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Asymmetric Organocatalysis

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Aims and Scope

The series *Topics in Current Chemistry* presents critical reviews of the present and future trends in modern chemical research. The scope includes all areas of chemical science, including the interfaces with related disciplines such as biology, medicine, and materials science.

The objective of each thematic volume is to give the non-specialist reader, whether at the university or in industry, a comprehensive overview of an area where new insights of interest to a larger scientific audience are emerging.

Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5–10 years are presented, using selected examples to illustrate the principles discussed. A description of the laboratory procedures involved is often useful to the reader. The coverage is not exhaustive in data, but rather conceptual, concentrating on the methodological thinking that will allow the non-specialist reader to understand the information presented.

Discussion of possible future research directions in the area is welcome.

Review articles for the individual volumes are invited by the volume editors.

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Enough Organocatalysis?

These are exciting times for asymmetric organocatalysis. During the last decade, the chemical community finally began considering the previously overlooked field as the third pillar of asymmetric catalysis, complementing only enzymes and chiral metal complexes. Now, countless academic groups around the world are entering the area. And with regard to industrial applications, the question is not anymore, *if* the pharmaceutical industry is going to use organocatalysis, but rather whether or not there are still companies actually *not* using it.

Organocatalysts are purely organic molecules that function by removing or donating electrons or protons from or to reaction substrates or transition states. This situation defines four distinct areas: Brønsted acid and base catalysis and Lewis acid and base catalysis. The field has roots back to the beginning of the 20th century with Bredig's now legendary studies on the use of natural alkaloids as enantioselective catalysts. This line of research has subsequently been continued by others, including Pracejus and Wynberg. Parallel studies by Hajos and Wiechert using proline as aldolization catalyst were inspired by the seminal work of Knoevenagel in the late 19th century. Few other organocatalysts were described during those decades but, like proline and quinine, they were considered exotic, isolated examples with a poorly understood mode of action. The situation changed only at the beginning of this millennium when it was shown that aminocatalysis, the activation of carbonyl compounds via enamine and iminium ion intermediates, is a *general* catalysis concept. This discovery finally opened the door to understanding and designing organocatalysts and to predicting their behavior. The concept of aminocatalysis has since been applied to dozens of reaction types and literally hundreds of variants. Moreover, the working principles of other Lewis base catalysts such as carbenes and tertiary amines as well as that of Brønsted acid and base catalysts is now appreciated and new reactions and catalysts are being designed and published on a daily basis. These are fascinating developments, especially in light of a previous opinion we organic chemists have convinced ourselves of, namely that new reactions can *only* be expected from the realm of transition metal chemistry. The current developments leave us to either accept the fact that our perception may not have been entirely correct or to continue to be "right" simply by arguing that organocatalysis is not truly novel (and yet researching it anyway). Undebatable though, at least in my opinion, is the success and usefulness of organocatalysis, the

enormous amount of activities in the field, and the resulting constant need for reflection and knowledge updates such as this volume.

So why the provocative title then? The term “organocatalysis” has been quite useful in initially highlighting and subsequently popularizing an underappreciated though fundamental catalysis principle. However, as time goes by and as more and more organic catalyst motifs and concepts are being developed, the term might become less and less accurate. In the field of transition metal catalysis, we speak of “palladium catalysts” or invent a new “iron-catalyzed reaction” rather than stating we are investigating “transition metal catalysis”. Similarly, in biocatalysis, we specify which particular class of enzyme is being studied. I suggest that a similar specification will ultimately take place in organocatalysis. We will find more and more publications using “a phosphoric acid catalyst” or describing a “secondary amine-catalyzed transformation” rather than an “organocatalytic reaction”. In that sense: Yes, enough organocatalysis! Still, there is little doubt that the field will continue to grow massively. It appears to me that there are still many ripe and delicious fruits to be picked by creative and intrepid minds.

All four areas of organocatalysis are covered in this volume, providing an overview of the field from experts in their areas. I would like to wholeheartedly thank all those who have contributed to making this volume such a wonderful and original source of knowledge. I hope it will inspire you to apply organocatalytic methods to solve some of your problems but possibly also to contribute solving some of the remaining challenges of organocatalysis.

Mülheim, Summer 2009

Benjamin List

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