

CONTENTS

AROMATIC COMPOUNDS

PREFACE	VII
LIST OF PERIODICALS	XVIII
OFFICIAL PUBLICATIONS	XXIII
LIST OF COMMON ABBREVIATIONS AND SYMBOLS USED	XXIII

Chapter I. Introduction

1. The Benzene Nucleus <i>by</i> C. K. INGOLD	3
a. Theory of Aromatic Character	3
b. Physical Evidence of Mesomerism in Aromatic Nuclei.	16
(i) Electron Distribution (Spectral Evidence), 16 – (ii) Electronic Energy (Thermochemical Evidence), 16 – (iii) Electronic Mobility (Magnetic Evidence), 17	
2. Orientation in Electrophilic Aromatic Substitution <i>by</i> C. K. INGOLD.	20
a. Development of the Theory of Orientation.	20
b. Observations on Orientation and their Interpretation	26
(i) Orienting Effects of Poles and Polar Linkings, 26 – (ii) Orienting Effects of Formally Neutral Systems, 30 – (iii) Orienting Effects in Ionogenic Systems, 33	
c. Observations on Reactivity and their Interpretation	34
d. The Ortho-Para Ratio	41
3. Nucleophilic Aromatic Substitution <i>by</i> D. H. HEY and G. H. WILLIAMS	48
a. Mechanism of Substitution	49
(i) Unimolecular Substitution, 50 – (ii) Bimolecular Substitution, 51 – (iii) Activating and Deactivating Effects of Substituent Groups, 55 – (iv) Influence of the Nucleophilic Reagent, 57	
b. Nucleophilic Rearrangements	58
(i) The Smiles Rearrangement, 58 – (ii) Arylhydroxylamine Rearrangements, 58 – (iii) The von Richter Reaction, 59	
4. Homolytic Aromatic Substitution <i>by</i> D. H. HEY and G. H. WILLIAMS	60
a. Alkylation.	60
b. Amination and Hydroxylation	61
c. Arylation	62
5. Formation and Fission of the Benzene Nucleus <i>by</i> N. CAMPBELL	65
a. Formation of the Benzene Nucleus	65
(i) Pyrolysis, Condensation and Polymerisation Reactions, 66 – (ii) Aromatisation of Alicyclic Compounds by Dehydrogenation, 69 – (iii) Aromatisation by Isomerisation of Alicyclic Compounds, 74 – (iv) Aromatisation of 5-, 7- and 8-membered Ring Compounds and of Heterocyclic Compounds, 76	
b. Rupture of the Benzene Nucleus	77

Chapter II. Mononuclear Hydrocarbons: Benzene and its Homologues

by W. J. HICKINBOTTOM

1. Sources of the Hydrocarbons	81
Formation of Aromatic from Aliphatic Hydrocarbons	84
2. Reactions of the Hydrocarbons.	85
a. Additive Reactions.	85
(i) Hydrogenation, 85 - (ii) Addition of Halogens, 85 - (iii) Ozone, 86 - (iv) Hypochlorous Acid. 86 - (v) Polynitro Compounds and Quinones, 86 - (vi) Diazoacetic Ester. 86	
b. Oxidation.	87
c. Pyrolysis	90
d. Nuclear Substitution Reactions	90
(i) Halogenation, 90 - (ii) Nitration, 91 - (iii) Sulphonation, 93 - (iv) Friedel-Crafts Reaction. 94 - (v) Other Substitution Reactions, 99	
3. Individual Hydrocarbons	100
a. Benzene.	100
b. Homologues of Benzene; Alkylbenzenes.	102
(i) Preparation, 102 - (ii) Reactions of the Side Chain, 105 - (iii) Individual Alkylbenzenes. 106	

Chapter III. Halogen-, Nitro-, Nitroso-, and Hydroxylamino-Derivatives of Benzene and its Homologues

by W. J. HICKINBOTTOM

1. Halogen Derivatives of Benzene and its Homologues	113
a. Nuclear Halogen Derivatives	113
General Methods of Preparation, 113 - Properties and Reactions, 113	
(i) Halogeno-benzenes, 115 - (ii) Iodosobenzene, Iodoxybenzene and their Derivatives, 118 - (iii) Mixed Halogeno-benzenes, 120 - (iv) Halogen Derivatives of Alkylbenzenes, 121	
b. Alkylbenzenes with Halogen in the Side Chain	124
Preparation, 124	
(i) Benzyl Halides, 125 - (ii) Halogenophenylethanes, 128 - (iii) Benzylidene Halides; Benzotrihalides, 128	
2. Nitro Derivatives of Benzene and its Homologues	130
a. Nuclear Nitro Compounds.	130
Methods of Preparation. 130 - Properties and Reactions, 130	
(i) Mono- to Tetra-nitrobenzenes, 133 - (ii) Mono- to Tetra-nitrotoluenes, 135 - (iii) Nitro Derivatives of Higher Homologues, 138	
b. Halogen Derivatives of Nuclear Nitro Compounds	139
(i) Halogen in the Nucleus, 139 - (ii) Halogen in the Side Chain. 143	
c. Side Chain Nitro Compounds: Arylnitroparaffins	144
3. Nitroso Derivatives of Benzene and its Homologues.	148
4. N-Arylhydroxylamines	152

*Chapter IV. Aromatic Amines Derived from
Benzene and its Homologues*

by W. J. HICKINBOTTOM

I. Nuclear Monoamino Derivatives of Benzene and its Homologues . . .	159
a. Primary Amines	159
Methods of Formation, 159 – Properties and Reactions, 160 – Reactions of the Amino Group, 161 – Reactions of the Nucleus, 162	
(i) Aniline, 162 – (ii) Toluidines, 165 – (iii) Xylidines and Higher Homologues, 166 – (iv) Homologues of Aniline Halogenated in the Alkyl Group, 168	
b. Secondary and Tertiary Amines	169
Methods of Formation, 169 – Separation of Primary, Secondary and Tertiary Amines, 170	
(i) Monoalkylarylamines, 171 – (ii) Dialkylarylamines, 172 – (iii) Quaternary Ammonium Compounds, 175 – (iv) Dialkylarylamine Oxides, 176 – (v) Alkylarylamines with Substituents in the Alkyl Group, 177 – (vi) Alkylidenearylamines. Condensation Products of Arylamines with Aliphatic Aldehydes, 178 – (vii) Di- and Tri-arylamines, 180	
c. Arylamides of Inorganic Acids	182
(i) Thionylarylamines, 182 – (ii) Arylsulphamic Acids, 182 – (iii) Derivatives of Phosphorus Acids, 183 – (iv) Other Inorganic Acids, 184	
d. Arylamides of Monobasic Fatty Acids	184
e. Arylamides of Hydroxy- and Keto-acids.	189
f. Derivatives of Carbonic Acid	190
(i) Derivatives of Carbamic Acid, 190 – (ii) N-Aryl Derivatives of Urea, 191 – (iii) Derivatives of Phenylisourea, 193 – (iv) Phenylcarbonyl Derivatives of Hydroxylamine and Hydrazine, 193 – (v) Derivatives of Thio- and Dithio-carbamic Acids, 194 – (vi) Arylthioureas, 195 – (vii) Derivatives of Arylthiothioureas, 196 – (viii) Phenylthiocarbonyl Derivatives of Hydroxylamine and Hydrazine, 197 – (ix) Guanidine Derivatives (<i>in part</i> by E. HOGGARTH), 197 – (x) ArylisoCyanates, 201 – (xi) ArylisoThiocyanates, 203 – (xii) Phenylcyanamide and its Derivatives, 204	
g. Arylamides of Dicarboxylic Acids and their Derivatives	205
h. Phenylamino Derivatives of Fatty Aldehydes and Ketones	207
i. Phenylamino Derivatives of Fatty Acids	208
j. Phenylamino Derivatives of Aliphatic Dicarboxylic Acids	211
2. Nuclear Halogen Derivatives of Aniline	211
a. Monohalogen-substituted Anilines	213
b. Di-, Tri- and Poly-halogen-substituted Anilines	213
c. Halogen Derivatives of N-Alkylanilines and Diphenylamine	215
3. Nuclear Nitroso Derivatives of Aniline	217
4. Nuclear Nitro Derivatives of Aniline and Homologues	218
a. Nitroanilines.	219
b. Nitro Derivatives of Homologues of Aniline	221
5. Sulphonic Acids of Aniline and its Homologues	221
6. Amines with More than One Nuclear Amino Group	223
a. Diamines	223
b. Tri- and Poly-amines	228

*Chapter V. Sulphonic Acids, Sulphinic Acids
and Sulphenyl Compounds of the Benzene Series*

by W. J. HICKINBOTTOM

1.	Sulphonic Acids	230
a.	Nuclear Sulphonic Acids of Benzene and its Homologues	230
	General Methods of Formation, 230 – General Properties and Reactions, 230 – Replacement of the Sulphonyl Group, 231 – Reduction to Sulphinic Acids and Thiols, 233 – Preparation of Sulphonyl Halides, 233 – Properties and Reactions of Sulphonyl Halides, 234	
	(i) Monosulphonic Acids, 234 – (ii) Halogen-substituted Benzenesulphonic Acids, 237 – Nitro-substituted Sulphonic Acids, 238 – (iv) Di- and Trisulphonic Acids, 239 – (v) Aryl Selenonic Acids, 240	
	b. Acids with the Sulphonic Group in the Side Chain	240
2.	Sulphinic Acids	241
3.	Sulphenic Acid Derivatives	244
4.	Thiosulphonic Acids	246

Chapter VI. Nitrogen Derivatives of Anilines:

Nitrosamines; Nitramines; Diazo, Azo, Azoxy and Hydrazo Compounds

by Z. E. JOLLES

1.	Phenylnitrosamines	249
2.	Phenylnitramines.	252
3.	Diazo Compounds	256
a.	Methods of Formation and Properties.	258
	(i) Diazonium Salts, 258 [General, 258 – History and Constitution, 259 – Diazotisation of Amines: Theory, 259; Monoamines, 260; Diamines, 262 – Properties of Diazonium Salts; Stability: Solid Diazonium Salts, 264; Stability in Aqueous Media, 265; Diazo-oxides or Quinonediazides, 266; Diazoimines or Irninoquinonediazides, 267; Individual Diazonium Salts: from Monoamines, 268; from Diamines, 271] – (ii) Diazohydroxides and Diazotates, 272 [Isomerism of Aromatic Diazo Compounds, 272 – History and Constitution, 273 – Formation of n-Diazohydroxides and Diazotates, 274 – Formation of iso-Diazohydroxides and Diazotates, 276 – Diazobenzene-sulphonic Acids, 278] – (iii) Diazo Ethers, 279 – (iv) Diazomercaptans, Diazosulphides and Diazothioethers , 280 – (v) Diazosulphonates, 280 – (vi) Diazo-sulphinates and -sulphones , 282 – (vii) Diazocyanides, 283	
b.	General Reactions of Diazo Compounds	284
	(i) With Retention of Diazo Nitrogen, 284 – (ii) With Loss of Diazo Nitrogen, 286 [Replacement of Diazo Group by Hydrogen and by Various Groups, 287 – Reductive Replacement of the Diazo Nitrogen. Formation of Symmetrical Diaryls , 296 – Non-reductive Methods of Replacement of Diazo Nitrogen, 297 – Arylation of Quinones and of Unsaturated Compounds, 298]	

4. Diazoamino Compounds (or Triazens) and Bisdiazoamino Compounds (or Pentazdiens)	300
History and Constitution	301
a. Triazens (Diazoamino Compounds)	302
b. Pentazdiens (Bisdiazoamino Compounds)	303
5. Diazohydroxyamino Compounds, Triazen Oxides	307
6. Aryl Azides	309
7. Azoxy Compounds	312
8. Azo Compounds	319
a. General Methods of Formation	319
(i) Reduction of Nitro, Nitroso and Azoxy Compounds, 319 - (ii) Oxidation of Amines and Hydrazines, 320 - (iii) Condensation and Diazo-coupling Reactions, 320	
b. The Diazo-coupling Reaction	321
(i) Coupling with Amines, 322 - (ii) Coupling with Phenols and Phenol Ethers, 323 - (iii) Coupling with Substances Carrying a Reactive Methylene, Methine or Methyl Group, 323 - (iv) Theories of the Coupling Mechanism, 326	
c. Properties and Reactions	328
(i) General Properties, 328 - (ii) Reactions Affecting the Azo Group, 330 - (iii) Reactions of the Aromatic Nuclei, 332	
d. Azobenzene and Derivatives	333
(i) Azobenzene, 333 - (ii) Polyazo Compounds, 333 - (iii) Aminoazo Compounds, 335	
e. Mixed Azo Compounds	340
9. Hydrazine Derivatives	345
a. Aromatic Hydrazines	345
General Methods of Formation, 345	
(i) Monophenylhydrazines; Hydrazino Compounds, 345 - (ii) Diphenylhydrazines, 347 - (iii) Triphenylhydrazines, 348 - (iv) Tetraphenylhydrazines, 348	
Properties and Reactions, 348	
(i) Oxidation, 349 - (ii) Reduction, 351 - (iii) Action of Acids. Benzidine and Semidine Rearrangements, 351 - (iv) Action of Metals, 354 - (v) Reaction with Aldehydes and Ketones, 354 - (vi) Reaction with Unsaturated Compounds, 354 - (vii) Formation of Heterocyclic Compounds, 355	
Individual Compounds, 355	
(i) Monophenylhydrazines, 355 - (ii) <i>s</i> -Diphenylhydrazines; Hydrazobenzenes, 357 - (iii) <i>as</i> -Diarylhydrazines, 357	
b. Mixed Aliphatic-Aromatic Hydrazines	358
Methods of Formation, 358	
(i) Alkyl Derivatives of Monophenylhydrazines, 358 - (ii) Alkyl Derivatives of Diphenylhydrazines, 359	
Individual Compounds, 359	
c. Phenylhydrazones and Osazones	360
Methods of Formation, 360 - Reactions of Phenylhydrazones, 363	
d. Phenylhydrazine Derivatives of Inorganic Acids	364
e. Phenylhydrazides of Monocarboxylic Acids; Acylphenylhydrazines	365
Methods of Formation, 366 - Formation of Heterocyclic Compounds from Hydrazides, 367	
f. Phenylhydrazine Derivatives of Carbonic, Carbamic and Thiocarbonic Acids	367
g. Phenylhydrazine Derivatives of Dicarboxylic Acids	372

- h. Phenylhydrazidines (Amidrazones), Nitrazones, **Phenylhydrazoal-**
 oximes, Phenylazoaloximes (Nitrosazones), Formazyl Compounds . . . 373
 (i) Phenylhydrazidines or Phenylamidrazones, 373 - (ii) Nitrohydrazones or
 Nitrazones, 374 - (iii) Phenylhydrazoaloximes and Benzeneazoaloximes
 or Nitrosazones, 375 - (iv) Formazyl Compounds, 376
- i. **Nitroso Derivatives of Phenylhydrazines; Triazans, Tetrazens and**
 Tetrazans 378

Chapter VII. Aromatic Metal and Metalloid Compounds

by J. CHATT

Introduction	381
1. Aromatic Compounds of Elements of Group 1	383
2. Aromatic Compounds of Elements of Group 2	385
a. The Alkaline Earth Metals.	385
b. Typical Elements and B Sub-group, Be, Mg, Zn, Cd, Hg.	386
(i) Magnesium, 386 - (ii) Mercury, 387	
3. Aromatic Compounds of Elements of Group 3	389
(i) Boron, 389 - (ii) Aluminium, 390 - (iii) Gallium, 391 - (iv) Indium, 391 -	
(v) Thallium, 391	
4. Aromatic Compounds of Elements of Group 4	392
a. Silicon	392
b. Germanium, Tin and Lead	394
5. Aromatic Compounds of the Transition Elements.	397
a. Chromium, Manganese, Cobalt.	397
b. Copper, Silver, Gold	398
c. Metal Derivatives of Cyclopentadiene.	398
6. Aromatic Compounds of Elements of Group 5	399
a. Phosphorus	400
b. Arsenic	403
c. Antimony.	405
d. Bismuth	407
7. Aromatic Compounds of Elements of Group 6	408
a. Selenium	408
b. Tellurium	411
Bibliography	412

*Chapter VIII. Nuclear Hydroxy Derivatives of Benzene and
 its Homologues. Phenols*

by W. J. HICKINBOTTOM

1. Monohydric Phenols	413
Methods of Formation.	413
Properties and Reactions	415
Reactions of the Hydroxyl Group, 415 - Nuclear Substitution, 416	

a. Phenol and its Homologues	418
b. Functional Derivatives of Phenols	423
(i) Phenyl Alkyl Ethers, 423 - (ii) Unsaturated Ethers, 426 - (iii) Aryl Alkyl Ethers with Substituents in the Alkyl Group, 428 - (iv) Diaryl Ethers, 429 - (v) Esters of Phenols, 429 [Phenyl Esters of Inorganic Acids, 429 - Esters of Phenols with Carboxylic Acids, 431]	
c. Thiophenols and their Derivatives	432
(i) Thiophenols, 432 - (ii) Thioethers, Sulphides, 435 - (iii) Substituted Thiophenols and their Derivatives, 437	
d. Halogenophenols	438
e. Nitrophenols	442
Nitro Derivatives of Homologues of Phenol, 445	
f. Nitrosophenols	446
g. Aminophenols	449
h. Phenolsulphonic Acids	460
2. Dihydric Phenols	464
Methods of Formation	464
Reactions and Properties	464
a. <i>o</i> -Dihydric Phenols	465
(i) Catechol and its Derivatives, 465 [Cyclic Compounds from Catechol, 466 - Catechol Esters of Inorganic and Organic Acids, 468] - (ii) Halogen and Nitro Derivatives of Catechol, 469 - (iii) Homologues of Catechol, 469 - (iv) Thio Derivatives of Catechol, 470	
b. <i>m</i> -Dihydric Phenols	470
(i) Resorcinol and its Derivatives, 470 - (ii) Nitroso Derivatives, 472 - (iii) Nitro Derivatives, 472 - (iv) Homologues of Resorcinol, 473 - (v) Thio Derivatives, 474	
c. <i>p</i> -Dihydric Phenols	475
(i) Hydroquinone and its Derivatives, 475 - (ii) Substituted Quinols, 476 - (iii) Homologues of Hydroquinone, 477 - (iv) Thio Derivatives of Quinol, 478	
d. Amino Derivatives of Dihydric Phenols	479
3. Trihydric Phenols	480
a. 1:2:3-Trihydroxybenzene	480
b. 1:2:4-Trihydroxybenzene	482
c. 1:3:5-Trihydroxybenzene	482
4. Tetra-, Penta- and Hexa-hydric Phenols	485
a. Tetrahydric Phenols	485
b. Pentahydric and Hexahydric Phenols	486

Chapter IX. Aralkylamines,

Alcohols, Aldehydes and Ketones of the Benzene Series

by W. J. HICKINBOTTOM

1. Aralkylamines of the Benzene Series	487
Methods of Formation	487
a. Phenylalkylamines and their Homologues	488
b. Nuclear-substituted Aralkylamines	492
c. Benzyl Derivatives of Hydroxylamine	493

d. Benzyl Derivatives of Hydrazine	494
e. Diazo Compounds, Triazens and Azides Related to Benzylamine	495
2. Monohydric Alcohols of the Benzene Series and their Derivatives.	496
Methods of Formation	496
a. Phenyl Alcohols and their Homologues	498
b. Functional Derivatives of the Alcohols	502
c. Sulphur Derivatives of the Alcohols	503
d. Nuclear-substituted Benzyl Alcohols	504
3. Monoaldehydes of the Benzene Series	506
Methods of Formation	506
Aromatic Aldehydes, 506 - Methods Applicable to both Aromatic and Aryl-substituted Fatty Aldehydes, 508 - Special Methods for Aryl-substituted Aliphatic Aldehydes, 511	
a. Aromatic Aldehydes	511
General Properties and Reactions. 511 - (i) Benzaldehyde and its Homologues, 513 - (ii) Functional Derivatives of Benzaldehyde, 515 - (iii) Halogenobenzaldehydes, 521 - (iv) Nitrobenzaldehydes, 521 - (v) Hydroxyl-amino-, Nitroso-, Azoxy- and Azo-benzaldehydes, 523 - (vi) Aminobenzaldehydes, 524 - (vii) Benzaldehydesulphonic Acids, 527	
b. Aryl-substituted Fatty Aldehydes	527
4. Monoketones of the Benzene Series	528
Methods of Formation	529
General Methods, 529 - Special Methods for the Preparation of Alkyl Aryl Ketones, 530 - Special Methods for the Preparation of Aryl-substituted Aliphatic Ketones, 530	
a. Alkyl Aryl Ketones.	531
b. Nuclear-substituted Acetophenones	536
(i) Halogenoacetophenones, 536 - (ii) Nitroacetophenones, 537 - (iii) Aminoacetophenones, 537	
c. Monoaryl Derivatives of Dialkyl Ketones	538
d. Monoaryl Ketens	540

Chapter X. Monocarboxylic Acids of the Benzene Series

by W. J. HICKINBOTTOM

I. Aromatic Monocarboxylic Acids	541
Methods of Formation	541
a. Benzoic Acid and its Homologues	543
b. Functional Derivatives of Aromatic Monocarboxylic Acids.	545
(i) Esters, 546 - (ii) Aroyl Halides and Mixed Anhydrides with Inorganic Oxy-acids, 547 - (iii) Acid Anhydrides, 548 - (iv) Aroyl Peroxides and Peracids, 548 - (v) Thio- and Dithio-acids, 549 - (vi) Aromatic Amides, 551 - (vii) Benzoyl Derivatives of Amino-acids, 552 - (viii) Aroyl Hydrazines, 556 - (ix) Aroyl Azides, 557 - (x) Nitriles, Aryl Cyanides, 557 - (xi) Amidohalides, Iminoalides and Hydrazidohalides, 561 - (xii) Iminoethers, 563 - (xiii) Thioamides and Imino-thioethers, 563 - (xiv) Amidines, 564 - (xv) Hydrazidines or Amidrazones, 566 - (xvi) Hydroxamic Acid, and Hydroximic Acid Halides, 566 - (xvii) Nitrolic and Nitrosolic Acids, 568 - (xviii) Nitrile Oxides, 569 - (xix) Amidoximes and Related Compounds, 570 - (xx) Ortho-acid Derivatives, 571	

CONTENTS

XVII

c. Substituted Benzoic Acids.	571
(i) Halogen-substituted Benzoic Acids, 571 – (ii) Iodoso- and Iodoxy-benzoic Acids, 573 – (iii) Nitrobenzoic Acids, 573 – (iv) Nitrosobenzoic Acids, 575 – (v) Aminobenzoic Acids, 576 [Anthranilic Acid and its Derivatives, 577 – Nuclear-substituted Anthranilic Acids, 584 – Formation of Heterocyclic Compounds from Anthranilic Acid and its Derivatives, 585 – Other Aminobenzoic Acids, 586 – Diazo-, Azoxy- and Azo-compounds from Aminobenzoic Acids, 588] – (vi) Sulphobenzoic Acids, 590	
2. Aryl-substituted Saturated Fatty Acids	593
Methods of Formation	593
a. Aryl Fatty Acids.	595
b. Nitriles of the Aryl Fatty Acids	598
c. Substituted Aryl Fatty Acids	600
INDEX	603