

# CONTENTS

## ALICYCLIC COMPOUNDS

PREFACE . . . . .	VII
LIST OF PERIODICALS . . . . .	XVII
OFFICIAL PUBLICATIONS . . . . .	XXI
LIST OF COMMON ABBREVIATIONS AND SYMBOLS USED . . . . .	XXIII

### *Chapter I. Introduction*

by R. A. RAPHAEL

Saturated Ring Systems . . . . .	I
Isomerism of Alicyclic Compounds . . . . .	5
Physical Properties of Alicyclic Compounds. . . . .	7
Ring Expansions and Contractions . . . . .	II

### *Chapter II. Cyclopropane Group*

by R. A. RAPHAEL

1. Occurrence, Formation and Properties . . . . .	23
2. Saturated Hydrocarbons . . . . .	29
3. Unsaturated Hydrocarbons. . . . .	30
4. Halogen derivatives . . . . .	31
5. Alcohols . . . . .	32
6. Amines . . . . .	33
7. Aldehydes and Ketones . . . . .	34
8. Carboxylic Acids . . . . .	35
a. Monocarboxylic Acids . . . . .	35
b. Hydroxycarboxylic Acids . . . . .	37
c. Ketocarboxylic Acids . . . . .	39
d. Polycarboxylic Acids . . . . .	39

### *Chapter III. Cyclobutane Group*

by R. A. RAPHAEL

1. Occurrence, Formation and Properties . . . . .	46
2. Hydrocarbons . . . . .	50
a. Saturated Hydrocarbons. . . . .	50
b. Unsaturated Hydrocarbons. . . . .	51
3. Halogen Derivatives. . . . .	52
4. Alcohols . . . . .	55

5. Amines . . . . .	55
6. Aldehydes and Ketones . . . . .	56
7. Carboxylic Acids . . . . .	58
a. Cyclobutane Carboxylic Acids . . . . .	58
b. Truxillic and Truxinic Acids . . . . .	60
c. Cyclobutyl Derivatives of Aliphatic Acids . . . . .	65
d. Keto-acids . . . . .	67
e. Anemonin . . . . .	67

#### *Chapter IV. Cyclopentane Group*

*by R. A. RAPHAEL*

1. Occurrence, Formation and Properties . . . . .	71
2. Hydrocarbons . . . . .	76
a. Saturated Hydrocarbons. . . . .	76
b. Unsaturated Hydrocarbons. . . . .	78
(i) Cyclopentenes, 78 – (ii) Alkylidene- and Alkenyl-cyclopentanes, 80 –	
(iii) Cyclopentadienes, 81	
3. Halogen Derivatives. . . . .	84
4. Nitro- and Amino-derivatives. . . . .	85
5. Alcohols . . . . .	86
a. Hydroxyl Group in the Ring . . . . .	86
(i) Secondary Cyclopentanol, 86 – (ii) Tertiary Cyclopentanol, 87 – (iii) Cy-	
clopentane-diols, 89	
b. Exocyclic Alcohols . . . . .	90
6. Aldehydes . . . . .	91
7. Ketones . . . . .	92
a. Ring Ketones . . . . .	92
(i) Saturated Monoketones, 92 – (ii) Unsaturated Monoketones, 95 –	
(iii) Hydroxycyclopentenones, 98 [Pyrethrins, Cinerins and Jasmone, by	
L. CROMBIE, 98 – Synthesis of the Pyrethrins and their Degradation Products,	
102] – (iv) 1:2-Diketones, 105 – (v) 1:3-Diketones, 106 – (vi) Triketones, 107	
b. Exocyclic Ketones . . . . .	109
8. Carboxylic Acids . . . . .	110
a. Carboxyl Group Attached to the Ring . . . . .	110
b. Fatty Acids . . . . .	112
Naphthenic Acids, 114 – Hydnocarpic, Chaulmoogric, Gorlic and Related	
Acids, by L. CROMBIE, 117	
c. Hydroxy-acids . . . . .	120
d. Keto-acids . . . . .	121

#### *Chapter V. Cyclohexane Group*

*by R. A. RAPHAEL*

1. Occurrence, Formation and Properties . . . . .	124
a. Methods of Formation. . . . .	124
(i) The Reduction of Benzenoid Compounds, 124 – (ii) The Diels-Alder Diene	
Synthesis, 127 – (iii) Other Synthetic Methods, 129	
b. Configuration of the Cyclohexane Ring . . . . .	130
c. Differentiation between Cyclohexane and Cyclopentane Compounds . . . . .	134

2. Hydrocarbons . . . . .	135
a. Saturated Hydrocarbons . . . . .	135
Cyclohexanes (Hexahydrobenzenes or Cyclanes), 135	
b. Unsaturated Hydrocarbons. . . . .	139
(i) Cyclohexenes, 139 – (ii) Compounds with Unsaturated Side Chains, 145 –	
(iii) Cyclohexadienes (Dihydrobenzenes), 147 – (iv) Cyclohexylacetylenes, 150	
3. Halogen Derivatives of the Hydrocarbons . . . . .	151
a. Saturated Halogen Compounds . . . . .	151
b. Unsaturated Halogen Compounds . . . . .	155
4. Alcohols . . . . .	157
a. Saturated Ring Alcohols; Cyclohexanols . . . . .	157
(i) Monohydric Cyclohexanols, 157 – (ii) Dihydric and Polyhydric Alcohols,	
162 – (iii) Epoxycyclohexanes, 169	
b. Unsaturated Ring Alcohols. . . . .	171
(i) Cyclohexenols, 171 – (ii) Cyclohexadienols (Dihydrophenols), 172	
c. Acetylenic Alcohols . . . . .	173
d. Peroxides of the Cyclohexane Series. . . . .	174
(i) Cyclohexane Peroxides, 174 – (ii) Cyclohexene Peroxides, 174 – (iii) Cyclo-	
hexa-1:3-diene Peroxides, 175	
e. Halogenated Cyclohexanols . . . . .	175
f. Exocyclic Cyclohexane Alcohols . . . . .	177
5. Sulphur-containing Cyclohexane Compounds . . . . .	180
a. Mercaptans and Sulphides . . . . .	180
b. Sulphinic and Sulphonic Acids . . . . .	181
6. Nitro- and Amino-compounds . . . . .	182
a. Nitro-compounds . . . . .	182
b. Amines . . . . .	183
(i) Ring Amines, 183 – (ii) Ring Hydroxyamines, 185 – (iii) Exocyclic	
Amines, 186	
7. Aldehydes . . . . .	187
a. Saturated Aldehydes . . . . .	188
b. Unsaturated Aldehydes . . . . .	188
c. Hydroxyaldehydes . . . . .	191
d. Aminoaldehydes . . . . .	191
e. Side-chain Aldehydes . . . . .	191
8. Ketones . . . . .	192
a. Saturated Ring Ketones . . . . .	192
(i) Cyclohexanones, 192 – (ii) Halogenated Cyclohexanones, 199 – (iii) Hydr-	
oxycyclohexanones, 200 – (iv) Aminocyclohexanones, 201 – (v) Cyclo-	
hexanediones, 201 – (vi) Cyclohexanetriones, 204	
b. Unsaturated Ring Ketones. . . . .	205
(i) Cyclohexenones, 205 – (ii) Halogenated Cyclohexenones, 211 – (iii) Cyclo-	
hexadienones, 212	
c. Semicyclic and Exocyclic Unsaturated Ring Ketones . . . . .	214
d. Exocyclic Hydroaromatic Ketones . . . . .	214
9. Carboxylic Acids . . . . .	220
a. Monocarboxylic Acids . . . . .	220
(i) Cyclohexanecarboxylic Acids (Hexahydrobenzoic Acids), 220 – (ii) Cyclo-	
hexyl Fatty Acids, 224 – (iii) Cyclohexenecarboxylic Acids (Tetrahydro-	
benzoic Acids), 225 – (iv) Cyclohexenyl Fatty Acids, 227 – (v) Cyclohexa-	
dienecarboxylic Acids (Dihydrobenzoic Acids), 228	
b. Hydroxymonocarboxylic Acids . . . . .	229

(i) Hydroxycyclohexanecarboxylic Acids, 229 – (ii) Hydroxycyclohexyl Fatty Acids, 231	
c. Ketocarboxylic Acids . . . . .	232
(i) Ketocyclohexanecarboxylic Acids, 232 – (ii) Ketocyclohexenecarboxylic Acids, 234	
d. Dicarboxylic Acids . . . . .	235
(i) Cyclohexanedicarboxylic Acids, 235 – (ii) Cyclohexenedicarboxylic Acids, 236 – (iii) Cyclohexadienedicarboxylic Acids, 238 – (iv) Exocyclic Hydroaromatic Dicarboxylic Acids, 240 – (v) Hydroxycyclohexanedicarboxylic Acids, 242 – (vi) Ketocyclohexanedicarboxylic Acids, 245	
e. Polycarboxylic Acids . . . . .	246
(i) Tricarboxylic Acids, 246 – (ii) Tetra- and Hexacarboxylic Acids, 247	

*Chapter VI. Cycloheptane, Cyclo-octane and Macrocyclic Groups*

by R. A. RAPHAEL

1. Cycloheptane Group . . . . .	249
a. Hydrocarbons . . . . .	250
b. Halogen Compounds . . . . .	251
c. Alcohols . . . . .	251
d. Amines . . . . .	253
e. Aldehydes . . . . .	253
f. Ketones . . . . .	254
g. Carboxylic Acids . . . . .	255
2. Cyclo-octane Group . . . . .	257
a. Hydrocarbons . . . . .	258
b. Halogen Compounds . . . . .	263
c. Alcohols . . . . .	264
d. Amines . . . . .	265
e. Aldehydes and Ketones . . . . .	265
f. Carboxylic Acids . . . . .	266
3. Macrocyclic Compounds . . . . .	266
a. Hydrocarbons . . . . .	267
b. Alcohols . . . . .	269
c. Ketones . . . . .	270
(i) Saturated Ketones, 270 – (ii) Unsaturated Ketones, 275 – (iii) $\alpha$ -Hydroxyketones ( $\alpha$ -Ketols, Acyloins), 276 – (iv) Diketones, 276 [Muscone and Civetone, 277]	
d. Carboxylic Acids . . . . .	284
e. Benzenoid Compounds . . . . .	285
(i) Ortho-substituted Benzenes, 285 – (ii) Meta-substituted Benzenes, 286 – (iii) Para-substituted Benzenes, 287	

*Chapter VII. Polynuclear Alicyclic Compounds with Separate Ring Systems and Spiro Compounds*

by R. A. RAPHAEL

I. Rings United Directly or by a Carbon Chain. . . . .	290
Nomenclature . . . . .	291

a. Dicyclopropyl Compounds . . . . .	291
b. Dicyclobutyl Compounds . . . . .	291
c. Dicyclopentyl Compounds . . . . .	291
d. Cyclopentylcyclohexane Compounds. . . . .	293
e. Dicyclohexyl Compounds . . . . .	294
(i) Hydrocarbons, 294 – (ii) Alcohols, 294 – (iii) Ketones, 295 – (iv) Carboxylic Acids, 296	
f. Cyclohexylcycloheptane Compounds. . . . .	296
g. Dicycloheptyl Compounds . . . . .	296
h. Dicyclo-octyl Compounds . . . . .	298
2. Spiranes . . . . .	298
Nomenclature . . . . .	299
Methods of Formation . . . . .	299
a. Spiro[2:2]pentane Group . . . . .	300
b. Spiro[4:2]heptane Group . . . . .	301
c. Spiro[5:2]octane Group . . . . .	301
d. Spiro[6:2]nonane Group. . . . .	303
e. Spiro[3:3]heptane Group . . . . .	303
f. Spiro[4:3]octane Group . . . . .	303
g. Spiro[4:4]nonane Group. . . . .	303
h. Spiro[5:4]decane Group . . . . .	305
i. Spiro[5:5]undecane Group. . . . .	307
j. Spiro[6:5]dodecane Group. . . . .	307
k. Spiro[7:6]tetradecane Group. . . . .	307

*Chapter VIII. Polynuclear Alicyclic Compounds*

*Condensed Cyclic Systems*

by R. A. RAPHAEL

Nomenclature . . . . .	308
Stereochemistry of Condensed Ring Systems. . . . .	309
1. Bicyclic Ring Systems . . . . .	312
a. Bicyclo[1:1:0]butane Group . . . . .	312
b. Bicyclo[2:1:0]pentane Group . . . . .	313
c. Bicyclo[3:1:0]hexane Group. . . . .	314
d. Bicyclo[4:1:0]heptane Group . . . . .	314
e. Bicyclo[5:1:0]octane Group . . . . .	315
f. Bicyclo[2:2:0]hexane Group. . . . .	315
g. Bicyclo[3:2:0]heptane Group . . . . .	316
h. Bicyclo[4:2:0]octane Group . . . . .	316
i. Bicyclo[3:3:0]octane (Pentalane) Group. . . . .	317
j. Bicyclo[4:3:0]nonane (Hydrindane) Group . . . . .	319
k. Bicyclo[5:3:0]decane Group . . . . .	321
l. Bicyclo[4:4:0]decane (Decalin) Group. . . . .	323
(i) Saturated Compounds, 324 – (ii) Unsaturated Compounds, 328	
m. Bicyclo[5:4:0]undecane Group. . . . .	330
n. Bicyclo[5:5:0]dodecane Group . . . . .	331
2. Highly Condensed Alicyclic Systems. . . . .	331

*Chapter IX. Bridged Ring Systems**by R. A. RAPHAEL*

Nomenclature . . . . .	335
Synthesis and Properties. . . . .	336
a. Bicyclo[3:1:1]heptane Group . . . . .	339
b. Bicyclo[2:2:1]heptane Group . . . . .	339
Polymerisation Products of Cyclopentadiene, 343	
c. Bicyclo[2:2:2]octane Group . . . . .	346
d. Bicyclo[3:2:1]octane Group . . . . .	349
e. Bicyclo[3:3:1]nonane Group. . . . .	350
f. Bicyclo[3:2:2]nonanes . . . . .	350
g. Adamantane . . . . .	351

*Chapter X. The Carotenoid Group**by R. F. HUNTER*

1. Natural Occurrence, Properties and Constitution . . . . .	352
2. Carotenoid Hydrocarbons and Vitamin A . . . . .	354
a. The Carotenes . . . . .	354
b. Cis-trans Isomerism of Carotenoids . . . . .	363
c. Vitamin A . . . . .	365
Synthesis of Vitamin A and Related Compounds, 365	
d. Conversion of Carotenoids into Vitamin A and the Effect of Stereochemical Configuration on Biological Activity. . . . .	375
e. Biogenesis of the Carotenoids. . . . .	376
f. Lycopenes . . . . .	377
3. Carotenoids Containing Hydroxyl Groups; Xanthophylls . . . . .	379
4. Carotenoids Containing Ketonic Groups . . . . .	384
5. Carotenoid Carboxylic Acids . . . . .	387
6. Carotenoids of Partly Known Constitution . . . . .	388
7. Synthetic Higher Homologues of the Carotenes . . . . .	390

*Chapter XI. Open-chain and Cyclic Polymers Derived from Olefinic Compounds; Rubber and Rubber-like Compounds, Natural and Synthetic, and Their Derivatives*

*by R. G. R. BACON*

Introduction . . . . .	391
I. Polymerisation Products of Olefinic Compounds. . . . .	392
a. General Features of the Polymerisation of Olefinic Compounds . . . . .	392
b. Low Molecular-weight Polymers from Mono-olefinic Compounds . . . . .	393
(i) Open-chain Polymers Without Terminal Addend. 394 – (ii) Open-chain Polymers With Terminal Addenda (Telomers), 396 – (iii) Dimerisation Accompanied by Cyclisation between Carbon Chains and Aromatic Rings, 396 – (iv) Polymerisation Involving Alicyclic Ring-formation, 398	

c.	Low Molecular-weight Polymers of Diolefinic Compounds . . . . .	399
	(i) Open-chain Polymers Without Terminal Addenda, 399 – (ii) Open-chain Polymers With Terminal Addenda (Telomers), 399 – (iii) Cyclobutane-type Dimers, 400 – (iv) Cyclopentene-type Dimers, 400 – (v) Cyclohexene-type Dimers, 400 – (vi) Cyclo-octadiene-type Dimers, 402 – (vii) Bicyclic Dimers, 403 – (viii) Cyclic Trimers, Tetramers, etc., 403 – (ix) Allene Polymers, 403 – (x) Polymers of Non-conjugated Dienes, 404	
d.	Polymers of Trienes and Higher Polyenes . . . . .	404
e.	High Molecular-weight Polymers from Mono-olefinic Compounds; Vinyl and Vinylidene Plastics. . . . .	404
2.	Natural High Molecular-weight Isoprene Polymers . . . . .	407
a.	Natural Rubber and Its Derivatives . . . . .	407
	(i) Nature, Occurrence and Isolation of Natural Rubber, 407 – (ii) Composition and Properties of Rubber Latex, 409 – (iii) Rubber Solutions, 411 – (iv) Rubber Hydrocarbon: Purification, Heterogeneity, Structure and Molecular Size, 412 – (v) Physical Properties of Rubber, 415 – (vi) Chemical Properties of Rubber, 416 [(1) Thermal Decomposition and Cyclisation, 416; (2) Addition Reactions of Rubber, 417; (3) Reaction of Rubber with Chlorine and Other Halogens, 420; (4) Oxidation of Rubber, 421; (5) Vulcanisation of Rubber, 423; (6) Reaction of Rubber with Unsaturated and Resin-forming Substances, 426] – (vii) The Biogenesis of Rubber, 426	
b.	Polyisoprenes of Gutta-percha, Balata, etc.. . . . .	427
3.	Synthetic Elastomers . . . . .	428
a.	History of "Synthetic Rubber". . . . .	428
b.	Techniques Used in Preparing Elastomers from Dienes. . . . .	429
	(i) Relationship of Monomer Structure to Rubber-like Properties in the Derived Polymer, 430 – (ii) Alkali Metals as Polymerisation Catalysts, 430 – (iii) Polymerisation in Emulsion, 431 – (iv) Friedel-Crafts Polymerisation Catalysts, 432	
c.	Structure of Synthetic Elastomers from Dienes . . . . .	432
	(i) Physical Methods, 433 – (ii) Ozonolysis, 433 – (iii) Oxidation by Permanganate, 433 – (iv) Perbenzoic Acid Titration, 433	
d.	Properties of Individual Types of Elastomers Derived from Dienes. . . . .	434
	(i) Polymers and Copolymers of 1:3-Butadiene and Its Homologues, 434 – (ii) Polychloroprene (Neoprene), 434 – (iii) Butyl Rubbers, 435	
e.	Elastomers not Based on Dienes . . . . .	435
	(i) Polyesters, 435 – (ii) Polyacrylates, 435 – (iii) Polysulphides, 435 – (iv) Silicones, 436 – (v) Polyvinyl Chloride, 436	
	Additional General Bibliography . . . . .	436
	INDEX . . . . .	439

*For Contents of Vol. II B, see next page*