.ascenion.de