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Aromatic and Heteroaromatic Chemistry

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Aromatic and Heteroaromatic Chemistry

Volume 7

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Aromatic and Heteroaromatic Chemistry

Volume 7

Introduction

In this seventh Report the literature coverage is based essentially on volumes 87 and 88 of *Chemical Abstracts*. We have arranged the chapters as in Volume 6 except that the topics treated in the last two sections of the previous volume, namely 'Naturally Occurring Aromatic Oxygen-ring Compounds' and 'Other Naturally Occurring Aromatic Compounds' are now omitted. This, it was felt, was justified in view of the liberal treatment and accessibility of current reviews on natural products elsewhere.

We have again asked our contributors to comment on highlights in their subject. The synthesis of a stable tetrahedrane, one of the most attractive recent challenges, has now been achieved by a group of German workers (Chapter 1, ref. 40). Evidence for the existence of other elusive molecules, namely thiiren (Chapter 1, ref. 32), seleniren (Chapter 2, ref. 391), and azete (Chapter 1, ref. 80), the latter during the photolysis of an oxazinone, has been obtained. The interpretation of new i.r. data for cyclobutadiene as a non-square structure removes a troubling inconsistency between experiment and theory (Chapter 1, ref. 39). Five-membered heterocyclic systems continue to provide starting materials for fascinating chemistry: irradiation of tetrakis(trifluoromethyl)thiophen gives a Dewar-thiophen (Chapter 2, ref. 115) while that of a tetrazoline at low temperature provides the first example of a nitrogen analogue of trimethylenemethane (Chapter 2, ref. 419). 2-Chloro-3-ethylbenzoxazolium salts proved remarkably versatile reagents for the synthesis of ketones, isocyanates, isocyanides, and alkyl chlorides (Chapter 2, refs. 319—322). Among six-membered heterocycles, pyridine is still a favourite target for studying basic reactions. Thus, the first examples of direct alkylation, acylation, and regioselective metallation at the 3-position have been reported (Chapter 4, refs. 29, 30, and 33, respectively). A new non-cyclic cryptate derived from 8-hydroxyquinoline has been prepared which, in some respects, is superior to 18-crown-6 and is claimed to have the greatest complexation ability observed so far for neutral ligands (Chapter 4, ref. 93). Phase-transfer catalysts continue to provide useful synthetic aids (Chapter 4, refs. 91, 105, and 111).

There is an interesting claim pertaining to seven-membered rings (Chapter 5, ref. 43), namely that azatropolones have been prepared. If substantiated, this would represent a significant contribution to the heterocyclic field.

The first example of a medium-sized cyclic cumulene (Chapter 6, ref. 35) and of a bridged [10] annulene analogue of azulene (Chapter 6, ref. 57) are noted amongst a wealth of new annulenes.

Noteworthy points in the chapter on Electrophilic Substitution are the surprising findings, based on n.m.r. parameters of a model system, that the polar inductive effect of alkyl groups attached to sp^2-carbon is zero (ref. 12). The correlation of the *ortho*-directing effect in the metallation of aromatics (refs. 76—79) and a detailed study of the acylation of the pyrrole anion rationalizing the results on the HSAB principle (refs. 265, 266) are worthy of mention.

Noteable features described in the chapter on porphyrins include (i) the synthesis of porphyrin-*a* (ref. 22), (ii) increasing interest in synthesizing models for haemoglobin (ref. 31), and (iii) the biosynthetic work in the haem and vitamin B_{12} fields (Section 6).

We thank all our present Reporters for delivering and promptly dealing with their chapter within the required time, and our previous reviewers for their help. As always, the professional advice and invaluable assistance by the Editorial Staff of The Chemical Society is much appreciated by us.

H. SUSCHITZKY & O. METH-COHN

Contents

Chapter 1 Three- and Four-membered Ring Systems 1
By R. C. Storr

1 Three-membered Carbocyclic Systems 1

2 Three-membered Heterocyclic Systems 4

3 Four-membered Carbocyclic Systems 6

4 Fused Four-membered Carbocyclic Systems 9

5 Four-membered Heterocyclic Systems 11

Chapter 2 Five-membered Ring Systems 13
By G. V. Boyd

1 Introduction 13

2 Carbocyclic Compounds 13
Cyclopentadiene Radicals, Anions, and Ylides 13
Fulvenes 15
Cyclopentadienones 17
Pentalenes 19

3 Systems with One Heteroatom, and their Benzo-analogues 20
General 20
Furans and Benzofurans 23
  Formation 23
  Reactions 25
Thiophens and Benzothiophens 31
  General 31
  Formation 31
  Reactions 33
Selenophens 38
Tellurophen 39
Pyrroles 39
  Formation 39
  Reactions 40

Indoles 41
  Formation 41
  Reactions 44

4 Systems containing Two Identical Heteroatoms 46
Compounds containing Two Sulphur or Selenium Atoms in a Five-membered Ring 46
  Monocyclic Compounds and their Benzo-analogues 46
  Tetrathiafulvalenes and Selenium Analogues 49
Pyrazoles 51
  Formation 51
  Reactions 53
Indazoles 55
Imidazoles 56
Benzimidazoles 58

5 Systems containing Two Different Heteroatoms 60
General 60
Isoxazoles 60
Benzisoxazoles 62
Oxazoles 63
Benzoxazoles 64
Isothiazoles 64
Thiazoles 66
Benzothiazoles 67

6 Systems containing Three Heteroatoms 68
Triazoles and Benzotriazoles 68
  1,2,3-Triazoles 68
  1,2,4-Triazoles 70
Oxadiazoles 71
  1,2,4-Oxadiazoles 71
  1,2,5-Oxadiazoles 72
  1,3,4-Oxadiazoles 73
Thiadiazoles 73
  1,2,3-Thiadiazoles 73
  1,2,4-Thiadiazoles 75
  1,2,5-Thiadiazoles 76
  1,3,4-Thiadiazoles 76
Selenadiazoles 76
Dithiazoles 77

7 Systems containing Four Heteroatoms 77
Tetrazoles 77
Miscellaneous Ring Systems 79

8 Compounds containing Two Fused Five-membered Rings 80
Thienothiophens, Thienoselenophens, and Related Systems 80
Nitrogen Systems 81

Mixed Systems 82
Hypervalent Sulphur Compounds 85

9 Meso-ionic Compounds 87

Chapter 3 Six-membered Homocyclic Compounds 91
By A. W. Somerville

1 Introduction 91

2 Monocyclic Compounds 91
Benzene and its Alkylated Derivatives 91
Ethers 93
Alcohols and Phenols 95
Aldehydes, Ketones, and Quinones 98
Carboxylic Acids and Derivatives 102
Nitro- and Nitroso-derivatives and Hydroxylamines 104
Amines and Related Compounds 108
Azo- and Diazo-compounds, Hydrazines, Azides, and Related Compounds 113
Sulphur and Selenium Compounds 115
Halogeno-compounds 118

3 Polycyclic Compounds 120
Non-fused Systems 120
  Bi- and Ter-phenyls and Related Systems 120
Fused Systems 123
  Naphthalene and Derivatives 123
  Anthracene and Related Compounds 129
  Phenanthrene and Derivatives 133
  Polycyclic Systems 136
  Helicenes 139
  Cyclophanes 140

Chapter 4 Six-membered Heterocyclic Systems 145
By R. K. Smalley

1 Systems containing One Heteroatom, and their Benzo-derivatives 145
Pyridines 145
  Synthesis 145
  Reactions 149
Quinolines and Isoquinolines 164
Acridines, Phenanthridines, and Other Systems with One Nitrogen Atom 171
Pyrans and Pyrones 172
Coumarins, Chromones, Xanthones, and their Thio-analogues 175
Miscellaneous Systems 180

2 Systems containing Two Heteroatoms, and their Benzo-derivatives 181
Diazines 181
  Pyridazines, Cinnolines, and Phthalazines 181
  Pyrimidines and Quinazolines 185
  Pyrazines, Quinoxalines, and Phenazines 190
Purines, Pteridines, and Related Systems 193
Other Systems with Two Nitrogen Atoms 204
Oxazines, Thiazines, and their Benzo-derivatives 206

3 Systems containing Three and Four Heteroatoms 211
Triazines 211
Oxa- and Thia-diazines 214
Other Systems 216

Chapter 5 Seven-membered Ring Systems 218
By G. R. Proctor

1 Tropones 218

2 Tropolones 219

3 Tropylium Salts and Tropilidenes 219

4 Azulenes 222

5 Azepines and Benzazepines 222

6 Diazepines and Benzodiazepines 223

7 Miscellaneous 224

Chapter 6 Medium-sized Rings and Macrocycles 227
By O. Meth-Cohn

1 Reviews 227

2 General Topics 227

3 Eight-membered Systems 228
Homocyclic Systems 228
Heterocyclic Systems 234

4 Nine-membered Systems 235

5 Ten-membered Systems 235

6 Twelve-, Thirteen-, and Fourteen-membered Systems 237

7 Fifteen-, Sixteen-, and Seventeen-membered Systems 238

8 Eighteen-membered and Larger Systems 239

Chapter 7 Electrophilic Substitution 241
By D. J. Chadwick

1 Introduction 241
Theoretical Considerations 241

2 Reactions with Electrophilic Hydrogen 243
Exchange Reactions 243
Heteroaromatic Tautomerism 246

3 Metallation 248
Lithium and Magnesium Substitutions 248
Mercury Substitution 250
Other Metal Substitutions 250

4 Reactions with Electrophilic Carbon and Silicon 252
Alkylation 252
  Gas-phase Alkylation 252
  Alkylation with Alkenes 252
  Alkylation with Alkyl Halides 254
  Other Alkylations 256
  Heteroatom Alkylation 258
Acylation 260
Silicon Substitutions 265

5 Reactions with Electrophilic Nitrogen and Phosphorus 266
Nitration 266
Nitrosation 273
Amination 273
Diazo-coupling 274
Phosphorus Substitutions 274

6 Reactions with Electrophilic Oxygen and Sulphur 274
Oxygen Substitutions 274
Sulphur Substitutions 275

7 Halogenation 278
Fluorination 278
Chlorination 278
Bromination 280
Iodination 282

8 Miscellaneous Substitutions 282

Chapter 8 Nucleophilic Substitution Reactions 287
By G. M. Brooke

1 Introduction 287

2 Aromatic Systems 287
Substituted Benzenes 287
Fused Aromatic Systems 293

3 Heteroaromatic Systems 294
π-Deficient Heteroaromatic Systems 294
π-Excessive Heteroaromatic Systems 295
Fused Heteroaromatic Compounds 296

4 Meisenheimer and Related Compounds 299
Meisenheimer Complexes from Aromatic Systems 299
Meisenheimer Complexes from Heteroaromatic and Fused Ring Systems 302

5 Substitution in Polyhalogeno-compounds 303
Aromatic Polyhalogeno-compounds 303
Heteroaromatic Polyhalogeno-compounds 305

6 Other Reactions 305

Chapter 9 Aromatic Substitution by Free Radicals, Carbenes, and Nitrenes 307
By R. S. Atkinson

1 By Free Radicals 307

2 By Carbenes 311

3 By Nitrenes 314

Chapter 10 Porphyrins and Related Compounds 319
By A. H. Jackson

1 Introduction 319

2 Reviews 319

3 Porphyrins 320
Synthesis 320
Reactions and Properties 327
Biosynthesis 328

4 Metalloporphyrins 332
Synthesis 332
Properties and Reactions 333

5 Chlorophylls and Chlorins 334
Structure and Synthesis 334
Properties and Reactions 335
Biosynthesis 336

7 Vitamin B_{12}, Corrins, and Corroles 336
Structure and Synthesis 336
Properties and Reactions 338
Biosynthesis 338

7 Prodigiosins 339

8 Porphyrin Analogues 340

9 Bile Pigments 341
Structure and Synthesis 341
Properties and Reactions 342

Author Index 345

1

Three- and Four-membered Ring Systems

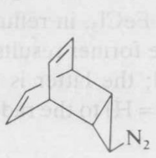
BY R. C. STORR

1 Three-membered Carbocyclic Systems

Calculations of the potential surfaces of the planar cyclopropenyl radical[1,2] and anion[1] indicate that both are subject to Jahn–Teller distortions such that the lowest energy configuration of the radical has one short and two long bonds whereas that of the anion has two short and one long bond. For the carbene (1), INDO calculations reveal a large singlet–triplet separation, the singlet state being stabilised by 2π aromatic character of the ring.[3]

Symmetry-allowed extrusion of the cyclopropenyl cation is not observed on loss of nitrogen from (2). Instead the ether (3) is formed in methanol, possibly *via* the pyramidally bridged cation (4).[4]

(1)



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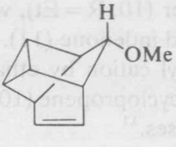

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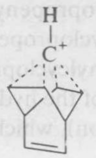
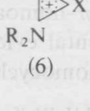


(4)

Yoshida and his co-workers have continued to contribute greatly to the field of cyclopropenium ion chemistry. In addition to describing a large number of cyclopropenium ions, cyclopropen-ones, and -thiones in the patent literature[5] they have produced the first triafulvalene dication (5).[6] This was obtained by treatment of (6; X = H) with butyl-lithium and then allowing the resulting carbenoid (6; X = Li) to react with (6; X = Cl). The transformation illustrates

(5)



(6)

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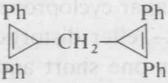
[1] E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, 1977, **67**, 2191.
[2] D. Poppinger, L. Radom, and M. A. Vincent, *Chem. Phys.*, 1977, **23**, 437.
[3] C.-K. Lee and W.-K. Li, *J. Mol. Structure*, 1977, **38**, 253.
[4] R. M. Magid and G. W. Whitehead, *Tetrahedron Letters*, 1977, 1951; see also R. M. Coates and E. R. Fretz, *ibid.*, p. 1955.
[5] Z. Yoshida, *Chem. Abs.*, 1976, **87**, 102 020, 134 027; 1978, **88**, 74 104, 74 107, 74 114, 104 762.
[6] Z. Yoshida, H. Konishi, S. Sawada, and H. Ogoshi, *J.C.S. Chem. Comm.*, 1977, 850.

the use of intermediates such as (6; X = Li) to effect formal electrophilic substitution in the cyclopropenium ion system.[7] The related (6; X = MgBr) produced from the iodocyclopropenium salt (6; X = I) and PhMgBr behaves as a typical Grignard reagent with electrophiles. In contrast to the iodo-cation (6; X = I), the chloro-cation (6; X = Cl) gives the aryldiamino-cyclopropenium cation (6; X = Ph) with PhMgBr.[8]

Hydride abstraction from (7) with trityl perchlorate does not give the dication (8), but rather the monocation (9) resulting from deprotonation of (8). ^{13}C n.m.r. spectroscopy reveals that the central carbon possesses a considerable amount of electron density, indicating that the dipolar form (9a) makes a significant contribution.[9] There is evidence that formation of dicyclopropene from cyclopropenyl cations under conditions of two-electron reduction proceeds through coupling of cyclopropenyl radicals produced by electron transfer from anion to cation.[10]



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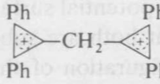

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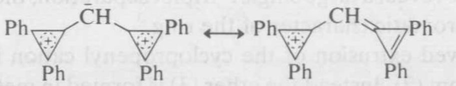
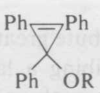


(9a) (9b)

The cyclopropenyl ether (10; R = Et), with $FeCl_3$, in refluxing ethanol, gives triphenylcyclopropene and indenone (11). The former results from reduction of the triphenylcyclopropenyl cation by ethanol; the latter is thought to involve oxidation of the hydroxy-cyclopropene (10; R = H) to the radical (12) (or further to the cation), which cyclises.[11]



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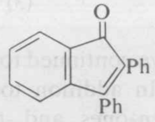

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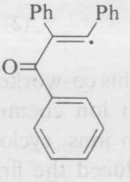


(12)

The cation (13), prepared from 11-methyl-11-bromotricyclo[4.4.1.0^{1,6}]-undecane in SbF_5–SO_2ClF at −120 °C, is neither a symmetrical cyclopropyl cation nor an allylic cation, but is best considered as a bent cyclopropyl cation showing significant 2π-homoaromatic nature.[12] An excellent review of the concept and experimental evidence for homoaromaticity includes sections on mono-, bis-, and tris-homocyclopropenium cations.[13]

---

[7] R. Weiss, C. Priesner, and H. Wolf, *Angew. Chem. Internat. Edn.*, 1978, **17**, 446.

[8] Z. Yoshida, H. Konishi, Y. Miura, and H. Ogoshi, *Tetrahedron Letters*, 1977, 4319.

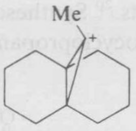
[9] K. Komatsu, K. Matsumoto, and K. Okamoto, *J.C.S. Chem. Comm.*, 1977, 232.

[10] R. W. Johnson, T. Widlanski, and R. Breslow, *Tetrahedron Letters*, 1976, 4685.

[11] A. S. Monahan, J. D. Frielich, J. J. Fong, and D. Kronenthal, *J. Org. Chem.*, 1978, **43**, 232.

[12] G. A. Olah, G. Liang, D. B. Ledlie, and M. G. Costopoulos, *J. Amer. Chem. Soc.*, 1977, **99**, 4196.

[13] L. A. Paquette, *Angew. Chem. Internat. Edn.*, 1978, **17**, 106.



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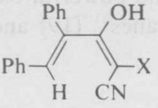
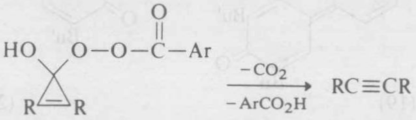


(14) X = CN or CO_2Et

Full details of the preparation of cyclopropenone have appeared in *Organic Syntheses.*[14] Under basic conditions, diphenylcyclopropenone reacts with malononitrile and ethyl cyanoformate at the carbonyl group to give the butadienes (14).[15] The key step in the oxidation of cyclopropenones (15) by peracid

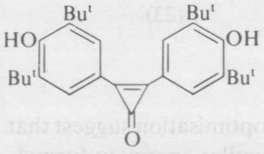


(15)

appears to be formation of the acetylene from attack by peracid at the carbonyl group, as shown, rather than formation of an oxabicyclobutanone. The acetylene then undergoes further oxidation.[16] CNDO/2 calculations have been reported for a number of cyclopropenones and cyclopropenethiones.[17] The first e.s.r. spectrum of a cyclopropenone radical anion has been observed for diphenylcyclopropenone. The anion is relatively unstable and undergoes loss of CO to give the radical anion of diphenylacetylene.[18] No spectra were obtainable for dialkylcyclopropenones.

A novel activation of diphenylcyclopropenone involving ring cleavage of the C–C double bond has been observed with $Pt_3(Me_3CNC)_6$.[19]

The reaction of cyclopropenones (16) with compounds containing active methylene groups leads to methylenecyclopropenes (17), which on oxidation give a new family of alkylidenequinocyclopropanes (18). These are highly coloured,



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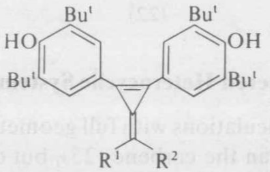

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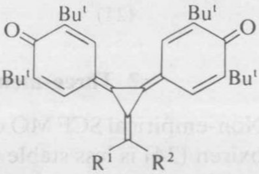
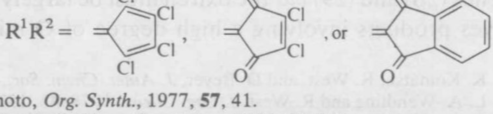


(18)

$R^1 = R^2 = CN$ or COMe; $R^1 = CN$, $R^2 = CO_2Et$



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[14] R. Breslow, J. Pecararo, and T. Sugimoto, *Org. Synth.*, 1977, **57**, 41.

[15] I. Agranat, G. V. Boyd, and M. A. Wirt, *Bull. Chem. Soc. Japan*, 1977, **50**, 765.

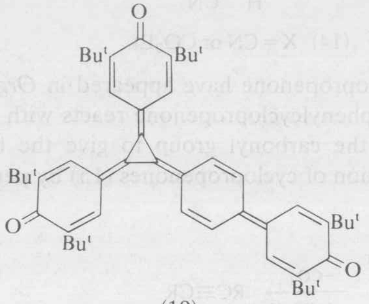
[16] J. K. Crandall and W. W. Conover, *J. Org. Chem.* 1978, **43**, 1323.

[17] N. J. Fitzpatrick and M. O. Fanning, *J. Mol. Structure*, 1977, **42**, 261.

[18] P. Fürderer, F. Gerson, and A. Krebs, *Helv. Chim. Acta*, 1977, **60**, 1226.

[19] W. E. Carroll, M. Green, J. A. K. Howard, M. Pfeffer, and F. G. A. Stone, *Angew. Chem. Internat. Edn.*, 1977, **16**, 793.

strongly dichroic, and powerful oxidising agents.[20] Syntheses and properties of the quinocyclopropanes[21] (19) and quinoiminocyclopropanes[22] (20) have also been reported.



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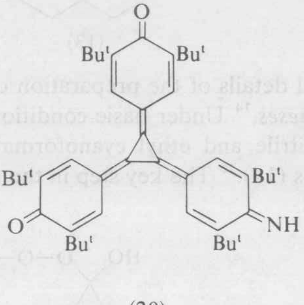
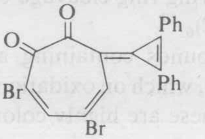


(20)

The *o*-tropoquinonecyclopropenide (21) is somewhat less stable than the previously prepared *para*-isomer. Spectral data indicate that it is nearly planar; however, the mono- and di-cations appear to be non-planar, owing to steric hindrance and electronic repulsion.[23] In agreement with previous *X*-ray studies, ^{35}Cl quadrupole resonance data for the cyclopentadiene cyclopropenide (22) indicate that the cyclopentadiene ring is largely dienoid.[24] The ^{13}C n.m.r. spectra of the highly stabilised thiocarbonyl ylides (23) suggest that they possess appreciable C=S character, as shown.[25]



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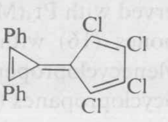

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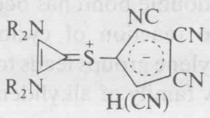

(23)

2 Three-membered Heterocyclic Systems

Non-empirical SCF MO calculations with full geometry optimisation suggest that oxiren (24) is less stable than the carbene (25), but of similar energy to formylcarbene, which is ~ 80 kcal mol^{-1} less stable than keten.[26] The role of oxiren in oxocarbene rearrangements is well established. Use of the labelled diazo-compounds (26) and (27) indicates that the equilibrium between the two oxocarbenes (28) and (29) *via* the oxiren must be largely displaced to the right, since (26) gives products involving a high degree of O migration on photolysis, whereas

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