The chemistry of
Organomagnesium Compounds
Part 1

Edited by
Zvi Rappoport
The Hebrew University, Jerusalem
and
Ilan Marek
Technion-Israel Institute of Technology, Haifa

2008

John Wiley & Sons, Ltd
An Interscience® Publication
The chemistry of
Organomagnesium Compounds
The Patai Series: The Chemistry of Functional Groups

A series of advanced treatises founded by Professor Saul Patai and under the general editorship of Professor Zvi Rappoport

The Patai Series publishes comprehensive reviews on all aspects of specific functional groups. Each volume contains outstanding surveys on theoretical and computational aspects, NMR, MS, other spectroscopic methods and analytical chemistry, structural aspects, thermochemistry, photochemistry, synthetic approaches and strategies, synthetic uses and applications in chemical and pharmaceutical industries, biological, biochemical and environmental aspects.

To date, 118 volumes have been published in the series.

Recently Published Titles

The chemistry of the Cyclopropyl Group (Volume 2)
The chemistry of the Hydrazo, Azo and Azoxy Groups (Volume 2, 2 parts)
The chemistry of Double-Bonded Functional Groups (Volume 3, 2 parts)
The chemistry of Organophosphorus Compounds (Volume 4)
The chemistry of Halides, Pseudo-Halides and Azides (Volume 2, 2 parts)
The chemistry of the Amino, Nitro and Nitroso Groups (2 volumes, 2 parts)
The chemistry of Dienes and Polynes (2 volumes)
The chemistry of Organic Derivatives of Gold and Silver
The chemistry of Organic Silicon Compounds (2 volumes, 4 parts)
The chemistry of Organic Germanium, Tin and Lead Compounds (Volume 2, 2 parts)
The chemistry of Phenols (2 parts)
The chemistry of Organolithium Compounds (2 volumes, 3 parts)
The chemistry of Cyclobutanes (2 parts)
The chemistry of Peroxides (Volume 2, 2 parts)
The chemistry of Organozinc Compounds (2 parts)
The chemistry of Anilines (2 parts)

Forthcoming Titles

The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids
The Chemistry of Metal Enolates

The Patai Series Online

Starting in 2003 the Patai Series is available in electronic format on Wiley InterScience. All new titles will be published as online books and a growing list of older titles will be added every year. It is the ultimate goal that all titles published in the Patai Series will be available in electronic format.

For more information see under Online Books on:

www.interscience.wiley.com

R – Mg
The chemistry of
Organomagnesium Compounds

Part 1

Edited by
ZVI RAPPOPORT
The Hebrew University, Jerusalem

and
ILAN MAREK
Technion-Israel Institute of Technology, Haifa

2008

John Wiley & Sons, Ltd

An Interscience® Publication
Dedicated to the memory of

Yair Avni
Contributing authors

Jaap Boersma  Chemical Biology & Organic Chemistry, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Katja Brade  Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Butenandtstr., 5-13, D-81377 München, Germany. Fax: +49-89-2180-77680

Gérard Cahiez  Laboratoire de Synthèse Organique Sélective et de Chimie Organométallique (SOSCO), UMR 8123 CNRS-ESCOM-UCP, 5 Mail Gay Lussac, Neuville /Oise, F-95092 Cergy-Pontoise, France. Fax: +3-313-425-7383; e-mail: g.cahiez@escom.fr

Christophe Duplais  Laboratoire de Synthèse Organique Sélective et de Chimie Organométallique (SOSCO), UMR 8123 CNRS-ESCOM-UCP, 5 Mail Gay Lussac, Neuville /Oise, F-95092 Cergy-Pontoise, France. Fax: +3-313-425-7383

Ben L. Feringa  Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands. Fax: +3-150-363-4296; e-mail: B.L.Feringa@rug.nl

Andrey Gavryushin  Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Butenandtstr., 5-13, D-81377 München, Germany. Fax: +49-89-2180-77680

Claude Grison  UMR CNRS-Université de Montpellier 2 5032, ENSCM, 8 rue de l’Ecole Normale, F-34296 Montpellier, France. Fax: +3-346-714-4342; e-mail: cgrison@univ-montp2.fr

Peter J. Heard  School of Science and Technology, North East Wales Institute, Mold Road, Wrexham LL112AW, UK; e-mail: p.heard@newi.ac.uk

Kenneth W. Henderson  Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, University of Notre Dame, Notre Dame, IN 46556, USA. Fax: +1-574-631-6652; e-mail: khenders@nd.edu

Katherine L. Hull  Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, University of Notre Dame, Notre Dame, IN 46556, USA. Fax: +1-574-631-6652
Contributing authors

Torkil Holm
Department of Chemistry, Technical University of Denmark, Building 201, DK-2800, Lyngby, Denmark. Fax: +45-4-593-3968; e-mail: th@kemi.dtu.dk

Kenichiro Itami
Department of Chemistry and Research Center for Materials Science, Nagoya University, Chikusa-ku, Nagoya 464-8602, Japan. Fax: +8-152-788-6098; e-mail: itami@chem.nagoya-u.ac.jp

Johann T. B. H. Jastrzebski
Chemical Biology & Organic Chemistry, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. Fax: +3-130-252-3615; e-mail: j.t.b.h.jastrzebski@uu.nl

Jan S. Jaworski
Faculty of Chemistry, Warsaw University, 02-093 Warszawa, Poland. Fax: +4-822-822-5996; e-mail: jaworski@chem.uw.edu.pl

Gerard van Koten
Chemical Biology & Organic Chemistry, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. Fax: +3-130-252-3615; e-mail: g.vankoten@uu.nl

Paul Knochel
Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Butenandtstr., 5-13, D-81377 München, Germany. Fax: +49-89-2180-77680; e-mail: paul.knochel@cup.uni-muenchen.de

Joel F. Liebman
Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, 1000 Hilltop Circle, Baltimore, Maryland 21250, USA. Fax: +1-410-455-2608; e-mail: jliebman@umbc.edu

Fernando López
Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela, Avda. de las ciencias, s/n, 15782, Santiago de Compostela, Spain; e-mail: qofer@usc.es

Adriaan J. Minnaard
Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands. Fax: ++3-150-363-4296; e-mail: A.J.Minnaard@rug.nl

Richard A. J. O’Hair
School of Chemistry, The University of Melbourne, Victoria 3010, Australia; Bio21, Molecular Science and Biotechnology Institute, The University of Melbourne, Victoria, 3010, Australia; ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Australia. Fax: +6-139-347-5180; e-mail: rohair@unimelb.edu.au

Koichiro Oshima
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo, Kyoto 615-8510, Japan. Fax: +8-175-383-2438; e-mail: oshima@orgrxn.mbox.media.kyoto-u.ac.jp

Mathias O. Senge
School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity College Dublin, Dublin 2, Ireland. Fax: +3-531-896-8536; e-mail: sengem@tcd.ie
Contributing authors

Natalia N. Sergeeva
School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity College Dublin, Dublin 2, Ireland. Fax: +3-531-896-8536

Tsuyoshi Satoh
Department of Chemistry, Faculty of Science, Tokyo University of Science; Ichigayafunagawara-machi 12, Shinjuku-ku, Tokyo 162-0826, Japan.
Fax: 8-135-261-4631; e-mail: tsatoh@rs.kagu.tus.ac.jp

Suzanne W. Slayden
Department of Chemistry, George Mason University, 4400 University Drive, Fairfax, Virginia 22030, USA.
Fax: +1-703-993-1055; e-mail: sslayden@gmu.edu

James Weston
Institut für Organische Chemie und Makromolekulare Chemie, Friedrich-Schiller-Universität, Humboldtstraße 10, D-07743 Jena, Germany.
Fax: +49(0)-36-419-48212; e-mail: c9weje@uni-jena.de

Shinichi Yamabe
Department of Chemistry, Nara University of Education, Takabatake-cho, Nara, 630-8528, Japan.
Fax: +81-742-27-9208; e-mail: yamabes@nara-edu.ac.jp

Shoko Yamazaki
Department of Chemistry, Nara University of Education, Takabatake-cho, Nara, 630–8528, Japan.
Fax: +81-742-27-9289; e-mail: yamazaks@nara-edu.ac.jp

Hideki Yorimitsu
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo, Kyoto 615-8510, Japan.
Fax: +81-75-383-2438; e-mail: yori@orgrxn.mbox.media.kyoto-u.ac.jp

Jun-Ichi Yoshida
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan.
Fax: +81-75-383-2727; e-mail: yoshida@sbchem.kyoto-u.ac.jp

Jacob Zabicky
Department of Chemical Engineering, Ben-Gurion University of the Negev, P. O. Box 653, Beer-Sheva 84105, Israel.
Fax: +9-72-8647-2969; e-mail: zabicky@bgu.ac.il
Foreword

The present book, *The Chemistry of Organomagnesium Compounds*, is a continuation of the sub-group of volumes in ‘The Chemistry of Functional Groups’ series that deals with organometallic derivatives. Closely related to it are the two volumes, *The Chemistry of Organolithium Compounds* (Zvi Rappoport and Ilan Marek, Eds., 2003 and 2005) in three parts and the two parts of *The Chemistry of Organozinc Compounds* (Zvi Rappoport and Ilan Marek, Eds., 2006). Organomagnesium (or Grignard) reagents play a key role in organic chemistry. Although considered as one of the oldest organometallic reagents in synthesis, there have been a complete renaissance of the field in the last decade.

The two parts of the present volume contain 17 chapters written by experts from 11 countries. They include chapters dealing with structural chemistry, thermochemistry and NMR of organomagnesium compounds, formation of organomagnesium compounds in solvent-free environment, photochemistry of magnesium derivatives of porphyrins and phthalocyanines, and electrochemistry, analysis and biochemistry of organomagnesium derivatives. Special chapters are devoted to special families of compounds, such as magnesium enolates, ate-complexes, carbenoids and bonded-complexes with groups 15 and 16 compounds. Processes such as enantioselective copper-catalyzed 1,4-addition of organomagnesium halides, the iron-catalyzed reactions of Grignard reagents, and theoretical aspects of their addition to carbonyl compounds as well as caromagnesiation reactions are covered in separate chapters. Both synthesis and reactivities of organomagnesium compounds are extensively discussed.

Unfortunately, the planned chapter on ‘Theoretical Aspects of Organomagnesium Compounds’ was not delivered. However, some theoretical aspects are covered in other chapters, especially Chapter 9. Another chapter on ‘Mechanisms of Reactions of Organomagnesium Compounds’ was not included after it was found that recent material on the topic was meager as compared with the coverage of the topic in Richey’s book *Grignard Reagents, New Developments*, published in 2000. We gratefully acknowledge the contributions of all the authors of these chapters.

The literature coverage is mostly up to and sometimes including 2007.

We will be grateful to readers who draw our attention to any mistakes in the present volume or to omissions, and to new topics which deserve to be included in a future volume on organomagnesium compounds.

Jerusalem and Haifa

November 2007

Zvi Rappoport

Ilan Marek
The Chemistry of Functional Groups
Preface to the series

The series ‘The Chemistry of Functional Groups’ was originally planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the preparation, properties and reactions of the functional group treated and on the effects which it exerts both in the immediate vicinity of the group in question and in the whole molecule.

A voluntary restriction on the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various ‘Advances’ and ‘Progress’ series and in textbooks (i.e. in books which are usually found in the chemical libraries of most universities and research institutes), should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the topic. Therefore each of the authors is asked not to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced postgraduate level.

It is realized that no plan can be devised for a volume that would give a complete coverage of the field with no overlap between chapters, while at the same time preserving the readability of the text. The Editors set themselves the goal of attaining reasonable coverage with moderate overlap, with a minimum of cross-references between the chapters. In this manner, sufficient freedom is given to the authors to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter deals with the general and theoretical aspects of the group.
(b) Chapters discuss the characterization and characteristics of the functional groups, i.e. qualitative and quantitative methods of determination including chemical and physical methods, MS, UV, IR, NMR, ESR and PES—as well as activating and directive effects exerted by the group, and its basicity, acidity and complex-forming ability.
(c) One or more chapters deal with the formation of the functional group in question, either from other groups already present in the molecule or by introducing the new group directly or indirectly. This is usually followed by a description of the synthetic uses of the group, including its reactions, transformations and rearrangements.
(d) Additional chapters deal with special topics such as electrochemistry, photochemistry, radiation chemistry, thermochemistry, syntheses and uses of isotopically labeled compounds, as well as with biochemistry, pharmacology and toxicology. Whenever applicable, unique chapters relevant only to single functional groups are also included (e.g. ‘Polyethers’, ‘Tetraaminoethylenes’ or ‘Siloxanes’).