311

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Bismuth-Mediated Organic Reactions
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Vol. 311, 2012

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Volume Editor: Timothy Deming
Vol. 310, 2012

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Volume Editor: Hans-Joachim Knölker
Vol. 309, 2012

Fluorous Chemistry
Volume Editor: István T. Horváth
Vol. 308, 2012

Multiscale Molecular Methods in Applied Chemistry
Volume Editors: Barbara Kirchner, Jadran Vrabec
Vol. 307, 2012

Solid State NMR
Volume Editor: Jerry C. C. Chan
Vol. 306, 2012

Prion Proteins
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Vol. 305, 2011

Microfluidics: Technologies and Applications
Volume Editor: Bingcheng Lin
Vol. 304, 2011

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Volume Editor: Carlo Alberto Bignozzi
Vol. 303, 2011

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Vol. 297, 2010

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Volume Editors: Wolfgang Bielke, Christoph Erbacher
Vol. 296, 2010

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Vol. 295, 2010

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Vol. 294, 2010

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Vol. 293, 2010

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– Aims and Scope
– Instructions for Authors
– Sample Contribution

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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.

In references *Topics in Current Chemistry* is abbreviated *Top Curr Chem* and is cited as a journal.

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Foreword

I have heard the following declaration made every l0 years or so: "Organic chemistry is all wrapped up. We are now able to prepare every possible molecule!". I believe this is far from true with respect to the actual status of organic synthesis. In fact, it is amazing to see how organic synthesis has changed and continues to evolve. Take, for instance, the total synthesis of a simple molecule of a natural product, which earlier required a period of 5–10 years, even with a number of postdocs devoting their time and expertise to the task. Nowadays, a single graduate student could synthesize the same complex natural molecule within a few years. I do think that this amazingly rapid growth far exceeds that which has occurred in other sciences. And I further believe that the study of organic synthesis should continue forever and that the number of future discoveries are limitless.

This book deals with only one element of the periodic table but still contains a large amount of new knowledge, all of which comes from a single element: bismuth! The history of bismuth in synthetic chemistry is relatively short. The most important features of this element, arising from its low toxicity and high reactivity, were first highlighted only recently. Each chapter describes a different aspect of the chemistry of bismuth, which I am confident will be rapidly recognized with increasing importance in future. Thus, I am already looking forward to reading the second volume of this book.

Science in its youth is always exciting to pursue. When I began my career forty years ago, aluminum chemistry was a newly emerging field. Thus, whatever I found was new and exciting. I am sure that every young researcher who is interested in bismuth chemistry will enjoy the still-unfolding era of this element prior to its full blooming – and I am also confident this book will provide a reliable compass for his or her journey of discovery.

Bon voyage!

The University of Chicago Hisashi Yamamoto

Preface

Bismuth in synthesis: an emerging area

These are exciting times for organic synthesis using green metals. During the last decade, the chemical community finally began considering the previously underused chemistry of organobismuth derivatives and bismuth catalysts. Today, many academic groups around the world are entering the area.

The roots of this field date back to the early 1850's with Löwig's studies of the synthesis of organic derivatives of bismuth, followed by Michaelis' in the late 1880's. Further studies by Gilman in the late 1930's and early 1940's, involving the synthesis of triaryl derivatives of bismuth, were inspired by the seminal work of Michaelis. Wittig in the 1950's also worked on the synthesis of pentaaryl derivatives of bismuth. This line of research was subsequently continued by Sir Barton in the 1980–90's reporting efficient phenylation reactions using triarylbismuth [(III) and (V)] compounds. Further studies by Suzuki involved the synthesis of organobismuth(V) derivatives and bismuthonium salts. In 2006–2007, Mukaiyama demonstrated the utility of organobismuth(V) derivatives as very efficient reagents for various phenylations and oxidations.

The role of bismuth(III) salts as Lewis acids has only been studied since the late 1980's. Pioneering work by Dubac, Wada and others paved the way to wide and general methods using bismuth(III) catalysts. The versatile use of bismuth salts in synthesis has clearly been highlighted by the increasing number of publications in the field. The low toxicity of bismuth salts, associated with low cost, make them attractive and practical catalysts to use. Synergistic effects with other Lewis acids have also been recently highlighted.

The discovery that some bismuth salts could be used as Lewis acids in aqueous conditions finally opened the door to designing catalysts and to broadening the concept of hydrocompatible Lewis acids, which has since been applied to various reaction types.

Moreover, the use of bismuth catalysts has definitively contributed to the area of environmentally benign catalysts, known as green catalysts. These are fascinating

developments since such green catalysts are now widely appreciated and new reactions and catalysts are being designed and published on a regular basis.

The current developments allow us to demonstrate that bismuth chemistry truly is an emerging field. Efficient catalytic transformations using bismuth are definitively high potential processes, which encompass asymmetric catalysis using chiral bismuth(III) complexes as one of their most promising challenges to reach. The expanding activity in the field and the resulting constant need for knowledge developments make this volume an essential update in organic synthesis using bismuth.

Both areas of bismuth chemistry – organobismuth derivatives and the use of bismuth salts as catalysts – are covered in this volume, providing an overview of the field from experts in their respective 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 new methods using bismuth derivatives to solve some of your specific problems, but possibly also contribute to meeting some of the remaining challenges of synthetic organic chemistry.

Québec, Winter 2011 Thierry Ollevier

Contents