

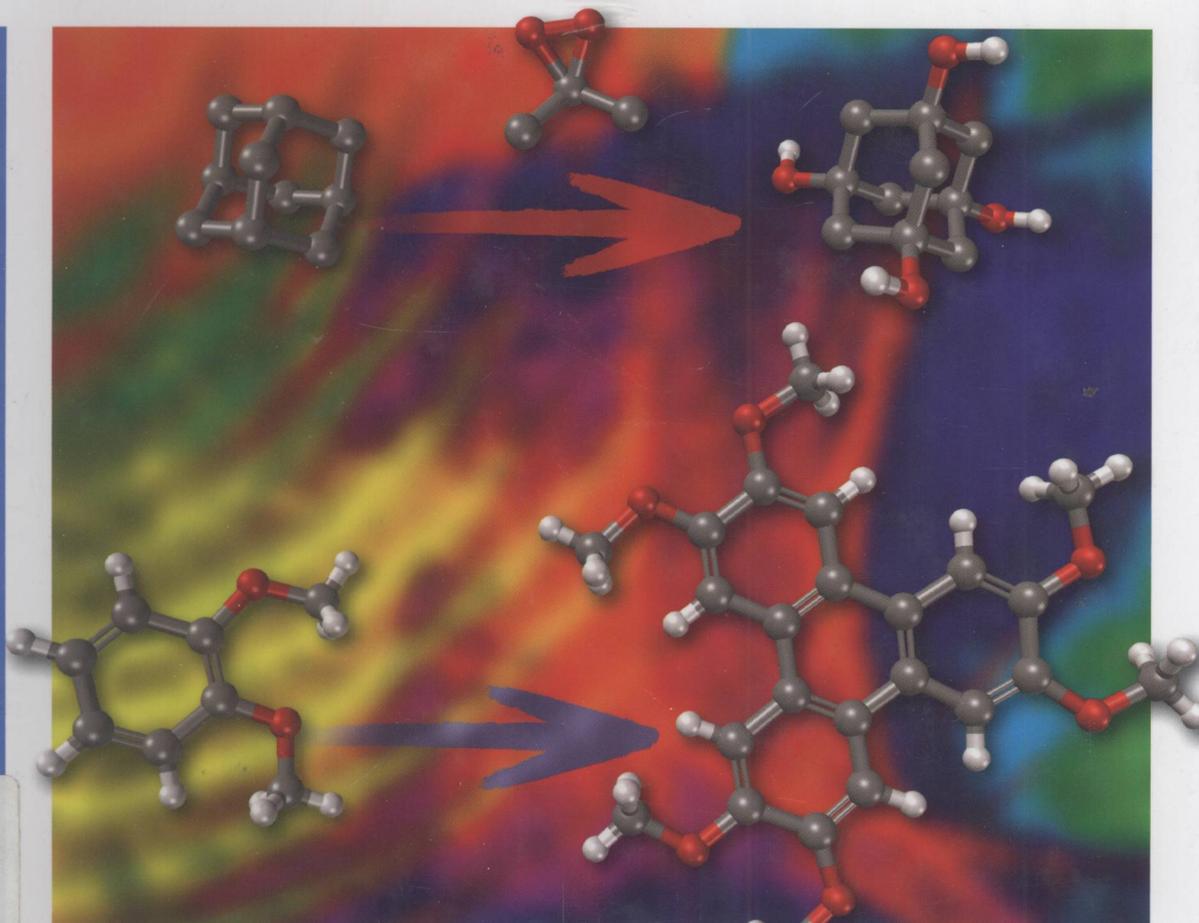
Edited by Gerald Dyker

 WILEY-VCH

Handbook of C–H Transformations

Applications in Organic Synthesis

Volume 2



0621.3-62

H236.4

v.2

Handbook of C–H Transformations

Applications in Organic Synthesis

Volume 2

Edited by

Gerald Dyker



WILEY-
VCH



E200601298

WILEY-VCH Verlag GmbH & Co. KGaA

Editor

Prof. Gerald Dyker

Department of Chemistry
Bochum University
44780 Bochum
Germany

■ All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

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 Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <<http://dnb.ddb.de>>.

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation into other languages).
No part of this book may be reproduced in any form – nor transmitted or translated into machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

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

Typesetting Kühn & Weyh, Satz und Medien, Freiburg
Printing betz-druck GmbH, Darmstadt
Bookbinding J. Schäffer GmbH, Grünstadt

ISBN-13: 978-3-527-31074-6
ISBN-10: 3-527-31074-6

**Handbook of
C–H Transformations**

Volume 2

*Edited by
Gerald Dyker*

Further Titles of Interest

R. Mahrwald (Ed.)

Modern Aldol Reactions

2004, ISBN 3-527-30714-1

A. de Meijere, F. Diederich (Eds.)

Metal-Catalyzed Cross-Coupling Reactions

2 Vols.

2004, ISBN 3-527-30518-1

M. Beller, C. Bolm (Eds.)

Transition Metals for Organic Synthesis

2004, ISBN 3-527-30613-7

K. C. Nicolaou, S. A. Snyder (Eds.)

Classics in Total Synthesis II

2003, ISBN 3-527-30685-4

M. M. Green, H. A. Wittcroft

Organic Chemistry Principles and Industrial Practice

2003, ISBN 3-527-30289-1

C. Reichardt

Solvent and Solvent Effects in Organic Chemistry

2003, ISBN 3-527-30618-8

Preface

The direct transformation of C-H bonds is a fundamental task in organic synthesis, regularly facing reactivity and selectivity problems but simultaneously promising substantial benefits. The intention of this handbook, written by renowned authors who have contributed substantially to this research area, is to present, very concisely within its 66 sections, the whole range of modern methods for C-H-transformation.

Most of the sections follow a general concept and are therefore divided into five parts which cover the most important features of the reaction in focus. "Introduction and Fundamental Examples" gives general information about the reaction, especially the scientific background and related reactions. This part also includes reactions which might be important to understanding although not necessarily of preparative value. "Mechanism" presents current mechanistic considerations, eventually including critical remarks. "Scope and Limitations" concentrates on examples which lead to interesting structures, usually with yields in excess of 50%. "Experimental" presents instructive, comprehensible examples, including work-up procedures. Information about appropriate methods for monitoring the reaction (TLC data or diagnostic NMR spectroscopy) are also given. If a special catalyst is needed, the procedure for its synthesis is also included. "References and Notes", of course, leads to significant publications where further details are available.

You may notice that this preface is as concise as the contents of this handbook. Nevertheless, as editor I should not forget to thank all authors and the team from Wiley-VCH, who made this project possible. The transformation of C-H bonds is certainly one of the most important fields of research in preparative organic chemistry; let us hope this handbook will further motivate research, simultaneously accelerating the change from new developments to established synthetic tools.

Gerald Dyker

Bochum, April 2005

List of Contributors

Editor

Gerald Dyker

Fakultät für Chemie/
AG Organische Chemie
Ruhr-Universität Bochum
Universitätsstr. 150
44780 Bochum
Germany

Authors

Part I

Sigurd Buchholz

Bayer Technology Services GmbH
Process Technology-RPT
Geb. E 41
51368 Leverkusen
Germany

Leslaw Mleczko

Bayer Technology Services GmbH
Process Technology-RPT
Geb. E 41
51368 Leverkusen
Germany

Christian Munnich

Bayer Technology Services GmbH
Process Technology-RPT
Geb. E 41
51368 Leverkusen
Germany

Dalibor Sames

Department of Chemistry
Columbia University
3000 Broadway, MC 3101
New York, NY 10027
USA

Bengü Sezen

Department of Chemistry
Columbia University
3000 Broadway, MC 3101
USA

Part II

Christian Bruneau

UMR 6509 : CNRS – Université de
Rennes
Organometalliques et Catalyse
Campus de Beaulieu, Bât. 10C
Avenue du Général Leclerc
35042 Rennes Cedex
France

Emilio Bustelo Gutiérrez

UMR 6509 : CNRS – Université de
Rennes
Laboratoire de Chimie de Coordination
et Catalyse
Campus de Beaulieu, Bât 10C
Avenue du General Leclerc
35042 Rennes Cedex
France

Erick M. Carreira

Laboratorium für Organische Chemie
ETH-Hoenggerberg HCI H 335
8093 Zürich
Switzerland

Anupama Datta

Institut für Anorganische Chemie
Petersenstr. 18
64287 Darmstadt
Germany

Pierre H. Dixneuf

UMR 6509 : CNRS – Université de
Rennes
Laboratoire de Chimie de Coordination
et Catalyse
Campus de Beaulieu, Bât 10C
Avenue du General Leclerc
35042 Rennes Cedex
France

Beatrice Felber

Schillerstraße 9a
85386 Eching
Germany

Herbert Plenio

Institut für Anorganische Chemie
Petersenstr. 18
64287 Darmstadt
Germany

Tobias Ritter

Laboratorium für Organische Chemie
ETH-Hoenggerberg HCI H 335
8093 Zürich
Switzerland

Peter Siemsen

Schillerstraße 9a
85386 Eching
Germany

Dieter Vogt

Laboratory of Homogeneous Catalysis
Eindhoven University of Technique
STW3.29, P. O. Box 513
5600 MB Eindhoven
The Netherlands

Jos Wilting

Lab. of Homogeneous Catalysis
Eindhoven University of Technique
STW3.29, P. O. Box 513
5600 MB Eindhoven
The Netherlands

Part III

Marco Bandini

Dipartimento di Chimica G. Ciamician
Università di Bologna
Via Selmi 2
40126 Bologna
Italy

Käthe Baumann

Bayer HealthCare AG
Chemical Development –
Process Research
Business Group Pharma
42096 Wuppertal
Germany

Robin B. Bedford

School of Chemistry
University of Exeter
Stocker Road
EX4 4QD Exeter
UK

Robert G. Bergman

Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460
USA

Michael Betham

School of Chemistry
University of Exeter
Stocker Road
EX4 4QD Exeter
UK

Marta Catellani

Dipartimento di Chimica Organica e
Industriale
Parco Area delle Scienze 17/A
43100 Parma
Italy

Catherine S. J. Cazin

School of Chemistry
University of Exeter
Stocker Road
EX4 4QD Exeter
UK

Naoto Chatani

Department of Applied Chemistry
Faculty of Engineering
Osaka University,
Suita
Osaka 565-0871
Japan

Jonathan A. Ellman

Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460
USA

Yuzo Fujiwara

Department of Chemistry
Graduate School of Engineering
Kyushu University
Hakozaki
Fukuoka 812-8581
Japan

Lukas J. Goßßen

Max-Planck-Institut
für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim
Germany

Vladimir V. Grushin

DuPont de Nemours & Co., Inc.
Central Research and Development
Experimental Station, E328/306
Wilmington, DE 19880-0328
USA

T. Brent Gunnoe

Department of Chemistry
North Carolina State University
Raleigh, NC 27695-8204
USA

Lucas Hintermann

Institut für Organische Chemie
der RWTH
Prof.-Pirlet-Str. 1
52074 Aachen
Germany

Tatsuo Ishiyama

Division of Molecular Chemistry
Graduate School of Engineering
Hokkaido University
060-8628 Sapporo
Japan

Chul-Ho Jun

Department of Chemistry
Yonsei University
Seoul 120-749
Korea

Fumitoshi Kakiuchi

Department of Applied Chemistry
Faculty of Engineering
Osaka University
Suita
Osaka 565-0871
Japan

Tsugio Kitamura

Department of Chemistry
Graduate School of Engineering
Kyushu University
Hakozaki
Fukuoka 812-8581
Japan

Shu Kobayashi

Graduate School of Pharmaceutical
Sciences,
University of Tokyo
Hongo, Bunkyo-ku
113-0033 Tokyo
Japan

Richard C. Larock

Department of Chemistry
Iowa State University
Ames, Iowa 50011
USA

Piet W. N. M. van Leeuwen

DSM Pharma Chemicals
Advanced Synthesis, Catalysis &
Development
PO Box 18
6160 MD Geleen
The Netherlands

Alfonso Melloni

Dipartimento di Chimica G. Ciamician
Università di Bologna
Via Selmi 2
40126 Bologna
Italy

Francesco Minisci

Dipto. di Chimica del Politecnico
via Mancinelli 7
20131 Milano
Italy

Daniela Mirk

Organisch-Chemisches Institut
Universität Münster
Corrensstr. 40
48149 Münster
Germany

Masahiro Miura

Dept. of Applied Chemistry
Osaka University
2-1 Yamada-oka
565-0871 Osaka
Japan

Norio Miyaura

Division of Molecular Chemistry
Graduate School of Engineering
Hokkaido University
060-8628 Sapporo
Japan

Elena Motti

Dipartimento di Chimica Organica e Industriale
Parco Area delle Scienze 17/A
43100 Parma
Italy

Shinji Murai

Department of Applied Chemistry
Faculty of Engineering
Osaka University
Suita
Osaka 565-0871
Japan

Young Jun Park

Department of Chemistry
Yonsei University
Seoul 120-749
Korea

Roy A. Periana

Department of Chemistry
North Carolina State University
Raleigh, NC 27695-8204
USA

Fabio Piccinelli

Dipartimento di Chimica G. Ciamician
Università di Bologna
Via Selmi 2
40126 Bologna
Italy

Ombretta Porta

Dipto. di Chimica del Politecnico
via Mancinelli 7
20131 Milano
Italy

Manfred T. Reetz

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim an der Ruhr
Germany

Vsevolod V. Rostovtsev

Research Chemist
DuPont Central Research and Development
Experimental Station
P.O. Box 80328
Wilmington
DE 19880-0328
USA

Tetsuya Satoh

Dept. of Applied Chemistry
Osaka University
2-1 Yamada-oka
565-0871 Osaka
Japan

Victor Snieckus

Department of Chemistry
Queen's University
K7L 3N6 Kingston
Canada

Knut Sommer

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim an der Ruhr
Germany

Johannes G. de Vries

DSM Pharma Chemicals
Advanced Synthesis, Catalysis & Development
PO Box 18
6160 MD Geleen
The Netherlands

Siegfried R. Waldvogel

Organisch-Chemisches Institut
Universität Münster
Corrensstr. 40
48149 Münster
Germany

Sean H. Wiedemann

Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460
USA

Xiaoxia Zhang

Department of Chemistry
Iowa State University
Ames, Iowa 50011
USA

Part IV

Waldemar Adam

221 Guajataca Street
Villas de la Playa
Vega Baja, Puerto Rico 00693
USA

Gan B. Bajracharya

Department of Chemistry
Graduate School of Science
Tohoku University
Sendai, 980-8578
Japan

Gaurav Bhalla

Loker Hyocarbon Research Institute
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661
USA

Carsten Bolm

Institut für Organische Chemie
RWTH Aachen
Professor-Pirlet-Str. 1
52056 Aachen
Germany

Armin Börner

Institut für Organische
Katalyseforschung
Universität Rostock e.V.
Albert-Einstein-Str. 29a
18059 Rostock
Germany

Bruno Bühler

Department of Biochemical and
Chemical Engineering
University of Dortmund
Emil-Figge-Strasse 66
44227 Dortmund
Germany

Jesus Angel Varela Carrete

Departamento de Quimica Organica
Facultade de Quimica
Universidade de Santiago de
Compostela
15782 Santiago de Compostela
Spain

Remle Çelenligil-Çetin

University of Missouri
Department of Chemistry
315A Schrenk Hall
Rolla, MO 65409
USA

Andrea Christiansen

Institut für Organische
Katalyseforschung
Universität Rostock e.V.
Albert-Einstein-Str. 29a
18059 Rostock
Germany

Armando Cordova

Departement of Organic Chemistry
Stockholm University
Arrhenius Laboratory
Arrhenius gatan
106 91 Stockholm
Sweden

Robert H. Crabtree

Department of Chemistry
Yale University
225 Prospect Street
New Haven, CT 06201-8107
USA

Huw M. L. Davies

Department of Chemistry
University at Buffalo
The State University of New York
Buffalo, NY 14260-3000
USA

David C. Ebner

Division of Chemistry and Chemical
Engineering, M/C 164-30
California Institute of Technology
1200 East California Boulevard
Pasadena, CA 91125
USA

Aney A. Fokin

Institut für Organische Chemie
Justus-Liebig-Universität
Heinrich-Buff-Ring 58
35392 Giessen
Germany

Jean-Cécil Frison

Institut für Organische Chemie
RWTH Aachen
Professor-Pirlet-Str. 1
52056 Aachen
Germany

A. Ganesan

Department of Chemistry
University of Southampton
Highfield
SO17 1BJ Southampton
UK

Rajshekhar Ghosh

Rutgers University
Chemistry Department
610 Taylor Road
Piscataway, NJ 08854-8087
USA

Alan S. Goldman

Rutgers University
Chemistry Department
610 Taylor Road
Piscataway, NJ 08854-8087
USA

Yoshitaka Hamashima

Institute of Multidisciplinary Research
For Advanced Materials (IMRAM)
Tohoku University
Katahira
Miyagi 980-8577
Japan

John F. Hartwig

Department of Chemistry
Yale University
225 Prospect Street
New Haven CT 06520-8107
USA

Minsheng He

152 Davey Lab, C28
Department of Chemistry
Penn State University
University Park, PA 16802
USA

C. J. Jones

Loker Hyocarbon Research Institute
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661
USA

Stefan Kaskel

Max-Planck-Institut für
Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim an der Ruhr
Germany

Salma Kiani

University of Missouri
Department of Chemistry
315A Schrenk Hall
Rolla, MO 65409
USA

Joshua D. Lawrence

Dept. of Chemistry
Yale University
P.O. Box 20 81 07
06520-8107 New Haven
USA

Julien Legros

Institut für Organische Chemie
RWTH Aachen
Professor-Pirlet-Str. 1
52056 Aachen
Germany

Aiwen Lei

152 Davey Lab, C28
Department of Chemistry
Penn State University
University Park, PA 16802
USA

Seijiro Matsubara

Kyoto University
Graduate School of Engineering
Department of Material Chemistry
Kyoutodaigaku-Katsura
Nishikyo, Kyoto 615-8510
Japan

Francesco Minisci

Dipto. di Chimica del Politecnico
via Mancinelli 7
20131 Milano
Italy

Oleg Mironov

Loker Hyocarbon Research Institute
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661
USA

Shun-ichi Murahashi

Department of Applied Chemistry
Okayama University of Science
Ridai-cho 1-1, Okayama 700-0005
Japan

Satoshi Nakamura

Loker Hyocarbon Research Institute
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661
USA

Claudio Palomo Nicolau

Departamento de Química Orgánica I
Facultad de Químicas. Universidad del
País Vasco
20018 San Sebastián
Spain

Mikel Oiarbide

Departamento de Química Orgánica I
Facultad de Químicas. Universidad del
País Vasco
20018 San Sebastián
Spain

Patrino Paraskevopoulou

University of Missouri
Department of Chemistry
315A Schrenk Hall
Rolla, MO 65409
USA

Roy A. Periana

Loker Hyocarbon Research Institute
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661
USA

Devender Pinnareddy

University of Missouri
Department of Chemistry
315A Schrenk Hall
Rolla, MO 65409
USA

Ombretta Porta

Dipto. di Chimica del Politecnico
via Mancinelli 7
20131 Milano
Italy

Toshiyasu Sakakura

National Institute of Advanced
Industrial Science & Technology (AIST)
1-1-1 Higashi, Central 5
Tsukuba 305-8565
Japan

Dalibor Sames

Department of Chemistry
Columbia University
3000 Broadway, MC 3101
New York, NY 10027
USA

Robert Schlögl

Fritz-Haber-Institut der Max-Planck-
Gesellschaft
Faradayweg 4-6
14195 Berlin
Germany

Andreas Schmid

Department of Biochemical and
Chemical Engineering
University of Dortmund
Emil-Figge-Strasse 66
44227 Dortmund
Germany

Peter R. Schreiner

Institut für Organische Chemie
Justus-Liebig-Universität
Heinrich-Buff-Ring 58
35392 Giessen
Germany

Barry Snider

Department of Chemistry MS 015
Brandeis University
415 South Street
Waltham, MA 02454-9110
USA

Mikiko Sodeoka

Institute of Multidisciplinary Research
for Advanced Materials (IMRAM)
Tohoku University
Katahira
Miyagi 980-8577
Japan

Pericles Stavropoulos

University of Missouri
Department of Chemistry
315A Schrenk Hall
Rolla, MO 65409
USA

Brian M. Stoltz

Division of Chemistry and Chemical
Engineering, M/C 164-30
California Institute of Technology
1200 East California Boulevard
Pasadena, CA 91125
USA

Hiroshi Suginome

Organic Synthesis Division
Hokkaido University
Kita-ku, 060 Sapporo
Japan

Amy Tapper

University of Missouri
Department of Chemistry
315A Schrenk Hall
Rolla, MO 65409
USA

William J. Tenn III

Loker Hydrocarbon Research Institute
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661
USA

Jesús A. Varela

Dept. de Química Orgánica
Univ. de Santiago de Compostela
15782 Santiago de Compostela
Spain

Pablo Wessig

Institut fuer Chemie
Humboldt-Universität zu Berlin
Brook-Taylor-Str. 2
12489 Berlin
Germany

Yoshinori Yamamoto

Department of Chemistry
Graduate School of Science
Tohoku University
Sendai, 980-8578
Japan

Takehiko Yoshimitsu

Meiji Pharmaceutical University
2-522-1, Noshio, Kiyose
Tokyo 204-8588
Japan

Xumu Zhang

152 Davey Lab, C28
Department of Chemistry
Penn State University
University Park, PA 16802
USA

Cong-Gui Zhao

221 Guajataca Street
Villas de la Playa
Vega Baja, Puerto Rico 00693
USA

Contents

Volume 1

Preface V

List of Contributors XVII

I General 1

1 What is C–H Bond Activation? 3

Bengü Sezen and Dalibor Sames

1.1 Introduction 3

1.2 Activation or “Activation” 3

1.3 The Origin and Historical Context of the “Organometallic Definition” 4

1.4 What Do We Do With Two Definitions? 6

1.5 Conclusions 9

2 C–H Transformation in Industrial Processes 11

Leslaw Mleczko, Sigurd Buchholz, Christian Münnich

2.1 Introduction 11

2.2 Alkane Activation 11

2.3 C–H Transformation at Olefins 17

2.4 Basic Chemicals from Aromatic Hydrocarbons 19

2.5 Fine Chemicals 22

2.5.1 Fine Chemicals by Organometallic Catalysis 23

2.5.2 Metal-free Synthesis of Fine Chemicals 24