

Organocatalysis in the Chemical Transformations

Adriana Maria da Silva 

Instituto Nacional de Metrologia, Qualidade e Tecnologia (INMETRO), Duque de Caxias 25250-020, RJ, Brazil;
amdasilva@inmetro.gov.br

Organocatalysis has been a breakthrough in chemical transformations becoming viable the conversion of challenging reactions through the sustainable use of small organic molecules as catalysts. Although organic molecules have been utilized in the past, the emergence of organocatalysis as new field occurred only in the last two decades. This was brought about because of their distinct set of advantages, such as operational simplicity, catalyst stability, and the availability of a vast amount of small, naturally occurring organic molecules, including natural sources of chiral amino acids and alkaloids, to mention few [1]. The recognition of organocatalysis as a tool for controlling the chirality of molecules was accomplished through the Nobel Prize in Chemistry 2021 being awarded for “the development of asymmetric organocatalysis”. In addition to asymmetric conversion, other organocatalyzed reactions have been exploited, such as forming and breaking reactions, and photo- and electrocatalysis.

Thus, this Special Issue is dedicated to the field of organocatalysis and the latest developments regarding the optimization of the organocatalysts using distinct methodologies, with the commitment of meeting the environmental requirements, highlighting the importance of green solvents and catalyst recycling, as well as the need to correlate the waste produced in relation to the useful product for upscaling purposes [2–8], as briefly described in the following paragraphs.

Zalewska et al. [2] reported the benefits resulting from the association of Chiral Ionic Liquids (CIL) using L-proline as a cation or anion, combined with suitable counterions, and their performance in the asymmetric Michael addition reactions of ketones and aldehydes to nitro-olefins. The CIL-Proline organocatalysis exhibited better catalytic results in comparison to the L-Proline, achieving good conversions and enantioselectivities (e.g., upwards of 95%). According to the authors, products could be recovered with good efficiency via supercritical CO₂ extraction. Likewise, Jacoby et al. [3] demonstrated the feasibility of recovering products and catalysts through the development of novel polyester-supported catalysts (PCL) prepared from poly(ϵ -caprolactones), modulating the molecular weights in order to control the catalyst/polymer weight ratio, ensuring homogeneous catalysis, while allowing the catalysts to recover through CO₂ supercritical extraction. In terms of catalyst performance, the presence of amide groups decorating the catalysts' structures was more effective than the presence of their ester group counterparts toward the aldol product, achieving a higher degree of stereoselectivity. Fleisher et al. [4] evaluated the substitution of the nucleophilic core, N-alkylimidazole or 4-aminopyridine, decorated through the benzyl substituent by an extensive secondary-sphere envelope in the acylation and phosphorylation of butyric anhydride and diphenylphosphoryl chloride reactions, respectively. The results revealed significant differences between the two transformations according to the catalyst's nature, with the BMAP-type catalysts being much more active than the imidazole-type (Im-) analogues.

In view of the fact that solvents have a pivotal role in organic reactions, Martelli et al. [5] made a comprehensive review of the recent advances in asymmetric organocatalysis using bio-based solvents in order to replace the toxic organic reagents often used with greener ones. The authors emphasize the need for considering solvents derived from renewable



Citation: da Silva, A.M.

Organocatalysis in the Chemical Transformations. *Catalysts* **2023**, *13*, 1282. <https://doi.org/10.3390/catal13091282>

Received: 30 August 2023

Accepted: 4 September 2023

Published: 7 September 2023



Copyright: © 2023 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

sources, including biomass. The application of bio-based solvents such as ethyl alcohol, 2-methyltetrahydrofuran, ethyl acetate, ethyl lactate, supercritical carbon dioxide, and diethyl carbonate in asymmetric organocatalysis reactions was discussed.

A detailed review of the use of sulfur ylides such as organocatalysts in reactions such as Corey–Chaykovsky reactions, cyclopropanations, forming C-H and C-X, and X-H insertions was discussed by Hayashi et al. [6]. Despite the fact that the use of sulfur ylides for metal carbene formation is well established, their application in organocatalysis is still in its early stages. The authors discussed the mechanisms and activation modes of this class of organocatalysts, and identified the potential challenges to be circumvented, such as the need for research on sulfonium ylide organocatalysts in formal insertion reactions and sulfoxonium ylides in cyclization.

Antenucci et al. [7] discussed the foundations of upscaling of some of the relevant organocatalytic reactions not yet achieved on a large scale, wherein key factors such as the availability of equipment, purity, and a lack of traces of certain metal impurities are pivotal in the design of the process. At the same time, a sustainability approach was evaluated through global E factor (Eg) and E factor (E), from which the ratio of useful product to waste generated, including catalyst waste, was to be measured.

Finally, I believe this Special Issue will contribute to the existing knowledge in the field and motivate further research in organocatalysis, contributing to green process development.

I would like to express my gratitude to the journal, *Catalysts*, for the opportunity to serve as a Guest Editor, contributing to this exciting developing field, as well as to the editorial team, especially to Ms. Rita Lin, who was instrumental to the successful publication of this Special Issue. I would also like to extend my sincerest gratitude to the authors, who shared their research, and to the referees for their invaluable contributions.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Lassaletta, J.M. Spotting trends in organocatalysis for the next decade. *Nat. Commun.* **2020**, *11*, 3787.
2. Zalewska, K.; Pinto, I.; Cabrita, L.; Zakrzewska, M.; Noronha, J.; da Ponte, M.; Branco, L. Development of L-Proline-Based Chiral Ionic Liquids for Asymmetric Michael Reaction. *Catalysts* **2023**, *13*, 270. [\[CrossRef\]](#)
3. Jacoby, C.; Sbardelotto, J.; Daitx, T.; Dalberto, B.; Mauler, R.; Schneider, P. Poly(ϵ -caprolactones) Initiated by Chiral Compounds: A New Protocol to Support Organocatalysts. *Catalysts* **2023**, *13*, 164. [\[CrossRef\]](#)
4. Fleischer, O.; Targel, T.; Saady, F.; Portnoy, M. Similarities and Differences between Site-Selective Acylation and Phosphorylation of Amphiphilic Diols, Promoted by Nucleophilic Organocatalysts Decorated with Outer-Sphere Appendages. *Catalysts* **2023**, *13*, 361. [\[CrossRef\]](#)
5. Martelli, L.; Machado, I.; dos Santos, J.; Corrêa, A. Recent Advances in Greener Asymmetric Organocatalysis Using Bio-Based Solvents. *Catalysts* **2023**, *13*, 553. [\[CrossRef\]](#)
6. Hayashi, M.; Burtoloso, A. Organocatalytic Transformations from Sulfur Ylides. *Catalysts* **2023**, *13*, 689. [\[CrossRef\]](#)
7. Antenucci, A.; Dughera, S. Usefulness of the Global E Factor as a Tool to Compare Different Catalytic Strategies: Four Case Studies. *Catalysts* **2023**, *13*, 102. [\[CrossRef\]](#)
8. Nikiforov, A.; Panina, N.; Blinou, D.; Gurzhiy, V.; Nashchekina, J.; Korzhikova-Vlakh, E.; Eremin, A.; Stepanova, M. Ring-Opening Polymerization of rac-Lactide Catalyzed by Octahedral Nickel Carboxylate Complexes. *Catalysts* **2023**, *13*, 304. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.