

# RODD'S CHEMISTRY OF CARBON COMPOUNDS

*A modern comprehensive treatise*

SECOND EDITION

*Edited by*

S. COFFEY

M.Sc. (London), D.Sc. (Leyden), F.R.I.C.

*formerly of*

*I.C.I. Dyestuffs Division, Blackley, Manchester*

VOLUME III PART E

AROMATIC COMPOUNDS

Monobenzenoid hydrocarbon derivatives with functional groups in separate side-chains; dihydric and polyhydric aralkanols and their oxidation products; monobenzenoid hydrocarbons with unsaturated side-chains and their derivatives



ELSEVIER SCIENTIFIC PUBLISHING COMPANY

AMSTERDAM OXFORD NEW YORK

1974

# CONTENTS

## VOLUME III E

Aromatic Compounds: Monobenzenoid hydrocarbon derivatives with functional groups in separate side-chains; dihydric and polyhydric aralkanols and their oxidation products; monobenzenoid hydrocarbons with unsaturated side-chains and their derivatives

PREFACE . . . . .	VII
OFFICIAL PUBLICATIONS; SCIENTIFIC JOURNALS AND PERIODICALS . . . . .	XIV
LIST OF ABBREVIATED NAMES OF CHEMICAL FIRMS MENTIONED IN PATENT REFERENCES . . . . .	XV
LIST OF COMMON ABBREVIATIONS AND SYMBOLS USED . . . . .	XVI

*Chapter 17. Dihydric and Polyhydric Aralkanols and Their Oxidation Products with Functional Groups in Separate Side-chains*  
by G. V. BOYD

1. Side-chain halogenated alkylbenzenes . . . . .	2
a. $\alpha,\alpha$ -Dihalogenoxylenes, bis(halogenomethyl)benzenes (xylylene dihalides) and other dihalides . . . . .	2
b. Tetra- and poly-halogeno compounds . . . . .	4
2. Di- and poly-hydric aralkanols, thiols and amines . . . . .	5
a. Aralkanols . . . . .	5
b. Thiols, amines, etc. . . . .	6
c. Phenolic di- and tri-hydric alcohols . . . . .	9
d. Phenol-formaldehyde resins . . . . .	10
3. Hydroxyalkylarene-carbaldehydes and hydroxyalkylaryl ketones . . . . .	11
4. Arene-di- and -poly-carbaldehydes . . . . .	13
a. Arenedicarbaldehydes . . . . .	13
(i) Methods of formation and preparation, 13 – (ii) Phthalaldehyde, 14 – (iii) Iso-, tere- and homo-phthalaldehydes, 17 – (iv) Phenolic dialdehydes, 18 –	
b. Tri- and tetra-arene-carbaldehydes . . . . .	19
5. Di- and tri-acyl compounds . . . . .	19
a. Di- and tri-acylarenes . . . . .	19
b. Di- and tri-acylphenols . . . . .	20
6. Hydroxyalkylarene-carboxylic acids, lactones and lactams. Phthalides . . . . .	20
a. Hydroxyalkylbenzoic acids . . . . .	20
b. Phthalide and related compounds . . . . .	21
(i) Preparation, 21 – (ii) Properties and reactions, 22 –	
c. Nitrogen and sulphur analogues of phthalide . . . . .	23
d. Phenolic phthalides . . . . .	24
e. Alkylphthalides . . . . .	25
7. Oxoaralkanecarboxylic acids . . . . .	26
a. Aldehydic acids . . . . .	26
(i) Phthaldehydic acid and related compounds, 27 – (ii) Hydroxy- and alkoxy-phthaldehydic acids, 30 – (iii) Other aldehydic acids, 31 –	

b. Dialdehydic carboxylic acids . . . . .	31
c. Oxo-carboxylic acids . . . . .	32
8. Arene-di-, -tri- and -poly-carboxylic acids . . . . .	34
a. Phthalic acid and its derivatives . . . . .	34
(i) Phthalic acid, 34 – (ii) Phthalic anhydride and sulphur analogues, 35 – (iii) Phthaloyl halides, 38 – (iv) Peroxy-compounds, 39 – (v) Esters, 40 – (vi) Amides and related compounds, 43 – (vii) Hydrazine derivatives of phthalic acid, 48 – (viii) Nitriles of phthalic acid, 48 – (ix) Substituted phthalic acids, 49 – (x) Hydroxyphthalic acids, 54 –	
b. Isophthalic acid and its derivatives . . . . .	55
Substituted isophthalic acids, 55 –	
c. Terephthalic acid and its derivatives . . . . .	59
Substituted terephthalic acids, 60 –	
d. Dicarboxylic acids with one nuclear and one side-chain carboxyl group . . . . .	62
(i) Homophthalic acid, 62 – (ii) Substituted homophthalic acids, 65 – (iii) Other acids, 65 –	
e. Dicarboxylic acids with carboxyl groups in separate side-chains . . . . .	56
f. Benzenepolycarboxylic acids . . . . .	67
(i) Tricarboxylic acids, 68 – (ii) Benzene-tetra-, -penta- and -hexa-carboxylic acids, 69 –	

*Chapter 18. Dihydric and Polyhydric Aralkanols and Their  
Oxidation Products*  
by A. B. TURNER

1. Aralkanediols, aralkanetriols and aminoaralkanols . . . . .	72
a. Aryl derivatives of dihydric alcohols; aralkanediols . . . . .	72
(i) General methods of preparation, 72 – (ii) Reactions, 72 – (iii) Individual aralkanediols, 73 –	
b. Aryl derivatives of trihydric alcohols; aralkanetriols . . . . .	78
c. Aryl derivatives of amino-alcohols; aminoaralkanols . . . . .	79
(i) Synthesis, 79 – (ii) Individual aminoaralkanols, 80 –	
2. Hydroxycarbonyl and aminocarbonyl derivatives of aralkanes . . . . .	90
a. Hydroxyaralkanecarbaldehydes . . . . .	90
b. Hydroxy- and amino-aralkanones . . . . .	92
3. Dicarbonyl derivatives of aralkanes . . . . .	99
a. 2-(or $\alpha$ -)Oxo-aralkanecarbaldehydes . . . . .	99
b. 3-(or $\beta$ -)Oxo-aralkanecarbaldehydes . . . . .	101
c. 4-(or $\gamma$ -) and 5-(or $\delta$ -)Oxo-aralkanecarbaldehydes . . . . .	102
d. 1-Aralkane-1,2-diones; 1,2-(or $\alpha, \beta$ -)dioxo-1-aralkanes . . . . .	102
e. Aralkane-1,3-diones; 1,3-(or $\alpha, \gamma$ -)dioxoaralkanes . . . . .	103
4. Hydroxy- and amino-aralkanecarboxylic acids . . . . .	105
a. 2-(or $\alpha$ -)Monohydroxy- and 2-(or $\alpha$ -)monoamino-arylacetic acids . . . . .	105
(i) Mandelic acid and related compounds, 105 – (ii) 2-(or $\alpha$ -)Aminoarylacetic acids, 109 –	

b. Arylhydroxy- and amino(aryl)propionic acids . . . . .	110
(i) Arylhydroxypropionic acids, 110 – (ii) Amino(aryl)propionic acids, 112 –	
c. Higher arylhydroxy- and amino(aryl)-alkanoic acids . . . . .	122
d. Aryldihydroxy- and aminohydroxyaralkanoic acids . . . . .	123
5. Carbonyl derivatives of aralkanoic acids . . . . .	125
a. Formylaralkanoic acids . . . . .	125
b. Aryloxoalkanoic acids . . . . .	126
(i) Aryl-2-(or $\alpha$ -)oxoalkanoic acids, 126 – (ii) Aryl-3-(or $\beta$ -)oxoalkanoic acids, 129 – (iii) Aryl-4-(or $\gamma$ -) and -5-(or $\delta$ -)oxoalkanoic acids, 131 –	
c. Arylhydroxyoxoalkanoic acids . . . . .	134
d. Aryldioxoalkanoic acids . . . . .	134
6. Aralkane-di- and -tri-carboxylic acids . . . . .	135
a. Aralkanedicarboxylic acids . . . . .	135
b. Arylhydroxyalkanedicarboxylic acids . . . . .	138
c. Aryloxoalkanedicarboxylic acids . . . . .	138
d. Arakanetricarboxylic acids . . . . .	139

*Chapter 19. Benzene Derivatives with One or More  
Unsaturated Side-Chains*  
by J. H. P. UTLEY

1. Unsaturated hydrocarbons and their nuclear-substituted derivatives . . . . .	141
a. Aralkenes . . . . .	141
(i) Styrene, 142 – (ii) Side-chain substitution products of styrene, 145 – (iii) Homologous alkenylbenzenes, 149 –	
b. Phenylacetylenes; phenylalkynes . . . . .	152
(i) Preparation, 152 – (ii) Reactions, 153 –	
c. Phenyl-dienes and -diynes . . . . .	155
d. Hydroxyphenyl-alkenes and -alkynes and their derivatives . . . . .	158
(i) Monohydroxyphenylalkenes, 159 – (ii) Dihydroxyphenylalkenes, 163 – (iii) Trihydroxyphenylalkenes, 171 – (iv) Tetrahydroxyphenylalkenes, 172 – (v) Hydroxyphenylalkynes, 173 – (vi) Hydroxyphenylpolyenes, 173 –	
2. Phenyl derivatives of unsaturated alcohols . . . . .	174
a. Phenylalkenols and their derivatives . . . . .	174
b. Hydroxyphenylalkenols and their derivatives . . . . .	177
c. Phenylalkynols and their derivatives . . . . .	178
3. Phenyl derivatives of unsaturated aldehydes and ketones . . . . .	179
a. Aralkenylcarbaldehydes . . . . .	179
b. Hydroxyaralkenecarbaldehydes . . . . .	182
c. Aralkylpolyenecarbaldehydes . . . . .	183
d. Aralkynecarbaldehydes . . . . .	184
e. Aralkenyl ketones . . . . .	184
f. Hydroxyaralkenyl ketones . . . . .	187
g. Aralkynyl ketones . . . . .	187
h. Arakadienyl ketones . . . . .	188
i. Aryl hydroxyalkenyl ketones . . . . .	189
j. Aralkenediones . . . . .	190

4. Aralkenecarboxylic acids . . . . .	190
a. Nuclear carboxylic acids . . . . .	190
b. Aralkenecarboxylic acids . . . . .	191
<i>(i)</i> Cinnamic acid and allocinnamic acid, 193 – <i>(ii)</i> Cinnamic acids substituted in the side-chain, 197 – <i>(iii)</i> Nuclear-substituted cinnamic acids, 199 – <i>(iv)</i> Cinnamic acids substituted in both ring and side-chain, 201 – <i>(v)</i> Homologous cinnamic acids, 201 – <i>(vi)</i> Atropic and related acids, 203 – <i>(vii)</i> Higher aralkenecarboxylic acids, 204 –	
c. Hydroxyarenecarboxylic acids with an unsaturated side-chain . . . . .	207
d. Phenolic aralkenecarboxylic acids and their derivatives . . . . .	208
<i>(i)</i> Monohydroxyaralkenecarboxylic acids, 208 – <i>(ii)</i> Dihydroxyaralkenecarboxylic acids, 213 – <i>(iii)</i> Trihydroxycinnamic acids, 215 –	
e. Aralkynecarboxylic acids . . . . .	216
f. Aralka-di- and -tri-enecarboxylic acids . . . . .	220
g. Aralkenehydroxycarboxylic acids . . . . .	224
h. Oxoaralkenecarboxylic acids . . . . .	226
i. Aralkene-di- and -tri-carboxylic acids . . . . .	228
j. Alkylidene compounds: unsaturated oxidation products of the dialkylbenzenes . . . . .	232

*Appendix to Chapter 19. Benzene Derivatives with One or More  
Unsaturated Side-Chains*

by MALCOLM SAINSBURY

1. Aralkenes . . . . .	237
a. Styrene and its homologues . . . . .	237
b. Halogenostyrenes . . . . .	241
c. Nitrostyrenes . . . . .	242
2. Natural products related to styrene . . . . .	243
3. Natural products related to cinnamyl alcohol . . . . .	244
4. Allyl phenols and related compounds . . . . .	245
5. Conjugated arylpolyenes . . . . .	246
6. Arylpropenes, arylbutenes and derivatives . . . . .	247
7. Aralkenecarbaldehydes . . . . .	248
8. Aralkenyl ketones . . . . .	249
9. Aralkenecarboxylic acids and their derivatives . . . . .	250
a. Cinnamic acid derivatives and related compounds . . . . .	250
b. Natural products . . . . .	254
10. Aralkynes . . . . .	255
a. Preparative methods . . . . .	255
b. Reactions and properties . . . . .	256
11. Aralkynols and derivatives . . . . .	258
a. Reactions . . . . .	258
12. Aralkynals and aralkynones . . . . .	260
13. Aralkynoic acids . . . . .	260

INDEX . . . . .	263
-----------------	-----