

Cambridge University Press
0521445809 - Half a Century of Free Radical Chemistry
Derek H. R. Barton
Frontmatter
[More information](#)

This book presents an expansion of the highly successful lectures given by Professor Barton at the Polytechnical Institute of Milan under the auspices of the Accademia Nazionale dei Lincei.

The book explores the invention of new chemical reactions for use in the synthesis of biologically and economically important compounds. It begins with a mechanistic study of the industrial importance of the pyrolysis of chlorinated alkanes. It continues with a theory on the biosynthesis of phenolate derived alkaloids involving phenolate radical coupling. Included in the book is a description of the work on nitrite photolysis (the Barton Reaction) which involved the invention of new radical chemistry leading to a simple synthesis of the hormone, aldosterone. In two final chapters Dr Shyamal Parekh views Professor Barton's pioneering work from the modern perspective, with a review of recent applications in industry and research.

The book should prove to be an enlightening and exciting review of over fifty years of creative chemical research.

Cambridge University Press
0521445809 - Half a Century of Free Radical Chemistry
Derek H. R. Barton
Frontmatter
[More information](#)

*Half a century of
free radical chemistry*

Cambridge University Press
0521445809 - Half a Century of Free Radical Chemistry
Derek H. R. Barton
Frontmatter
[More information](#)

Lezioni Lincee

Sponsored by *Fondazione IBM Italia*

Editor: Luigi A. Radicati di Brozolo, Scuola Normale Superiore, Pisa

This series of books arises from lectures given under the auspices of the Accademia Nazionale dei Lincei and is sponsored by *Fondazione IBM Italia* .

The lectures, given by international authorities, will range on scientific topics from mathematics and physics through to biology and economics. The books are intended for a broad audience of graduate students and faculty members, and are meant to provide a 'mise au point' for the subject they deal with.

The symbol of the Accademia, the Lynx, is noted for its sharp sightedness; the volumes in the series will be penetrating studies of scientific topics of contemporary interest.

Already published

Chaotic Evolution and Strange Attractors: D. Ruelle

Introduction to Polymer Dynamics: P. de Gennes

The Geometry and Physics of Knots: M. Atiyah

Attractors for Semigroups and Evolution Equations:

O. Ladyzhenskaya

Cambridge University Press
0521445809 - Half a Century of Free Radical Chemistry
Derek H. R. Barton
Frontmatter
[More information](#)

Half a century of free radical chemistry

DEREK H. R. BARTON
in collaboration with
SHYAMAL I. PAREKH

*Department of Chemistry
Texas A & M University, USA*



Cambridge University Press
0521445809 - Half a Century of Free Radical Chemistry
Derek H. R. Barton
Frontmatter
[More information](#)

Published by the Press Syndicate of the University of Cambridge
The Pitt Building, Trumpington Street, Cambridge CB2 1RP
40 West 20th Street, New York, NY 10011-4211, USA
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1993

First published 1993

A catalogue record for this book is available from the British Library

Library of Congress cataloguing in publication data

Barton, Derek, Sir, 1918–

Half a century of free radical chemistry/Derek H. R. Barton in
collaboration with S. I. Parekh.

p. cm. – (Lezioni Lincee)

Includes index.

ISBN 0–521–44005–X

I. Free radical reactions. 2. Organic compounds – Synthesis.

I. Parekh, S. I. (Shyamal I.) II. Title. III. Series.

QD471.B313 1992

547 – dc20 92–24681CIP

ISBN 0 521 44005 X hardback

ISBN 0 521 44580 9 paperback

Transferred to digital printing 2004

Contents

<i>Preface</i>	ix
1 The pyrolysis of chlorinated hydrocarbons	1
2 Phenolate radical coupling in synthesis and biosynthesis; Pummerer's ketone	7
3 Nitrite photolysis (the Barton reaction)	21
4 Radical deoxygenation (the reaction of Barton and McCombie)	34
5 Disciplined radicals and disciplinary radical reactions (Barton decarboxylation) SHYAMAL I. PAREKH in collaboration with DEREK H. R. BARTON	46
6 Some recent synthetic applications of Barton radical methodologies SHYAMAL I. PAREKH	91
<i>Author index</i>	148
<i>Subject index</i>	160

Preface

First, I must express my appreciation for the honour of being invited by the President, Prof. Giorgio Salvini, of the Accademia Nazionale dei Lincei to give the Lezioni Lincee for 1990–1991. The added responsibility of writing a short book summarizing these lessons was also stimulating. In view of the long-standing research interests of my host at the Dipartimento di Chimica of the Politecnico di Milano, Professor Francesco Minisci, a very distinguished radical chemist, I decided to talk about my 50 years of research on the chemistry of free radicals. Some of my audience will surely demand how something that happened in chemistry fifty years ago could have any relevance to the present day. I hope to show that lessons can be learnt from the past about the philosophy of chemical research. Older chemists always seem to be interested in this subject, although many also become interested in the origins of life.

I have always tried to select a problem whose solution would be significant. On the other hand, the problem must be one that could be solved with the means at one's disposal. Frequently, I have chosen problems relevant to the chemistry of natural products.

The first problem that I discuss in this book was the major part of my PhD thesis. The problem, the synthesis of vinyl chloride, was chosen for me by the circumstance of war. It was of national importance. When the problem has been chosen, one has to think about it. The thought process is based on known literature, but the creative process is to imagine the solution to the problems in terms of the unknown. The creative thinking in the first chapter is about the interpretation of what

seemed a baffling problem of experimental observations. The comprehension of the meaning of the observations led to a theory of considerable predictive value.

The second chapter is initiated by thoughts about the problem of the biosynthesis of morphine. Ever since Sir Robert Robinson deduced the correct constitution for morphine in the early 1920s, he speculated about the biosynthesis. Of course, he was right in proposing that morphine was an oxidized and cyclized benzyl isoquinoline alkaloid. However, he and later Schöpf were wrong in assuming that the structure of Pummerer's ketone was correct. Anyone who read Pummerer's paper critically would have seen that it was wrong. Anyone? In fact, the wrong formula was accepted for 30 years before someone (I) saw what the true constitution should be. Then, logic led from the right formula for Pummerer's ketone to right biosynthetic proposals for morphine and many other phenolic alkaloids.

The third chapter concerns the synthesis of aldosterone and its congeners. The problem of synthesis arose because of the scarcity of the hormone and a pressing need to study its biological effects. An elegant solution to the problem required the invention of a new reaction. So the creative thought was in thinking what that might be; and it was.

The fourth chapter concerns a family of radical reactions which were invented to solve the problem of how to remove secondary hydroxyl groups in complicated amino-glycoside antibiotics. This biologically important problem was solved by the invention of a new reaction. It changed carbohydrate chemistry and introduced many chemists to high yielding radical reactions for the first time.

The fifth chapter has been mainly written by Dr Shyamal I. Parekh, who has also been responsible for all the production process in preparing the final manuscript. The general philosophy is again apparent. A new reaction was needed to manipulate the carboxyl group in peptides and in compounds

Cambridge University Press
0521445809 - Half a Century of Free Radical Chemistry
Derek H. R. Barton
Frontmatter
[More information](#)

Preface

xi

of the arachidonic acid cascade, and it was invented for the purpose.

The final chapter, written by Dr Parekh, is a summary of recent applications by other groups of the reactions invented and discussed in Chapters 4 and 5.

I take this occasion to thank Prof. Minisci and his colleagues for their kindness in making my stay in Milano so enjoyable and initiating the project of writing this book.

D. H. R. Barton
Milano, June 17th, 1991