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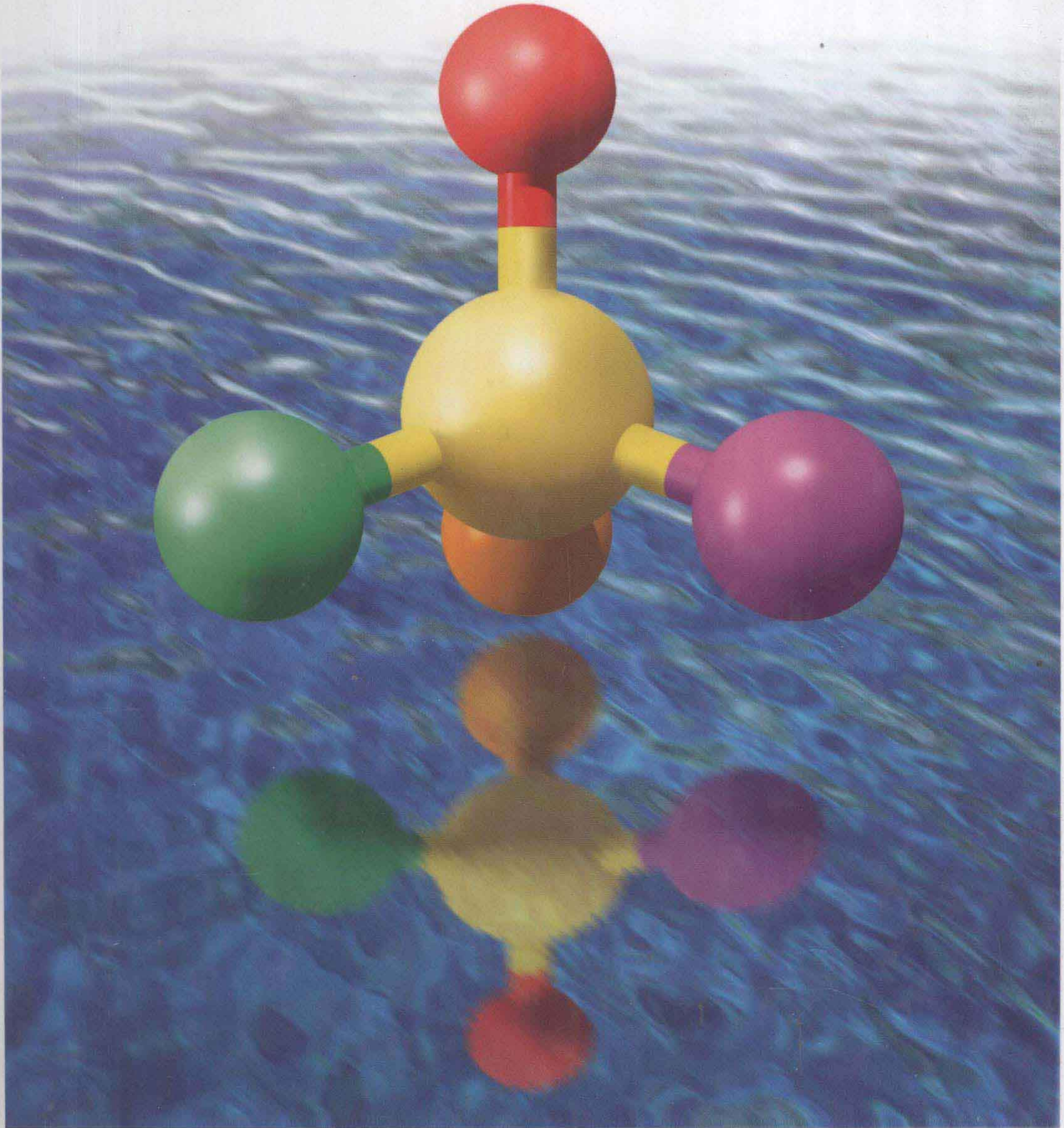
Takeshi Toru and Carsten Bolm

WILEY-VCH

Organosulfur Chemistry in Asymmetric Synthesis



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WILEY-VCH
WILEY-VCH Verlag GmbH & Co. KGaA

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

Bibliographic information published by the Deutsche Nationalbibliothek
Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Printed in the Federal Republic of Germany
Printed on acid-free paper

Cover design Adam Design, Weinheim
Typesetting Asco Typesetters, Hong Kong
Printing Strauss GmbH, Mörlenbach
Bookbinding Litges & Dopf GmbH, Heppenheim

ISBN 978-3-527-31854-4

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Preface

Sulfur has the atomic number 16, and is denoted by the symbol, S. In Nature, sulfur may be found in elemental form, and it is also widely present in gases such as H_2S or SO_2 and inorganic materials such as sulfates and sulfide-based minerals. The key role of sulfur in living systems (such as plants and animals) is exemplified by the importance of the sulfur-containing amino acids cysteine and methionine in polypeptides and proteins. Interestingly, both compounds are chiral and, even more so, they are enantiomerically pure. As they have stereogenic centers at carbon, a number of chiral sulfur-containing pharmaceuticals have also been developed. In having an interest in chirality on sulfur, many organic chemists have realized the synthetic opportunities and today, various chiral – and even achiral – organosulfur reagents have been recognized as highly effective tools to face the challenges of the asymmetric synthesis of complex organic molecules. In this book, *Organosulfur Chemistry in Asymmetric Synthesis*, we summarize various aspects of this fascinating area, the intention being to provide guidelines for new developments in modern organic chemistry. In this respect, the editors appreciate the scientific contributions of all authors, who all impressively demonstrated their high-level expertise in this emerging field of asymmetric synthesis.

The overview begins with a presentation by Kagan, who summarizes asymmetric processes directed towards the synthesis of enantiopure sulfoxides. Related reactions can be applied in preparations of enantiomerically enriched sulfinic acid esters and chiral sulfinamides, as described by Drabowicz *et al.* and Senanayake *et al.*, respectively. Once the stereogenic center at sulfur is established, the respective molecule can serve as a chiral auxiliary, which directs subsequent reactions. Along these lines, asymmetric transformations mediated by sulfinyl groups are presented by García Ruano *et al.* The use of enantiopure sulfoxides as ligands in asymmetric catalysis is summarized by Fernandez and Khiar, while Bulman Page and Buckley report on the chemistry of dithioacetals having stereogenic centers at both carbon and sulfur. If a sulfide is alkylated, sulfonium salts result, and these may be deprotonated by bases to yield sulfonium ylides. The syntheses and applications of chiral reagents of this type are presented by Brière and Metzner. Sulfoximines form the focus of the overview by Bolm and coworkers. Enantiopure derivatives are accessible by a variety of methods, including stereospecific iminations

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ISBN: 978-3-527-31854-4

of sulfoxides, and alternative approaches, as well as the applications of sulfoximines in asymmetric synthesis, are described. In sulfones, the sulfur atom is in its highest oxidation state, and several asymmetric catalyses have utilized that class of organosulfur reagent, as summarized by Carretero and coworkers. Metallations of sulfides give rise to α-sulfenyl carbanions, the properties and chemical behavior of which in asymmetric reactions are presented by Nakamura and Toru. If sulfoxides are deprotonated with strong bases, then α-sulfinyl carbanions result, and their use in stereoselective C–C bond formation is highlighted by Volonterio and Zanda. Gais discusses structural aspects and the asymmetric reactions of α-sulfonyl carbanions. Finally, an insight into the theoretical background of asymmetric reactions with sulfur reagents is provided by Balcells and Maseras.

Once again, the editors wish to express their sincere thanks to all contributors of this book. It has been an exciting enterprise, which began at a high energy level and seldom required any 'human catalysis' for adding essential activation energy. Hopefully, it will lead to a stable (market) product!

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ISBN: 978-3-527-31854-4