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METHODS OF
ORGANIC CHEMISTRY
METHODS OF ORGANIC CHEMISTRY
(HOUBEN-WEYL)

ADDITIONAL AND SUPPLEMENTARY VOLUMES TO THE 4TH EDITION

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Preface

There was a time when stereoselectivity of a reaction was mostly of mechanistic interest and reactions that could result in the formation of stereoisomers were considered a nuisance and had to be avoided at best. However, this situation has changed over the past two decades, during which stereoselective synthesis has grown into a reliable methodology. This development began with the remodelling of readily available chiral compounds from nature. More recently, these “ex-chiral-pool” synthetic strategies have been complemented and, in many cases, surpassed by the powerful techniques of asymmetric synthesis.

Originally, only a few laboratories were concerned with the design of routes to enantiomerically pure compounds. Since the demand for nonracemic chiral drugs and pesticides has enormously increased, methods of asymmetric synthesis are now bound to be applied by almost every practising chemist. However, newcomers to the field soon find themselves confronted with a confusing vocabulary, with no guidance as to the appropriate method to solve their problem, and with lack of well-documented procedures. This situation frequently leads to frustration or at least to unnecessary work.

This called for the present volume set of the HOUBEN-WEYL series Methods of Organic Chemistry. Since the 1950s HOUBEN-WEYL has served the synthetic community by giving comprehensive critical reviews of the existing synthetic methods in a consistent style and with high reliability. The editors, authors and publisher of HOUBEN-WEYL “Stereoselective Synthesis” have worked together to confer this philosophy to the field of asymmetric synthesis. Thus, we hope to supply a treatise which should become the standard reference in the field.

“Stereoselective Synthesis” gives a comprehensive treatment of chemical transformations in which a new stereocenter is created, i.e., all enantio- and those diastereodifferentiating reactions which allow the absolute and relative configuration of a new stereogenic unit to be controlled. Consequently, mechanism-controlled reactions (e.g. $S_N2$ displacements), “ex-chiral-pool” syntheses which do not lead to new stereogenic units, and $E/Z$ selective formation of alkenes are not covered.

Following the general introductory chapters covering principles, nomenclature, separation and analysis, the chapters on individual synthetic methods are organized by the type of bond that is broken or formed. Only starting material and products are considered as a basis for the classification, not the reaction mechanism. In the typical HOUBEN-WEYL style, the scope of the most important methods is illustrated with tables of selected examples. Insight into the practical application of the methods can be obtained from the experimental procedures provided.
The wealth of material forced us to break up the work into five volumes (E21a through f). Access to and properties of the common chiral auxiliaries, solvents, reagents and catalysts which are used in various different reactions is covered comprehensively in Volume E 21e avoiding duplication of information in the individual chapters.

The transition of HOUBEN-WEYL from German to English brought about changes in the layout and in the style of presentation without, however, sacrificing the high standard of quality and reliability that is the hallmark of HOUBEN-WEYL.

Special thanks go to our 101 authors who have spent a great deal of time and effort to achieve the goals we have set. We are also indebted to the editorial staff in Stuttgart, who had to cope with the special challenges of editing and publishing a gigantic amount of complex material.

May 1995

Günter Helmchen
Reinhard W. Hoffmann
Johann Mulzer
Ernst Schumann
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Appendix

Survey of Chiral Auxiliaries, Solvents, Reagents, and Catalysts

R. Herrmann

Introduction

The purpose of this appendix is to survey chiral auxiliaries, solvents, reagents, and catalysts which are often used in stereoselective bond-forming reactions, thus avoiding repetition of details on the synthesis of these compounds in the other sections of Houben-Weyl Volume E21 which discuss specific reaction types. It will not contain every chiral compound ever used in asymmetric synthesis, but will focus on compounds mentioned in this Houben-Weyl volume. Reagents used exclusively for the resolution of racemates are not included, as these are treated in more detail in Section A.2. Enzymes, which can also be considered as chiral catalysts, are also not discussed; they are beyond the scope of this section, which concentrates on chemical techniques.

This survey is structured by functional groups and/or common structures present in the compounds considered. This implies that structural analogy rather than synthetic logic defines the place where a specific compound can be found; there are only a few exceptions to this principle. For example, compounds mimicking the typical reactivity of others are treated together, such as chiral oxaziridines and sultams, which are included in Section 3.4.11., although they do not contain the bicyclo[2.2.1]skeleton which is the general topic of Section 3.4. This section also contains a subsection on ring-enlarged (3.4.9.) and ring-cleaved (3.4.10.) derivatives of camphor, where synthetic logic has been chosen as the ordering principle. In cases of doubt, the reader should use the tabular survey at the end of the section which they expect to contain the compound. Generally, the logic is applied that a compound should appear as early as possible if it can be attributed to more than one section. A few exceptions are made for closely related compounds such as phosphorus and sulfur compounds which are listed in specific sections, as their syntheses are often closely related. Wherever possible, cross-references are made to sections where their precursors are described.

Table 1. Abbreviations Used for Commercial Suppliers

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>Supplier</th>
<th>Address</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Sigma-Aldrich-Chemie</td>
<td>Postfach 1120, D-89555 Steinheim</td>
</tr>
<tr>
<td></td>
<td>GmbH &amp; Co. KG</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Boehringer Ingelheim KG</td>
<td>Chemicals Division, D-55216 Ingelheim</td>
</tr>
<tr>
<td>C</td>
<td>Carl Roth GmbH &amp; Co.</td>
<td>Schoemperlenstr. 1–5, D-76185 Karlsruhe</td>
</tr>
<tr>
<td>D</td>
<td>Degussa AG</td>
<td>GB Industrie- und Feinchemikalien, Postfach 11053, D-60287 Frankfurt</td>
</tr>
<tr>
<td>F</td>
<td>Fluka Chemie AG</td>
<td>Industriestr. 25, CH-9470 Buchs</td>
</tr>
<tr>
<td>J</td>
<td>Acros Chimica</td>
<td>Postfach 23, D-61130 Nidderau</td>
</tr>
<tr>
<td>M</td>
<td>Merck KGaA</td>
<td>D-84271 Darmstadt</td>
</tr>
<tr>
<td>R</td>
<td>Riedel-de-Haën AG</td>
<td>Postfach 100262, D-30918 Seelze</td>
</tr>
<tr>
<td>T</td>
<td>Tokyo Kasei Kogyo Co. Ltd. (TCI)</td>
<td>3-1-13, Nihonbashi-Honcho, Chuo-Ku, Tokyo 103, Japan</td>
</tr>
</tbody>
</table>

for references see p 5765