

Organic photochemistry

Cambridge Texts in Chemistry and Biochemistry

GENERAL EDITORS

S. J. Benkovic

Professor of Chemistry Pennsylvania State University

I. Lewis

Professor of Inorganic Chemistry University of Cambridge

K. Schofield

Professor of Organic Chemistry University of Exeter

J. M. Thomas

Professor of Physical Chemistry University of Cambridge

B. A. Thrush

Professor of Physical Chemistry University of Cambridge



Organic photochemistry

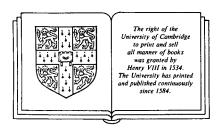
J.M.COXON

University of Canterbury, NZ

B.HALTON

Victoria University of Wellington, NZ

SECOND EDITION



CAMBRIDGE UNIVERSITY PRESS
Cambridge
London New York New Rochelle
Melbourne Sydney



> CAMBRIDGE UNIVERSITY PRESS Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo, Delhi, Dubai, Tokyo, Mexico City

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521189729

© Cambridge University Press 1974, 1986

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 1974 Second edition 1986 First paperback edition 2011

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

Library of Congress Cataloguing in Publication data

Coxon, J. M. (James Morriss), 1941– Organic photochemistry.

(Cambridge texts in chemistry and biochemistry)
Includes bibliographies and index.

1. Photochemistry.
2. Chemistry, Organic.
1. Halton, B. (Brian)
11. Title.
111. Series.

QD708.2.096
1986
547.1'35
85-24251

ISBN 978-0-521-32067-2 Hardback ISBN 978-0-521-18972-9 Paperback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party internet websites referred to in this publication, and does not guarantee that any content on such websites is, or will remain, accurate or appropriate.



CONTENTS

	Preface to the first edition page Preface to the second edition	vii viii
1	Introduction – excitation and the excited state	1
1.1	The interaction of electromagnetic radiation with matter	1
1.2	Excitation	2
1.3	The excited state	9
1.4	The transfer of excitation energy - sensitisation and	
	quenching	13
	References	17
2	Intramolecular reactions of the alkene bond	18
2.1	Geometrical isomerisation	18
2.2	Cyclisation reactions of conjugated alkenes	25
2.3	Rearrangements – 1,4-dienes and the di- π -methane	
	or Zimmerman rearrangement	49
2.4	Rearrangements – 1,5-dienes and the sigmatropic reaction	57
	References	71
3	Intramolecular reactions of the carbonyl group	72
3.1	Saturated acyclic carbonyl compounds	72
3.2	Saturated cyclic carbonyl compounds	86
3.3	βγ-Unsaturated carbonyl compounds	95
3.4	αβ-Unsaturated carbonyl compounds	103
3.5	Cyclohexadienones	110
	References	120
4	Intermolecular cycloaddition reactions	123
4.1	[2+2] cycloaddition reactions of alkenes	123
4.2	[2+2] cycloaddition reactions of carbonyl compounds to	
	alkenes – oxetane formation	139
4.3	[2+2] cycloaddition reactions of $\alpha\beta$ -unsaturated carbonyl	
	compounds	145



vi		Contents	
	4.4	Other cycloadditions	152
	4.5	Cycloaddition of benzene and its derivatives	162
		References	178
	5	Oxidation, reduction, substitution and elimination reactions	180
	5.1	Incorporation of molecular oxygen	180
	5.2	Oxidative coupling	19
	5.3	Reduction reactions	196
	5.4	Substitution reactions	205
	5.5	Molecular rearrangements involving elimination and	
		substitution	216
	5.6	Formation of reactive intermediates by molecular elimination	222
		References	232
		Index	234



PREFACE TO THE FIRST EDITION

The use of light to effect chemical change has been recognised for many years, but it is only recently that sufficient knowledge has been attained to place photochemical reactions in the realm of organic synthesis. The recent application, by Woodward and Hoffmann, of the principle of conservation of orbital symmetry to concerted reactions has made an important contribution to the understanding of many photochemical processes. This book has been written to provide an introduction to the principles and applications of organic photochemistry at a level suitable for senior undergraduate and graduate students in universities and technical institutes. It is not intended to provide an exhaustive survey of the field but rather to provide the student with an up-to-date background of the subject, on which a more detailed study can be based.

The authors gratefully acknowledge many helpful comments from Dr K. Schofield. We also thank Dr B. G. Odell for critically reading the entire manuscript, and Professors M. F. Grundon and J. Vaughan, and Dr M. P. Halton and Mr A. D. Woolhouse for many helpful suggestions. Any errors are the sole responsibility of the authors. Finally we thank our wives.

J. M. C.

New Zealand, 1972

B. H.



PREFACE TO THE SECOND EDITION

In the decade since this book first appeared research involving organic photochemistry has been prolific. In this edition we have attempted to summarise those classes of reaction which best illustrate the types of photochemical behaviour commonly observed for simple organic molecules. Wherever possible reference is given to review-type material for the student or teacher wishing to pursue the topic in more detail; the annual Royal Society of Chemistry specialist periodical report *Photochemistry* provides an excellent route to the primary literature for those who seek such detail.

We anticipate that the use of lasers to investigate photochemically induced reactions will become more common in the next ten years. Thus much more detailed information on known reactions and of specific excited states and their chemistry is likely to become available.

The authors acknowledge many helpful comments from Professor K. Schofield. We also thank Dr P. J. Steel and Dr M. P. Halton for reading the manuscript and for their constructive suggestions. We also appreciate the many helpful and encouraging comments from colleagues around the world who have used the first edition for their courses.

J. M. C. B. H.

New Zealand, 1986