International
Review of Science

Heterocyclic Compounds

Organic Chemistry
Series Two
Volume 4

Consultant Editor
D H Hey FRS
Volume Editor
K Schofield

Butterworths

062
068
V.2/4
7962459
5

International Review of Science

Organic Chemistry
Series Two

Volume 4
Heterocyclic Compounds

Edited by **K. Schofield,**
University of Exeter

华南工学院
外国教材
中心图书室藏书

E7952459

BUTTERWORTHS
LONDON - BOSTON
Sydney - Wellington - Durban - Toronto

THE BUTTERWORTH GROUP

ENGLAND
Butterworth & Co (Publishers) Ltd
London: 88 Kingsway, WC2B 6AB

AUSTRALIA
Butterworths Pty Ltd
Sydney: 586 Pacific Highway, NSW 2067
Melbourne: 343 Little Collins Street, 3000
Brisbane: Commonwealth Bank Building, King George Square, 4000

CANADA
Butterworth & Co (Canada) Ltd
Toronto: 2265 Midland Avenue, Scarborough, Ontario M1P 4S1

NEW ZEALAND
Butterworths of New Zealand Ltd
Wellington: 26–28 Waring Taylor Street, 1

SOUTH AFRICA
Butterworth & Co (South Africa) (Pty) Ltd
Durban: 152–154 Gale Street

USA
Butterworths (Publishers) Inc
Reading: 161 Ash Street, Boston, Mass., 01867

Library of Congress Cataloging in Publication Data

Schofield, Kenneth, 1921–
Heterocyclic compounds.

(Organic chemistry, series two; v. 4) (International review of science)

Includes bibliographical references and index.

1. Heterocyclic compounds. I. Title. II. Series. III. Series: International review of science.

QD245.073 vol. 4 [QD400] 547′.008s [547′.59]
ISBN 0 408 70616 3 75–19465

First Published 1975 and © 1975
BUTTERWORTH & CO (PUBLISHERS) LTD

All rights reserved. No part of this publication may be reproduced or transmitted in any form or by any means, including photocopying and recording, without the written permission of the copyright holder, application for which should be addressed to the publisher. Such written permission must also be obtained before any part of this publication is stored in a retrieval system of any nature.

This book is sold subject to the Standard Conditions of Sale of Net Books and may not be re-sold in the UK below the net price given by the Publishers in their current price list.

Typeset, printed and bound in Great Britain by
REDWOOD BURN LIMITED
Trowbridge & Esher

International Review of Science

Organic Chemistry
Series Two

Consultant Editor
D. H. Hey, F.R.S.

Publisher's Note

The International Review of Science is an important venture in scientific publishing presented by Butterworths. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. Chemistry was taken first as the problems of literature survey are probably more acute in this subject than in any other. Biochemistry and Physiology followed naturally. As a matter of policy, the authorship of the Review of Science is international and distinguished, the subject coverage is extensive, systematic and critical.

The Review has been conceived within a carefully organised editorial framework. The overall plan was drawn up and the volume editors appointed by seven consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence the 500 or so contributions to the Review of Science come from many countries of the world and provide an authoritative account of progress. The publication of Organic Chemistry Series One was completed in 1973 with ten text volumes and one index volume; in accordance with the stated policy of issuing regular reviews to keep the series up to date, volumes of Series Two will be published between the middle of 1975 and early 1976; Series Two of Physical Chemistry will be published at the same time, while Inorganic Chemistry Series Two was published during the first half of 1975. Volume titles are the same as in Series One but the articles themselves either cover recent advances in the same subject or deal with a different aspect of the main theme of the volume. In Series Two an index is incorporated in each volume and there is no separate index volume.

Butterworth & Co. (Publishers) Ltd.

此为试读，需要完整PDF请访问： www.ertongbook.com

ORGANIC CHEMISTRY SERIES TWO

Consultant Editor
D. H. Hey, F.R.S., *formerly of the Department of Chemistry, King's College, University of London*

Volume titles and Editors

1 **STRUCTURE DETERMINATION IN ORGANIC CHEMISTRY**
Professor L. M. Jackman, *Pennsylvania State University*

2 **ALIPHATIC COMPOUNDS**
Professor N. B. Chapman, *University of Hull*

3 **AROMATIC COMPOUNDS**
Professor H. Zollinger, *Eidgenossische Technische Hochschule, Zurich*

4 **HETEROCYCLIC COMPOUNDS**
Professor K. Schofield, *University of Exeter*

5 **ALICYCLIC COMPOUNDS**
Professor D. Ginsburg, *Technion-Israel Institute of Technology, Haifa*

6 **AMINO ACIDS, PEPTIDES AND RELATED COMPOUNDS**
Professor H. N. Rydon, *University of Exeter*

7 **CARBOHYDRATES**
Professor G. O. Aspinall, *York University, Ontario*

8 **STEROIDS**
Dr. W. F. Johns, *G. D. Searle & Co., Chicago*

9 **ALKALOIDS**
Professor K. Wiesner, F.R.S., *University of New Brunswick*

10 **FREE RADICAL REACTIONS**
Professor W. A. Waters, F.R.S., *formerly of the University of Oxford*

INORGANIC CHEMISTRY SERIES TWO

Consultant Editor
H. J. Emeléus, C.B.E., F.R.S.
Department of Chemistry University of Cambridge

Volume titles and Editors

1 **MAIN GROUP ELEMENTS—HYDROGEN AND GROUPS I–III**
Professor M. F. Lappert, *University of Sussex*

2 **MAIN GROUP ELEMENTS—GROUPS IV AND V**
Dr. D. B. Sowerby, *University of Nottingham*

3 **MAIN GROUP ELEMENTS—GROUPS VI AND VII**
Professor V. Gutmann, *Technical University of Vienna*

4 **ORGANOMETALLIC DERIVATIVES OF THE MAIN GROUP ELEMENTS**
Professor B. J. Aylett, *Westfield College, University of London*

5 **TRANSITION METALS—PART 1**
Professor D. W. A. Sharp, *University of Glasgow*

6 **TRANSITION METALS—PART 2**
Dr. M. J. Mays, *University of Cambridge*

7 **LANTHANIDES AND ACTINIDES**
Professor K. W. Bagnall, *University of Manchester*

8 **RADIOCHEMISTRY**
Dr. A. G. Maddock, *University of Cambridge*

9 **REACTION MECHANISMS IN INORGANIC CHEMISTRY**
Professor M. L. Tobe, *University College, University of London*

10 **SOLID STATE CHEMISTRY**
Dr. L. E. J. Roberts, *Atomic Energy Research Establishment, Harwell*

PHYSICAL CHEMISTRY SERIES TWO

Consultant Editor
A. D. Buckingham, F.R.S.,
Department of Chemistry University of Cambridge

Volume titles and Editors

1 **THEORETICAL CHEMISTRY**
Professor A. D. Buckingham, F.R.S., *University of Cambridge* and Professor C. A. Coulson, F.R.S., *University of Oxford*

2 **MOLECULAR STRUCTURE AND PROPERTIES**
Professor A. D. Buckingham, F.R.S., *University of Cambridge*

3 **SPECTROSCOPY**
Dr. D. A. Ramsay, F.R.S.C., *National Research Council of Canada*

4 **MAGNETIC RESONANCE**
Professor C. A. McDowell, F.R.S.C., *University of British Columbia*

5 **MASS SPECTROMETRY**
Professor A. Maccoll, *University College, University of London*

6 **ELECTROCHEMISTRY**
Professor J. O'M Bockris, *The Flinders University of S. Australia*

7 **SURFACE CHEMISTRY AND COLLOIDS**
Professor M. Kerker, *Clarkson College of Technology, New York*

8 **MACROMOLECULAR SCIENCE**
Professor C. E. H. Bawn, C.B.E., F.R.S., *formerly of the University of Liverpool*

9 **CHEMICAL KINETICS**
Professor D. R. Herschbach *Harvard University*

10 **THERMOCHEMISTRY AND THERMODYNAMICS**
Dr. H. A. Skinner, *University of Manchester*

11 **CHEMICAL CRYSTALLOGRAPHY**
Professor J. M. Robertson, C.B.E., F.R.S., *formerly of the University of Glasgow*

12 **ANALYTICAL CHEMISTRY —PART 1**
Professor T. S. West, *Imperial College, University of London*

13 **ANALYTICAL CHEMISTRY —PART 2**
Professor T. S. West, *Imperial College, University of London*

BIOCHEMISTRY SERIES ONE

Consultant Editors
H. L. Kornberg, F.R.S.
Department of Biochemistry University of Leicester and
D. C. Phillips, F.R.S., *Department of Zoology, University of Oxford*

Volume titles and Editors

1 **CHEMISTRY OF MACROMOLECULES**
Professor H. Gutfreund, *University of Bristol*

2 **BIOCHEMISTRY OF CELL WALLS AND MEMBRANES**
Dr. C. F. Fox, *University of California, Los Angeles*

3 **ENERGY TRANSDUCING MECHANISMS**
Professor E. Racker, *Cornell University, New York*

4 **BIOCHEMISTRY OF LIPIDS**
Professor T. W. Goodwin, F.R.S., *University of Liverpool*

5 **BIOCHEMISTRY OF CARBOHYDRATES**
Professor W. J. Whelan, *University of Miami*

6 **BIOCHEMISTRY OF NUCLEIC ACIDS**
Professor K. Burton, F.R.S., *University of Newcastle upon Tyne*

7 **SYNTHESIS OF AMINO ACIDS AND PROTEINS**
Professor H. R. V. Arnstein, *King's College, University of London*

8 **BIOCHEMISTRY OF HORMONES**
Professor H. V. Rickenberg, *National Jewish Hospital & Research Center, Colorado*

9 **BIOCHEMISTRY OF CELL DIFFERENTIATION**
Professor J. Paul, *The Beatson Institute for Cancer Research, Glasgow*

10 **DEFENCE AND RECOGNITION**
Professor R. R. Porter, F.R.S., *University of Oxford*

11 **PLANT BIOCHEMISTRY**
Professor D. H. Northcote, F.R.S., *University of Cambridge*

12 **PHYSIOLOGICAL AND PHARMACOLOGICAL BIOCHEMISTRY**
Dr. H. K. F. Blaschko, F.R.S., *University of Oxford*

PHYSIOLOGY SERIES ONE

Consultant Editors
A. C. Guyton,
Department of Physiology and Biophysics, University of Mississippi Medical Center and
D. F. Horrobin,
Department of Physiology, University of Newcastle upon Tyne

Volume titles and Editors

1 **CARDIOVASCULAR PHYSIOLOGY**
Professor A. C. Guyton and Dr. C. E. Jones, *University of Mississippi Medical Center*

2 **RESPIRATORY PHYSIOLOGY**
Professor J. G. Widdicombe, *St. George's Hospital, London*

3 **NEUROPHYSIOLOGY**
Professor C. C. Hunt, *Washington University School of Medicine, St. Louis*

4 **GASTROINTESTINAL PHYSIOLOGY**
Professor E. D. Jacobson and Dr. L. L. Shanbour, *University of Texas Medical School*

5 **ENDOCRINE PHYSIOLOGY**
Professor S. M. McCann, *University of Texas*

6 **KIDNEY AND URINARY TRACT PHYSIOLOGY**
Professor K. Thurau, *University of Munich*

7 **ENVIRONMENTAL PHYSIOLOGY**
Professor D. Robertshaw, *University of Nairobi*

8 **REPRODUCTIVE PHYSIOLOGY**
Professor R. O. Greep, *Harvard Medical School*

Consultant Editor's Note

The ten volumes in Organic Chemistry in the Second Series of the biennial reviews in the International Review of Science follow logically from those of the First Series. No major omissions have come to light in the overall coverage of the First Series. The titles of the ten volumes therefore remain unchanged but there are three new Volume Editors. The volume on Structure Determination in Organic Chemistry has been taken over by Professor Lloyd M. Jackman of Pennsylvania State University, that on Alicyclic Compounds by Professor D. Ginsburg of Technion-Israel Institute of Technology, and that on Amino Acids, Peptides and Related Compounds by Professor H. N. Rydon of the University of Exeter. The international character of the Series is thus strengthened with four Volume Editors from the United Kingdom, two each from Canada and the U.S.A., and one each from Israel and Switzerland. An even wider pattern is shown for the authors, who now come from some sixteen countries. The reviews in the Second Series are mainly intended to cover work published in the years 1972 and 1973, although relevant results published in 1974 and 1975 are included in some cases, and earlier work is also covered where applicable.

It is my pleasure once again to thank all the Volume Editors for their helpful cooperation in this venture.

London D. H. Hey

Preface

This volume closely resembles its predecessor in the subject matter and organisation of ten of its chapters, which again deal with the major heterocyclic families. In the place of 'Macromolecules Derived from Pyrroles', treated in the first series, this volume contains a chapter on 'The Heterocyclic Chemistry of Phosphorus, Arsenic, Antimony and Bismuth'. This latter is a growing field, and the report offered here covers the period from mid-1971 to the end of 1973, carrying on from a point reached by earlier reviews.

It is a pleasure to be able to thank authors for the promptness with which they completed their difficult tasks.

Exeter

K. Schofield

7962459
5
华南工学院
外国教材
中心图书室藏书

Contents

7962459

华南工学院
外国教材
中心图书室藏书

1

Small and Medium Ring Heterocycles

M. H. PALMER
University of Edinburgh

此为试读,需要完整PDF请访问: www.ertongbook.com

1.1 INTRODUCTION

The present review concentrates attention on conjugated systems since these are likely to show the greatest synthetic utility and have the highest intrinsic interest in terms of potential aromatic character. Thus most partially reduced, and all completely reduced, systems are omitted. There is also a restriction to monocyclic systems in most cases, i.e. benzo derivatives are largely omitted; bridged annulene rings where the primary conjugated system is restricted to the carbocyclic system are also omitted.

The review considers the theoretical background, spectroscopic properties, ring synthesis and interconversions.

The suggestion that the words arene/aromaticity/aromatic be replaced, or more strictly defined[1], has not been adopted here, since even if desirable this would of necessity require that the reviewer was required to re-interpret the original author's decisions without necessarily being in full possession of the facts.

1.2 PHYSICAL ASPECTS

1.2.1 Theoretical

There have been surprisingly few molecular orbital calculations on the medium size hetero-annulenes. In a modification of the Hückel procedure which recognises the energy of the $C_{sp^2}—C_{sp^2}$ bond as well as $C_{sp^2}{=}C_{sp^2}$, Schaad and co-workers[2] have arrived at resonance energies for a large number of molecules related to and including the present systems (Tables 1.1 and 1.2). An assessment of this primitive method based upon results for benzene, naphthalene, pyrrole, furan and thiophene suggests that the results fit with qualitative organic chemical views, and in several cases with Pauling's mesomeric energies. Thus the results are worth considering in more detail. The monocyclic series $(CH{=}CH)_nS$ clearly shows the alternation in properties between aromaticity and antiaromaticity, but it is worth noting that the

Table 1.1 Resonance energies ($k\beta$) for heterocycles[2]

	k		*k*		*k*
Pyrrole	0.233	Furan	0.044	Thiophene	0.193
1*H*-Azepin	−0.291	Oxepin	−0.051	Thiepin	−0.232
1*H*-Azonine	0.139	Oxonin	0.001	Thionin	0.118
Indole	0.466	Benzofuran	0.356	Benzothiophene	0.443
Isoindole	0.292	Isobenzofuran	0.017	Isobenzothiophene	0.247
1*H*-Benzo[*b*]azepin	0.163	Benz[*b*]oxepin	0.287	Benzo[*b*]thiepin	0.196
2*H*-Benzo[*c*]azepin	−0.286	Benz[*c*]oxepin	−0.042	Benzo[*c*]thiepin	−0.233
3*H*-Benzo[*d*]azepin	0.178	Benz[*d*]oxepin	0.316	Benzo[*d*]thiepin	0.209

Table 1.2 Resonance energies ($k\beta$) for thia-annulenes[2]

	k		*k*
Thiirene	−0.457	Thia[13]annulene	0.100
Thiophene	0.193	Thia[15]annulene	−0.088
Thiepin	−0.232	Thia[17]annulene	0.099
Thionin	0.118	Thia[19]annulene	−0.047
Thia[11]annulene	−0.144	Thia[21]annulene	0.107

decline in antiaromaticity as ring size increases is quicker than the decline in aromaticity with ring size increase. The authors note that the procedure produces results which are similar to those of the empirical scheme devised by Dewar *et al.*[3], who obtain resonance energies of −7.5, 0.50 and −6.1 kJ mol^{-1} for 1*H*-azepin, oxepin and thiepin respectively. These values bear a qualitative relationship to those of Schaad, but the value of β is not a fixed constant, but a variable depending upon the ring atoms, whose value is *about* 1.3 eV (~125 kJ mol^{-1}). Thus from both sets of calculations the 8π-electron molecules C_6H_6X (X = NH, O, S) show a strong similarity to the very unstable cycloheptatrienyl anion, with only the extra electronegativity of the oxygen atom pulling the Hückel antibonding top occupied orbitals into the bonding region. It seems unlikely on the basis of other work that non-empirical calculations would find any of the electrons in these species antibonding. Overall, however, although the Hückel rule cannot strictly be applied on symmetry grounds, it does seem that the $(4n + 2)\pi$-electron sequence is more stable than other numbers. This is tantamount to observing that the perturbation induced by the heteroatom is comparatively small. It is interesting to note that the Hückel calculations (Tables 1.1 and 1.2) suggest that 1,4-dithiocin, a $(4n + 2)$ species, should be weakly antiaromatic.

A recent extended Hückel study of the energy differences between pairs within the *exo* and *endo* configurations in the azepin–azanorcaradiene sequence are ca. 0.14–0.18 eV (13.5–17.4 kJ mol^{-1})[4].

1.2.2 Molecular geometry

The conclusions above suggest that the heterocyclic derivatives of tropylidene, the azacyclo-octatetraenes and the heteronines, are unlikely to have much, if any, aromatic character. Some molecular structure determinations support these conclusions. Recent work on azepines[5, 6] support the earlier conclusions[7] that simple 1*H*-azepines are (a) non-planar with boat-type conformations, and (b) possess alternating double and single bonds with lengths appropriate for sp^2–sp^2 atoms. Iron tricarbonyl complexes of azepines show similar conformations, but with the metal bonded to four carbon atoms; the overall structures are thus unsymmetrical and the C—C/C=C lengths in the complexed portion nearly equal in length.

1*H*-1,2-Diazepines[8], a 1,3-oxazepin[9], a 3*H*-azepin[10] and a 4*H*-1,2-diazepin[11] all show boat conformations and it seems unlikely that planar seven-membered rings will emerge and even less likely that the bond alternation in these classical systems will be removed.

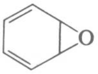
Little is known about the geometry of the larger, *potentially* 10π-electron aromatic systems, but *N*-(*N*,*N*-dimethylcarbamyl)azonine in the crystalline state exists in a boat form[12] not unlike that of cyclo-octatetraenes; however, a clear distinction between the N—H and *N*-substituted azonines has been drawn[13], and it remains to be seen whether the parent system is planar.

1.2.3 N.M.R. Spectra

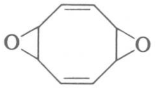
1.2.3.1 The oxygen series of tautomeric equilibria

Here we note generalisations which can be made for the shifts and coupling constants. Normally the ^{1}H n.m.r. spectrum has been used as the primary method of identification, and the Karplus relation between dihedral angle and vicinal coupling constant has been used to decide the conformation. The detailed examples are best obtained from the experimental sections below.

In the epoxides, the bridge protons absorb at 6.7 τ for non-allylic systems and near 6.3 τ for allylic environments. In the six-membered rings (1) the vinyl protons are nearly degenerate near 3.6 τ, while in the corresponding eight-membered rings (2) wider variation ($4.1 \pm 0.2\ \tau$) occurs. In the monocyclic systems there are again wide variations for vinyl hydrogen, with protons adjacent to oxygen at lower field in the eight-membered (3.4, 4.0 τ) than either the seven- (4.3 τ) or nine- (4.1 τ) membered rings. Full analyses of the coupling constants have been given in only a few instances, but the unusual ratio of $J_{5,6}/J_{6,7}$ in 1,4-dioxocin (8.00/9.22) is unexpected in view of the double and single bonds intervening; the explanation offered in terms of the heteroatom proximity is not convincing.



(1)

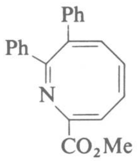


(2)

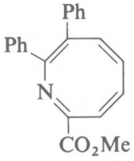
The ^{13}C resonance spectra of a range of molecules of the tropylidene–norcaradiene equilibrium, including oxepins, have been reported. A series of substituent constants were identified, and a correlation between the ^{13}C shift (δ) and the Hückel π-charge density (p) obtained[14]; this has the form $\delta = -216.7\,p + 349.9$ p.p.m., and leads to errors of ca. ± 3 p.p.m. in most cases. Of the other papers where detailed analysis of the n.m.r. spectra have been given, that on the azepines and diazepines systems is notable[15].

1.2.3.2 Azocines

The parent compound azocine rapidly decomposes above $-50\,^{\circ}$C, but the low-temperature ^{1}H n.m.r. spectrum shows non-equivalent α-protons, one of which is a singlet ($\delta_2 = 7.65$), the other a doublet ($\delta_8 = 7.0$) coupled ($J_{7,8} = 8$ Hz) to -H7 ($\delta_7 = 5.15$)[16]. 2-Methoxyazocine gives similar results[17]. A full ABMX analysis of the system (3) $\rightleftharpoons$ (4) yielded the results (δ) A, 6.02; B, 6.19; M, 6.40; X, 6.65; large (vicinal) couplings were[18] $J_{AB} = 11.8$, $J_{AM} = 4.2$ and $J_{BX} = 3.7$ Hz. These clearly show one large rather than two *cis*-olefinic couplings and hence assign the stable structure as (3) rather than (4). It is worth noting that very few coupling constants have been observed in cyclo-octatetraenes (COTs)[19], but that the temperature dependent 2-methoxy-COT yielded values $J_{6,7} = 11$ Hz (*cis*-olefin) and $J_{1,2} = 2.0$ Hz (vicinal HC—CH)[20]. Thus the diminution in $J_{\alpha\beta}$ observed in the pair benzene and pyridine occurs in the eight-membered rings also. The ^{1}H n.m.r. spectrum of 1,2-diaza-COT shows only singlets ($\delta_{4,5,6,7} = 6.08$, $\delta_{3,8} = 6.93$) at room temperature[21].



(3)



(4)

1.2.3.3 Heteronins

The ^{1}H n.m.r. spectra of oxonin, 1*H*-azonin and its *N*-ethoxycarbonyl derivative were reported earlier[13, 22], but attempts have subsequently been made to assess the extent of the ring current[23]. The method defines a term S by $S = \sigma_X - \sigma_{C_6H_{12}}/60$ where σ_X is the difference in chemical shift (60 MHz) between cyclohexane and acetonitrile in solvent X, and the analogous ($\sigma_{C_6H_{12}}$) difference in cyclohexane as solvent. Reference figures are: benzene, $+1.0$; naphthalene, $+1.35$; pyrrole, $+0.90$; furan, $+0.42$; cyclo-octatetraene, -0.19; the present series give 1*H*-azonin, $+1.35$; *N*-methylazonin, $+0.34$; and oxonin, -0.07. These values vary inversely with temperature; the higher value for azonin than for benzene was regarded as acceptable in the light of the naphthalene value, while the difference in values for the azonins was attributed to steric hindrance to planarity in the *N*-methyl case. The difference between furan and oxonin was thought to be enforced planarity in the former and not in the latter.

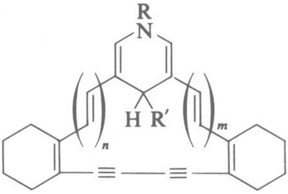
In an alternative approach[24], the ^{1}H n.m.r. spectral shifts of the amines and their anions were compared for pyrrole, azonin and indole. In the five-membered rings, formation of the anion has little effect upon the shifts, but in the azonin system the α-protons are shifted from 2.85 τ (amine) to 1.36 τ (salt), while the β, γ and δ protons are collapsed almost to a singlet. These changes are attributed to a planar 10 π-electron structure for the anion and are reminiscent of the behaviour of the cyclononatetraenyl anion.

In the 4,5-benzazonines, direct comparison of the benzylic shift remote from the nitrogen atom with the corresponding proton in the hydrocarbon

3,4-benzocyclonona-1,3,5,7-tetraene strongly suggests that the pair are non-aromatic in the larger ring[25].

1.2.3.4 Larger heteroannulenes

Some hetero [17]- and [21]-annulenes have been synthesised by stereospecific synthesis using Wittig condensations of pyridine derivatives with ethynylcyclohexenyl aldehydes[26]. These products (5; *n*, *m* = 1 or 2) show appreciable diamagnetic ring currents (diatropism), although these vary with the size of the alkyl substituent (R′); unsymmetrical species (5; $m \neq n$) have been made by similar routes and here the compounds showed the expected paramagnetic ring currents (paratropism)[26]. Related syntheses of the thia[17]-annulenes and their *S*,*S*-dioxides showed these to have weak diatropic and paratropic effects, respectively[27].

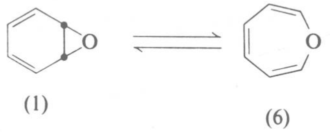


(5) $n = m = 1$
$n = m = 2$
$n = 1, m = 2$

In contrast, the aza- and oxa-[13]annulene derivatives prepared[28] by nitrene or oxygen addition to a cyclo-octatetraene dimer and photolysis show little evidence of temperature dependent spectra in the region +40 to −60 °C, and little evidence of ring currents. These compounds should be π-isoelectronic with [14]annulene and hence aromatic. It has been suggested[28] that they are polyolefinic and atropic in character; for the 1-aza compound the four inner protons absorb at 5.0 and 5.45 τ and the outer protons in the range 3.1–4.3 τ. There seems to be a genuine discrepancy here, and it seems possible that the extra flexibility in the latter series, whose members are completely monocylic, is leading to conformational mobility even at the lower temperatures used.

1.3 SYNTHESIS

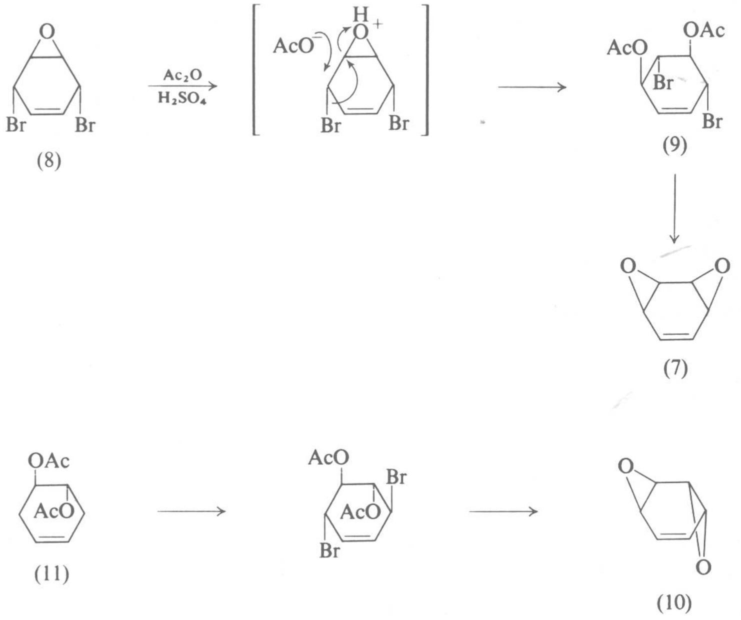
Many of the heterocyclic systems under discussion can exist as monocyclic or bicyclic systems strictly analogous to the cycloheptatriene–norcaradiene equilibrium. In these thermally allowed systems it is clear that synthetic routes directed to either one of the pair will lead to the mixture at some appropriate temperature. In the immediate vinyl homologues, the cyclononatetraene–bicyclo[6,1,0] system, equilibrium is achieved by a photochemically allowed process, but the same synthetic approach to the seven-membered system is normally used. Thus it is convenient to consider



approaches to these two sets of starting materials simultaneously, but to deal with the equilibria separately. A further complicating phenomenon is that other thermally allowed processes also occur in the larger systems; these are also treated separately. The corresponding hydrocarbon norcaradiene–cycloheptatriene equilibria have been reviewed[29], and it is important in Section 1.3 to note that the presence of the heteroatom does not *fundamentally* change the position compared with that for the hydrocarbons. Thus frequently it is necessary to make comparisons with the hydrocarbon chemistry.

1.3.1 Synthesis of hetero analogues of the bicyclo[*n*,1,0]alkane types

syn-Benzene dioxide (7) is formed[30] by the acetolysis of the *trans* epoxy dibromide (8), a neighbouring group participation leading to the intermediate (9) which yields (7). The *anti*-dioxide (10) was prepared[30] either in a



similar reaction from the *trans*-1,4-dibromo compound or better from the *trans*-diacetate (11) by allylic bromination.

此为试读，需要完整PDF请访问：www.ertongbook.com