CONTENTS

Special Topic Issue on Green Chemistry

iii Foreword, J. Miyamoto and T. Norin
v Preface, J. R. Bull

1207 Synthetic Pathways and Processes in Green Chemistry. Introductory Overview
P. Tundo, P. Anastas, D. StC. Black, J. Breen, T. Collins, S. Memoli, J. Miyamoto, M. Polyakoff, and W. Tumas

Symposium-in-Print

1231 Part 1: Introduction and Generic Aspects

1233 Atom efficiency and catalysis in organic synthesis
R. A. Sheldon

1247 Use of the life-cycle assessment (LCA) toolbox for an environmental evaluation of production processes
M. Herrchen and W. Klein

1253 Part 2: Use of Alternative Feedstocks

1255 Fats and oils as oleochemical raw materials
K. Hill

1265 Utilization of TiO$_2$ photocatalysts in green chemistry
M. Anpo

1271 Part 3: Use of Innocuous Reagents

1273 Oxidation reactions in the synthesis of fine and intermediate chemicals using environmentally benign oxidants and the right reactor system
W. F. Hoelderich and F. Kollmer

1289 Cleaner industrial processes using hydrogen peroxide
W. R. Sanderson
Heteropolyacids. Versatile green catalysts usable in a variety of reaction media
*M. Misono, I. Ono, G. Koyano, and A. Aoshima*

Solid acids and their use as environmentally friendly catalysts in organic synthesis
*K. Wilson and J. H. Clark*

Environment-friendly organic synthesis. The photochemical approach
*A. Albini, M. Fagnoni, and M. Mella*

Free radicals in synthesis. Clean reagents affording oxidative or reductive termination
*J. A. Murphy*

**Part 4: Employing Natural Processes**

Biocatalysis. Biological systems for the production of chemicals
*M. Held, A. Schmid, J. B. van Beilen, and B. Witholt*

**Part 5: Use of Alternative Solvents**

Dissolving biomolecules and modifying biomedical implants with supercritical carbon dioxide
*P. B. Webb, P. C. Marr, A. J. Parsons, H. S. Gidda, and S. M. Howdle*

Frontiers in green chemistry utilizing carbon dioxide for polymer synthesis and applications
*J. L. Young and J. M. DeSimone*

Diels–Alder reactions in water
*S. Otto and J. B. F. N. Engberts*

Green Lewis acid catalysis in organic synthesis
*S. Kobayashi and K. Manabe*

**Part 6: Design of Safer Chemicals**

The environmental issue. A challenge for new generation polyolefins
*U. Romano and F. Garbassi*

**Part 7: Developing Alternative Reaction Conditions**

Ionic liquids. Green solvents for the future
*M. J. Earle and K. R. Seddon*

Phase-transfer catalysis. A general green methodology in organic synthesis
*M. Makosza*
Modern chemistry is one of the essential tools in pursuing better medical care, more efficient telecommunications and informatics, and increased agricultural production.

However, certain chemicals produced and used in large quantities might cause various hazards in environmental sectors, owing to their global (trans-boundary) translocation, as well as their intrinsically hazardous properties. To reduce environmental risk of such chemicals, international regulatory measures have already been taken [e.g., in response to the initiatives of the Intergovernmental Forum in Chemical Safety (IFCS)], including legally binding implementations and national capacity building in developing countries. Herein lies the urgent need for promoting worldwide research into green chemistry (sustainable chemistry), in which the invention and application of chemical products and processes are designed to reduce or to eliminate the use and generation of hazardous substances.

Indeed, green chemistry should encompass a variety of disciplines of fundamental chemistry in IUPAC, to encourage new trends of chemical research. Moreover, results of these researches could be effectively applied for solving environmental problems related to the production and use of chemicals and to create a new chemical industry in the future. As such, green chemistry research conforms completely to the mission-oriented activity of IUPAC to meet regulatory requirements for achieving environmentally sound management of chemicals. We sincerely hope that the present special issue highlighting the state of the art and future prospects of green chemistry research will encourage all chemists who intend to serve society through their research efforts.

J. Miyamoto
Past-President of IUPAC Chemistry and the Environment Division

The increasing knowledge in natural sciences and the application of this knowledge are the driving forces for the development and welfare of mankind. Chemistry plays a central role in this development. Chemistry provides the molecular understanding of physical properties of materials and other matters and thus closely interacts with physics. Chemistry also provides the molecular understanding of living systems and is the basis for modern biology and medicine. The development and opportunities of synthetic chemistry have opened a new dimension for tailor-made materials and compounds for specific purposes. The driving forces for developments in chemistry have been very strong, and there is a demand for new and efficient processes and chemicals. Aspects of sustainable and environmentally friendly processes and chemicals have sometimes been lagging behind this demand.

Fortunately, chemistry also provides the tools for a green and sustainable development. Knowledge in this general area has to be integrated into the planning of all research and development in chemistry. There are specific research topics related to the development of green and sustainable processes, which need the input of new technology and novel chemistry. The present Symposium-in-Print provides an overview of recent research and development in the field. We hope that it will stimulate further activities in the field. It is planned as a first step in an IUPAC action on this subject. The IUPAC
Organic and Biomolecular Chemistry Division is grateful to its Subcommittee on Organic Synthesis and particularly Professor Pietro Tundo for initiating and engaging in this action, and to him and Profs. David StC. Black and Sofia Memoli for editing the Symposium-in-Print.

Torbjörn Norin
President of IUPAC Organic and Biomolecular Chemistry Division
The evolving face of contemporary chemistry is characterized by unprecedented societal demand for the goods and services of the chemical industry, tempered by growing awareness that finite resources must be conserved and their exploitation optimized. At the same time, environmental protection has become a global concern, and the chemical industry is increasingly obliged to reexamine conventional methodologies, and to seek ways of developing and applying more efficient and environmentally benign strategies for future sustainable growth. The tandem concepts of discovery and exploitation are obviously as old as the industry itself, but there is new urgency in the quest for solutions that will halt and reverse some of the negative effects of historical development and, at the same time, seize the opportunities offered by the extraordinary advances in chemical sciences during recent years.

The twin challenges of increasing synthetic efficiency in chemical transformations, and minimizing environmentally hostile waste offer irresistible opportunities for new-age ingenuity. It is in this climate that new approaches to these problems have coalesced into a distinctive discipline, which has been variously described and named but has, as its central thrust, the strategic objectives of increased efficiency, sustainability, and, ultimately, societal benefit. These objectives identify closely with the vision of IUPAC, which is eloquently expressed in two of the goals defined in the current strategic plan, namely to contribute to the advancement of research in the chemical sciences throughout the world and to assist chemistry-related industry in its contributions to sustainable development, wealth creation, and the improvement of the quality of life.

A Working Party on Synthetic Pathways and Processes in Green Chemistry was established in 1996, under the auspices of the Commission on Physical Organic Chemistry (Commission III.2) of the IUPAC Organic and Biomolecular Division, with a mandate to promote and disseminate awareness of environmentally compatible synthetic pathways (green chemistry), throughout the academic and industrial scientific research community. In 1999 this group, in close collaboration with the IUPAC Subcommittee on Organic Synthesis, initiated a project to publish a Symposium-in-Print on Green Chemistry, and undertook to compile a collection of expert reviews on aspects of the topic, underpinned by an introductory account of the evolution of the project, its rationale, and its interfaces with complementary initiatives and organisations.

This volume represents the culmination of that undertaking, and the introductory overview, comprising contributions by members of the Working Party, gives a detailed account of the role and interest of IUPAC in promoting this initiative, and sets the scene for the ensuing Symposium-in-Print, with an interpretation of the meaning of the term “green chemistry” and an account of the historical emergence of the concept. This is followed by a synoptic preamble, in which the content and purpose of individual reviews in the Symposium-in-Print are summarized. Although the preamble adopts a sequence of presentation based upon the logic imposed by the title theme of synthetic pathways and processes, the influential role of the Organization for Economic Cooperation and Development (OECD) is recognized by adoption of their recommended delineation of topics for grouping the ensuing reviews. The Symposium-in-Print sets out to capture the current status of the discipline and to project the boundless opportunities and challenges confronting contemporary organic synthesis and its practice in a changing world, increasingly sensitized to the finite bounds of natural resources and the vulnerability of the biosphere. It
offers evidence that current problems are being addressed and can be solved, and engenders expectations that future problems can be anticipated and prevented. Most importantly, the collective expertise and commitment of the contributors is expected to furnish inspirational guidance to practicing scientists and students of chemistry, to participate in shaping a more environmentally benign future, in which the synthetic pathways and processes in chemistry are fully reconciled with societal expectations for ever-improving quality of life.

J. R. Bull
IUPAC Special Topics Editor