

RODD'S  
CHEMISTRY  
OF  
CARBON COMPOUNDS

SECOND EDITION

EDITED BY

S. COFFEY

M. Sc., D. Sc., F.R.I.C.

VOLUME I

ALIPHATIC COMPOUNDS

PART C:

MONOCARBONYL DERIVATIVES  
OF ALIPHATIC HYDROCARBONS  
ANALOGUES AND DERIVATIVES

ELSEVIER PUBLISHING COMPANY

RODD'S CHEMISTRY OF CARBON COMPOUNDS

ELSEVIER PUBLISHING COMPANY  
335 JAN VAN GALENSTRAAT, P.O. BOX 211, AMSTERDAM

AMERICAN ELSEVIER PUBLISHING COMPANY, INC.  
52 VANDERBILT AVENUE, NEW YORK, N.Y. 10017

ELSEVIER PUBLISHING COMPANY LIMITED  
12B, RIPPLESIDE COMMERCIAL ESTATE  
RIPPLE ROAD, BARKING, ESSEX

LIBRARY OF CONGRESS CATALOG CARD NUMBER 51-14658

WITH 17 TABLES

ALL RIGHTS RESERVED  
THIS BOOK OR ANY PART THERE OF MAY NOT BE REPRODUCED IN ANY  
FORM, INCLUDING PHOTOSTATIC OR MICROFILM FORM,  
WITHOUT WRITTEN PERMISSION FROM THE PUBLISHERS

PRINTED IN THE NETHERLANDS

# RODD'S CHEMISTRY OF CARBON COMPOUNDS

---

## ADVISORS

Professor Sir ROBERT ROBINSON, O.M., M.A. (Oxon.), D.SC. (Manc.), HON. D.SC. (Lond., Liv., Wales, Dunelm, Sheff., Belfast, Bris. and Oxon.), HON. LL.D. (Manc., Edin., Birm., St. Andrews, Glas.), HON. D. PHARM. (Madrid and Paris), HON. F.R.S.E., F.R.S., *London*

*Chairman*

Sir JAMES COOK, PH.D., D.SC. (Lond.), HON. SC.D. (Dublin), HON. D.SC. (Nigeria), HON. D. DE L'U. (Rennes), F.R.S., F.R.I.C., *Exeter*

Professor R. N. HASZELDINE, M.A., PH.D., SC.D. (Cantab.), PH.D., D.SC. (Birm.), F.R.I.C., *Manchester*

Professor R. D. HAWORTH, D.SC., PH.D. (Manc.), B.SC. (Oxon.), F.R.S., F.R.I.C., *Sheffield*

Professor Sir EDMUND HIRST, M.A., PH.D. (St. Andrews), D.SC. (Birm.), F.R.S., F.R.I.C., *Edinburgh*

Professor Sir EWART JONES, M.A. (Oxon.), PH.D. (Wales), D.SC. (Manc.), F.R.S., F.R.I.C., *Oxford*

Dr. E. H. RODD, D.SC. (Lond.), F.C.G.I., F.R.I.C., *Limpley Stoke, Bath*

Professor Lord TODD, M.A. (Cantab.), D.PHIL. (Oxon.), D.SC., HON. LL.D. (Edin. and Glas.), DR. PHIL. NAT. (Frankfurt), HON. D.SC. (Exeter, Leics., Lond., Madrid and Wales), F.R.S., F.R.I.C., *Cambridge*

# RODD'S CHEMISTRY OF CARBON COMPOUNDS

VOLUME I

GENERAL INTRODUCTION

ALIPHATIC COMPOUNDS

\*

VOLUME II

ALICYCLIC COMPOUNDS

\*

VOLUME III

AROMATIC COMPOUNDS

\*

VOLUME IV

HETEROCYCLIC COMPOUNDS

\*

VOLUME V

MISCELLANEOUS

GENERAL INDEX

\*

# 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 I PART C

MONOCARBONYL DERIVATIVES  
OF ALIPHATIC HYDROCARBONS

THEIR ANALOGUES  
AND DERIVATIVES



ELSEVIER PUBLISHING COMPANY

AMSTERDAM LONDON NEW YORK

1965

## CONTRIBUTORS TO THIS VOLUME

M. F. ANSELL, D.SC., PH.D., F.R.I.C.

Department of Chemistry, Queen Mary College, London, E.1

J. G. BUCHANAN, M.A., PH.D.,

Department of Organic Chemistry, The University, Newcastle upon Tyne, 1

R. E. FAIRBAIRN, B.SC., PH.D., F.R.I.C.

Dyestuffs Division, I.C.I. Ltd., Hexagon House, Blackley, Manchester 9 (Index)

R. H. GIGG, B.SC., PH.D., A.R.I.C.,

National Institute for Medical Research, Mill Hill, London, N.W.7

R. HOWE, B.SC., PH.D., A.R.I.C.

Pharmaceuticals Division, I.C.I. Ltd., Alderley Park, Macclesfield

N. A. HUGHES, B.A., PH.D.

Department of Organic Chemistry, The University, Newcastle upon Tyne, 1

F. J. MCQUILLIN, M.A., D.PHIL.

Department of Organic Chemistry, The University, Newcastle upon Tyne, 1

G. A. SWAN, D.SC., PH.D., F.R.I.C.

Department of Organic Chemistry, The University, Newcastle upon Tyne, 1

## PREFACE TO VOLUME IC

THE reasons for this revised edition of *Rodd's* "Chemistry of Carbon Compounds", the general details with regard to Volume I, which deals with aliphatic (acyclic) compounds and the method adopted for splitting up the primary volume into a series of smaller sub-volumes for the greater convenience of the reader, are set out in the Prefaces to Volumes IA and IB.

The descriptive chapters in Volume IA dealt with aliphatic hydrocarbons and their halogen-substituted derivatives; those in Volume IB described the remaining singly-linked, mono-substituted aliphatic hydrocarbons.

The present book, Volume IC, contrives to describe a single broad class of compounds, namely, aliphatic monocarbonyl compounds, their analogues and derivatives, *i.e.* derivatives of aliphatic hydrocarbons in which one carbon atom carries a doubly-linked oxygen, sulphur or nitrogen atom, or two or more such atoms linked singly or by both modes of attachment. Aldehydes and ketones and their derivatives are discussed in Chapter 8, monocarboxylic acids and their analogues in Chapter 9, while Chapter 10 describes the chemistry of carbon monoxide, isocyanides and fulminic acid, compounds containing a single "bivalent" carbon atom, and Chapter 11, that of carbonic acid and its wide range of derivatives. Again, for obvious chemical reasons, halogeno- and nitro-aldehydes and -ketones are also described in Chapter 8 and halogeno-alkanemonocarboxylic acids are included in Chapter 9; nitroalkanemonocarboxylic acids will be described in Chapter 15 (Volume ID) along side aminoalkanecarboxylic acids.

S. COFFEY

January, 1965



This page intentionally left blank

## CONTENTS

Preface . . . . .	VII
List of common abbreviations and symbols used . . . . .	XIV
Official publications . . . . .	XVI
Scientific journals and periodicals . . . . .	XVI

### *Chapter 8. Aldehydes and Ketones*

by J. G. BUCHANAN, N. A. HUGHES, F. J. MCQUILLIN AND G. A. SWAN

1. Introduction . . . . .	I
2. Saturated aldehydes . . . . .	3
a. Aldehydes, alkanals, $C_nH_{2n+1}CHO$ . . . . .	3
(i) Formation and preparation, 4 - (ii) Reactions of the aldehydes, 10 -	
(iii) Aldehydes in synthetic reactions, 14 - (iv) Individual compounds, 18	
b. Halogen substitution products of the saturated aldehydes . . . . .	24
c. Nitro-aldehydes . . . . .	26
d. Aldehyde peroxides . . . . .	26
e. Ethers and esters of the aldehyde hydrates . . . . .	27
(i) Hemiacetals; 1-alkoxyalkan-1-ols, 27 - (ii) Acetals; 1,1-dialkoxyalkan-	
nes, 28 - (iii) 1,1-Dihalogenoalkanes, 1-halogeno-1-hydroxyalkanes and 1-	
alkoxy-1-halogenoalkanes, 30 - (iv) Carboxylic esters of the aldehyde	
hydrates, 31 - (v) Aldehyde bisulphite compounds and aldehyde sulph-	
oxylates, 32	
f. Sulphur derivatives of the saturated aldehydes . . . . .	33
(i) Alkane-1,1-dithiols, 34 - (ii) Thioaldehydes; alkanethials, polymeric	
thioaldehydes and their sulphones, 34 - (iii) Thioacetals; 1,1-bisalkylthio-	
alkanes and alkylidenesulphones; 1,1-bisalkylsulphonylalkanes, 37 - (iv)	
Alkane-1,1-disulphonic acids, 39	
g. Nitrogen-containing derivatives of the aldehydes . . . . .	40
(i) Compounds derived from aldehydes and ammonia, 40 - (ii) Compounds	
derived from aldehydes and alkylamines, 44 - (iii) Aldoximes, 45 - (iv)	
Azines and substituted hydrazones, 47	
3. Unsaturated aldehydes . . . . .	48
a. Olefinic aldehydes; alkenals, $C_nH_{2n-1}CHO$ . . . . .	48
b. Acetylenic aldehydes; alkynals, $C_nH_{2n-3}CHO$ . . . . .	51
c. Di- and poly-olefinic aldehydes . . . . .	52
4. Saturated ketones . . . . .	52
a. Ketones; alkanones; oxoalkanes, $C_nH_{2n}O$ . . . . .	52
(i) Methods of formation and preparation, 53 - (ii) Properties and re-	
actions, 58 - (iii) Individual ketones, 65	
b. Halogen substitution products of the ketones . . . . .	70
c. Nitrosoketones . . . . .	71
d. Nitroketones . . . . .	71

e. Derivatives of the ketone hydrates . . . . .	72
(i) Ketone acetals; ketals; dialkoxyalkanes, 72 - (ii) Ketone halides, 72 - (iii) Ketone bisulphite compounds and sulphoxylates, 73	
f. Sulphur analogues of the saturated ketones . . . . .	73
(i) Alkane- <i>gem</i> -dithiols, 73 - (ii) Thioketones, polymeric thioketones and their sulphones, 74 - (iii) Thioketals; bisalkylthioalkanes and derived sulphones, 75	
g. Nitrogen analogues of the ketones . . . . .	76
(i) Nitro compounds, 76 - (ii) Compounds with ammonia, 76 - (iii) Compounds with alkylamines, 76 - (iv) Hydroxylamine derivatives; ketoximes, 76 - (v) Hydrazine derivatives, 78 - (vi) Ketone semicarbazones, 80 - (vii) Miscellaneous derivatives, 80	
5. Unsaturated ketones and ketens. . . . .	81
a. Ketens, $RR'C:CO$ . . . . .	81
(i) Formation and preparation, 81 - (ii) Properties, 82	
b. Olefinic ketones, $C_nH_{2n-1} \cdot CO \cdot C_nH_{2n+1}$ . . . . .	83
(i) Formation and preparation, 83 - (ii) Reactions, 84	
c. Diolefinic ketones . . . . .	87
(i) Individual compounds, 87 - (ii) The action of ammonia on acetone, mesityl oxide and phorone, 88 - (iii) Action of hydroxylamine and semicarbazide on mesityl oxide and phorone, 89	
d. Acetylenic ketones . . . . .	90

### Chapter 9. Monobasic Carboxylic Acids

by M. F. ANSELL AND R. H. GIGG

i. Introduction . . . . .	92
2. Saturated monocarboxylic acids . . . . .	96
a. Formic acid and its derivatives . . . . .	96
(i) Formic acid, 96 - (ii) Metal formates, 100 - (iii) Halides of formic acid, 101 - (iv) Esters of formic acid (formates), 101 - (v) Formamides, 102 - (vi) Hydrogen cyanide, 104 - (vii) Functional derivatives of formic acid, 109 - (viii) Derivatives of orthoformic acid, 112	
b. Saturated fatty acids . . . . .	114
(i) Formation and preparation of primary and secondary fatty acids, 115 - (ii) Synthesis of acids with tertiary groups, 123 - (iii) Physical properties of fatty acids, 124 - (iv) Chemical properties and reactions of fatty acids, 126 - (v) Individual fatty acids, 130	
3. Functional derivatives of the fatty acids . . . . .	139
a. Esters . . . . .	139
(i) Methods of formation, 139 - (ii) Properties, 144 - (iii) Reactions, 144 - (iv) Individual esters, 146	
b. Acid or acyl halides . . . . .	150
(i) Formation, 150 - (ii) Properties and reactions of acyl halides, 152 - (iii) Individual acyl halides, 154	
c. Mixed anhydrides with inorganic oxy-acids . . . . .	155
d. Carboxylic acid anhydrides . . . . .	156
(i) Formation of simple anhydrides, 156 - (ii) Formation of mixed anhydrides, 158 - (iii) Properties and reactions of acid anhydrides, 158 - (iv) Individual anhydrides, 159	
e. Peroxy-acids (per-acids) and acyl peroxides . . . . .	160
(i) Formation of peroxy-acids, 160 - (ii) Properties of peroxy-acids, 162 - (iii) Reactions of peroxy-acids, 162 - (iv) Peroxy-esters, 163 - (v) Diacyl peroxides, 164	

f. Amides . . . . .	165
(i) General methods of preparation, 166 – (ii) Properties and reactions of amides, 171 – (iii) Individual carboxamides, 173	
g. Carbohydrazides . . . . .	173
(i) Preparation, 173 – (ii) Properties and reactions, 174 – (iii) Individual carbohydrazides, 174	
h. Acyl azides . . . . .	175
(i) Preparation, 175 – (ii) Properties, 175 – (iii) Reactions, 175	
i. Nitriles or alkyl cyanides . . . . .	177
(i) General methods of preparation, 177 – (ii) Properties and reactions, 179 – (iii) Individual nitriles, 182	
j. Carboxamide chlorides and imidoyl chlorides . . . . .	182
k. Alkyl imidates . . . . .	183
l. Amidines . . . . .	185
m. Hydroxamic acids and hydroximoyl chlorides . . . . .	189
(i) Hydroxamic acids, 189 – (ii) Hydroximoyl chlorides, 190	
n. Amidoximes . . . . .	191
o. Hydroxamic acid-oximes (oxyamidoximes) and nitroso-oximes . . . . .	191
p. Hydrazidines, amidrazones and 1,2-dihydroformazans . . . . .	192
4. Thiocarboxylic acids . . . . .	193
a. Monothiocarboxylic acids and esters . . . . .	194
(i) Preparation of thiocarboxylic acids, 194 – (ii) Preparation of thiol- or S-alkyl thio-esters, 195 – (iii) Preparation of thion-esters or O-alkyl thio-esters, 195 – (iv) Reactions of monothiocarboxylic acids, 196 – (v) Individual monothiocarboxylic acids, 196	
b. Dithiocarboxylic acids and their derivatives . . . . .	196
(i) Preparation, 196 – (ii) Reactions, 196 – (iii) Individual dithiocarboxylic acids, 197	
c. Nitrogen derivatives of thiocarboxylic acids . . . . .	197
(i) Thionamides; thioamides, 197 – (ii) Thiolimidates (isothioamides, iminothioethers, thiolimidic esters, S-alkyl thioimidates), 200	
5. Halogen substitution products of the fatty acids . . . . .	201
a. Halogenated acetic acids . . . . .	207
b. Halogenated propionic acids . . . . .	212
c. Halogen derivatives of higher fatty acids . . . . .	214
6. Derivatives of ortho-fatty acids . . . . .	215
a. Ortho-esters . . . . .	215
(i) Preparation, 215 – (ii) Reactions, 216 – (iii) Individual ortho-esters, 217	
b. Other ortho-compounds . . . . .	218
7. Unsaturated aliphatic monocarboxylic acids . . . . .	218
a. Introduction . . . . .	218
(i) Methods of isolation and analysis of unsaturated acids, 218 – (ii) Biological significance of unsaturated acids, 219 – (iii) General references, 220	
b. Synthesis of unsaturated acids . . . . .	220
(i) $\alpha\beta$ -Ethylenic acids, 220 – (ii) $\beta\gamma$ - and $\gamma\delta$ -Ethylenic acids, 221 – (iii) Ethylenic acids with isolated double bonds, 222 – (iv) $\alpha\beta$ -Acetylenic acids, 222 – (v) Acetylenic acids with isolated triple bonds, 223 – (vi) Allenic acids, 223	
c. Properties and reactions . . . . .	224
(i) Hydrogenation and reduction, 224 – (ii) Polymerisation, 225 – (iii) Oxidation, 225 – (iv) Action of alkalis, 226 – (v) Action of sulphuric acid, 226 – (vi) Addition of halogens, 227 – (vii) Addition of mercuric acetate, 227 – (viii) Characteristic reactions of $\alpha\beta$ -unsaturated acids, 227	

d. Unsaturated acids with three carbon atoms . . . . .	228
e. Unsaturated acids with four carbon atoms . . . . .	230
f. Unsaturated acids with 5-10 carbon atoms . . . . .	233
(i) C <sub>5</sub> -acids, 223 - (ii) C <sub>6</sub> -acids, 234 - (iii) C <sub>7</sub> -acids, 237 - (iv) C <sub>8</sub> -acids, 238 - (v) C <sub>9</sub> -acids, 239 - (vi) C <sub>10</sub> -acids, 239	
g. Unsaturated acids with 11-17 carbon atoms . . . . .	240
(i) C <sub>11</sub> -acids, 240 - (ii) C <sub>12</sub> -acids, 241 - (iii) C <sub>13</sub> -acids, 242 - (iv) C <sub>14</sub> -acids, 242 - (v) C <sub>15</sub> -acids, 243 - (vi) C <sub>16</sub> -acids, 243	
h. Unsaturated acids with 18 carbon atoms . . . . .	244
(i) -Enoic and -ynoic acids, 244 - (ii) -Dienoic and -enynoic acids, 246 - (iii) -Trienoic and -enediynoic acids, 247 - (iv) -Tetraenoic acids, 249	
i. Unsaturated with more than 18 carbon atoms . . . . .	249
(i) C <sub>20</sub> -acids, 249 - (ii) C <sub>22</sub> -acids, 251 - (iii) C <sub>23</sub> -acids, 252 - (iv) C <sub>24</sub> -acids, 252 - (v) C <sub>26</sub> -acids, 252 - (vi) C <sub>27</sub> -acids, 252	

*Chapter 10. Carbon Monoxide, Isocyanides and Fulminic Acid*

by M. F. ANSELL

1. Introduction . . . . .	253
2. Carbon monoxide . . . . .	254
a. Metal carbonyls . . . . .	255
(i) Formation and preparation, 255 - (ii) Structure, 256	
b. Carbonyl hydrides or hydrocarbonyls . . . . .	257
c. Synthetic uses of carbon monoxide . . . . .	258
3. Isocyanides, isonitriles or carbylamines . . . . .	262
4. Fulminic acid . . . . .	264

*Chapter 11. Carbonic Acid and its Derivatives*

by R. HOWE

1. Metacarbonic acid and its esters . . . . .	268
a. Esters of carbonic acid. . . . .	271
(i) Primary esters of carbonic acid; alkyl hydrogen carbonates, 271 - (ii) Neutral esters, dialkyl carbonates, alkoxycarbonyloxyalkanes, 272 - (iii) Percarbonates, 274	
b. Anhydrides of primary esters of carbonic acid . . . . .	274
(i) Esters of dicarbonic acid, 274 - (ii) Mixed anhydrides of primary carbo- nates and monocarboxylic acids; alkoxycarbonyl esters, 275	
2. Halides of carbonic acid . . . . .	276
a. Monohalide esters . . . . .	277
(i) Chloroformic esters, alkyl chloroformates, chlorocarbonates or alkoxy- carbonyl chlorides, 277 - (ii) Alkyl fluoroformates, 278	
b. Carbonyl halides . . . . .	279
3. Sulphur analogues of carbonic acid and their derivatives . . . . .	281
a. Carbon oxysulphide and carbon disulphide . . . . .	282
b. Thiocarbonic acids . . . . .	284
(i) Monothiocarbonic acids, 284 - (ii) Dithiocarbonic acids, 285 - (iii) Trithiocarbonic acid, 287	
c. Halides of the thiocarbonic acids . . . . .	289
4. Amides and related derivatives of carbonic acid and the thiocarbonic acids. . . . .	290

a. Carbamic acid derivatives . . . . .	290
(i) Alkyl carbamates, urethanes, 291 – (ii) Carbamic acid derivatives of the amino-carboxylic acids, 297 – (iii) <i>N</i> -Halogeno-, nitroso- and nitro-urethanes, 299 – (iv) Carbamoyl chlorides, “urea chlorides”, 301 – (v) Carbamoyl phosphates, 302	
b. Urea and its derivatives . . . . .	303
Constitution of urea, 304 – Formation of urea, 305 – Manufacture of urea, 306 – Reactions of urea, 307 – Urea clathrate compounds, 308 – Determination of urea, 310	
(i) Alkylureas, 311 – (ii) Diureas, 314 – (iii) Halogenoureas, 314 – (iv) Nitroso- and nitro-ureas, 314 – (v) Ureides, 315	
c. Derivatives of iminodicarboxylic acid and nitrilotricarboxylic acid . . . . .	316
(i) Derivatives of iminodicarboxylic acid, 316 – (ii) Derivatives of nitrilotricarboxylic acid, 320	
d. Derivatives of iminocarbonic acid and isourea . . . . .	320
(i) Derivatives of iminocarbonic acid, 320 – Derivatives of isourea, 321	
e. Hydrazino, hydrazo, azo, azido and hydroxyamino derivatives of carbonic acid . . . . .	322
(i) Hydrazinecarboxylic acids and their derivatives, 322 – (ii) Azodicarboxylic acid and its derivatives, 326 – (iii) Azides of derivatives of carbonic acid, 327 – (iv) Hydroxyamino derivatives of carbonic acid, 327	
f. Sulphur analogues of carbamic acid and urea . . . . .	328
(i) Sulphur analogues of carbonic acid and its derivatives, 328 – (ii) Thiourea, isothiurea and their derivatives, 334 – (iii) Hydrazino, azo and azido derivatives of thiocarbonic acid, 339	
5. Guanidine and its derivatives . . . . .	341
6. Nitriles and imides of carbonic and thiocarbonic acids . . . . .	354
a. Cyanic acid and its derivatives . . . . .	354
(i) Esters of cyanic acid, 356 – (ii) Cyanogen halides, 361	
b. Sulphur compounds of cyanogen . . . . .	363
(i) Thiocyanic acid, 363 – (ii) Thiocyanogen halides, 366 – (iii) Alkyl thiocyanates, esters of thiocyanic acid, 367 – (iv) Alkyl isothiocyanates, esters of isothiocyanic acid, 369	
c. Cyanamide and its derivatives . . . . .	373
d. Derivatives of carbodi-imide . . . . .	376
7. Derivatives of orthocarbonic acid . . . . .	379
a. Esters, tetra-alkoxymethanes . . . . .	379
b. Amino-derivatives of orthocarbonic acid . . . . .	379
c. Sulphur derivatives of orthocarbonic acid . . . . .	380
(i) Esters, 380 – (ii) Sulphenyl halides and sulphonic acids, 381	
INDEX . . . . .	383

## VOLUMES IA, B, D, E, F AND G

Vol. IA	General Introduction; Hydrocarbons; Halogen Derivatives
Vol. IB	Monohydric Alcohols, Their Ethers and Esters; Sulphur Analogues; Nitrogen Derivatives; Organometallic Compounds
Vol. ID	Dihydric Alcohols, Their Oxidation Products and Derivatives
Vol. IE	Tri- and Tetra-hydric Alcohols, Their Oxidation Products and Derivatives
Vol. IF	Penta- and Higher-hydric Alcohols, Their Oxidation Products and Derivatives; Saccharides
Vol. IG	Enzymes; Macromolecules; Cumulative Index Vols. IA–IG

LIST OF COMMON ABBREVIATIONS AND  
SYMBOLS USED

A	acid
Å	Ångström units
Ac	acetyl
<i>a</i>	axial
<i>as</i>	asymmetrical
at.	atmosphere
B	base
Bu	butyl
b.p.	boiling point
C, mC and $\mu$ C	curie, millicurie and microcurie
conc.	concentrated
crit.	critical
D	Debye unit, $1 \times 10^{-18}$ e.s.u.
<i>D</i>	dissociation energy
D	dextro-rotatory
DL	optically inactive (externally compensated)
<i>d</i>	density
dec. or decomp.	with decomposition
deriv.	derivative
<i>E</i>	energy; extinction; electromeric effect
$E_1, E_2$	uni- and bi-molecular elimination mechanisms
E1cB	unimolecular elimination in conjugate base
E.S.R.	electron spin resonance
Et	ethyl
<i>e</i>	nuclear charge; equatorial
<i>f</i>	oscillator strength
f.p.	freezing point
<i>G</i>	free energy
G.L.C.	gas liquid chromatography
<i>g</i>	spectroscopic splitting factor, 2.0023
<i>H</i>	applied magnetic field; heat content
<i>h</i>	Planck's constant
<i>I</i>	spin quantum number; intensity; inductive effect
<i>K</i>	dissociation constant
<i>k</i>	Boltzmann constant; velocity constant
kcal.	kilocalories
L	laevorotatory
<i>M</i>	molecular weight; molar; mesomeric effect
Me	methyl
<i>m</i>	mass; mole; molecule; <i>meta</i> -

ml	millilitre
m.p.	melting point
[M]	molecular rotation
$N$	Avogadro number; normal
N.M.R.	nuclear magnetic resonance
$n$	normal; refractive index; principal quantum number
$o$	ortho-
$P$	polarisation; probability; orbital state
Pr	propyl
Ph	phenyl
$p$	<i>para</i> -; orbital
$R$	clockwise configuration
$S$	counterclockwise configuration; entropy; net spin of incompleated electronic shells; orbital state
$S_{N1}$ , $S_{N2}$	uni- and bi-molecular nucleophilic substitution mechanisms
$S_Ni$	internal nucleophilic substitution mechanisms
$s$	symmetrical; orbital
<i>sec</i>	secondary
soln.	solution
$T$	absolute temperature
Tosyl	<i>p</i> -toluenesulphonyl
Trityl	triphenylmethyl
$t$	time
temp.	temperature (in degrees centigrade)
<i>tert</i>	tertiary
$U$	potential energy
$v$	velocity
$\alpha$	optical rotation (in water unless otherwise stated)
[ $\alpha$ ]	specific optical rotation
$\alpha_A$	atomic susceptibility
$\alpha_E$	electronic susceptibility
$\epsilon$	dielectric constant; extinction coefficient
$\mu$	microns ( $10^{-4}$ cm); dipole moment; magnetic moment
$\mu_B$	Bohr magneton
$\lambda$	wavelength
$\nu$	frequency; wave number
$\chi$ , $\chi_d$ , $\chi_\mu$	magnetic, diamagnetic and paramagnetic susceptibilities
$\sim$	about
(+)	dextrorotatory
(-)	laevorotatory
$\ominus$	negative charge
$\oplus$	positive charge



## OFFICIAL PUBLICATIONS

B.P.	British (United Kingdom) Patent
F.P.	French Patent
G.P.	German Patent
Sw.P.	Swiss Patent
U.S.P.	United States Patent
B.I.O.S.	British Intelligence Objectives Sub-Committee Reports, H.M. Stationery Office, London.
C.I.O.S.	Combined Intelligence Objectives Sub-Committee Reports
F.I.A.T.	Field Information Agency, Technical Reports of U.S. Group Control Council for Germany
B.S.	British Standards Specification
A.S.T.M.	American Society for Testing and Materials

## SCIENTIFIC JOURNALS AND PERIODICALS

With few obvious and self-explanatory modifications the abbreviations used in references to journals and periodicals comprising the extensive literature on organic chemistry, are those used in the World List of Scientific Periodicals.

## Chapter 8

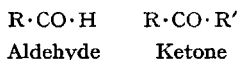
# Aldehydes and Ketones

J. G. BUCHANAN, N. A. HUGHES, F. J. McQUILLIN AND G. A. SWAN

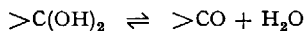
### 1. Introduction

The close relationship which exists, on the one hand, between the primary alcohols, the aldehydes and the carboxylic acids, and, on the other hand, between the secondary alcohols and the ketones has already been pointed out.

Aldehydes and ketones resemble each other in containing the carbonyl group CO; in aldehydes this is combined with either two hydrogen atoms, in formaldehyde, or with one alkyl group and a hydrogen atom, in the higher members of the series; in ketones it is combined with two alkyl groups:



Aldehydes and ketones can be regarded as the anhydrides of dihydroxy compounds in which both hydroxyl groups are attached to the same carbon atom. Where a reaction leads to a compound containing the group C(OH)<sub>2</sub>, the corresponding compound containing the CO group is formed by loss of water, except in a few cases where the dihydroxy compound, the aldehyde or ketone hydrate, is stable. In aqueous solution there is an equilibrium between the two forms,

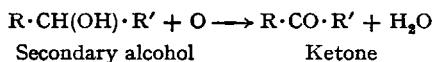
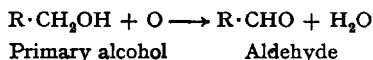


The ethers of the two hydrated forms R·CH(OR')<sub>2</sub> and R·C(OR')<sub>2</sub>·R", known as acetals and ketals, respectively, are stable compounds.

A comprehensive account of the chemistry of aldehydes is to be found in "Die Methoden der Organischen Chemie", *J. Houben* and *T. Weyl*, 4th Edn., Ed. *E. Müller*, Thieme, Stuttgart, 1954, Vol. VII, Part 1.

*Preparation.* The following methods are common to aldehydes and ketones.

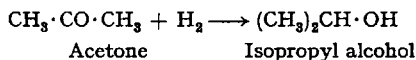
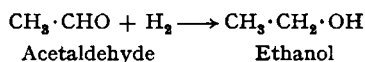
(1) Oxidation of the alcohols, whereby aldehydes are formed from the primary, and ketones from the secondary, alcohols:



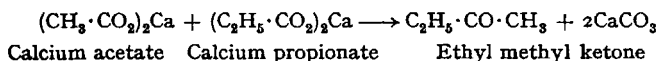
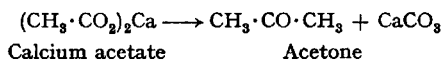
These reactions involve dehydrogenation and *H. Wieland* showed that they can occur in the absence of free oxygen, in the presence of finely divided palladium and a suitable hydrogen-acceptor, such as a quinone (Ber., 1912, 45, 484; 1913, 46, 3327). Biological oxidations may be similar in mechanism (*Wieland, ibid.*, 1914, 47, 2085; *E. Baldwin*, "Dynamic Aspects of Biochemistry", 2nd Edn., Cambridge, 1953, Chap. 6). More recently, the oxidation of alcohols by chromic acid has been shown to involve chromate esters as intermediates (*F. H. Westheimer*, Chem. Reviews, 1949, 45, 419; *W. A. Waters*, Quart. Reviews, 1958, 12, 277).

By further oxidation the aldehydes yield carboxylic acids having the same number of carbon atoms, whilst the ketones are broken down to smaller fragments.

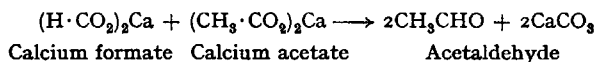
Conversely, aldehydes and ketones are reconverted into primary and secondary alcohols by the addition of hydrogen:



(2) The dry distillation of the calcium, barium or other heavy metal salts of monobasic fatty acids or of a mixture of salts of two different acids, gives in the first case symmetrical and in the second unsymmetrical ketones:



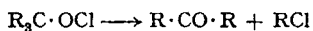
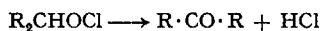
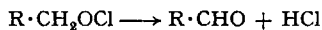
If one acid is formic acid, an aldehyde is produced:



When this reaction is applied to the calcium salts of dibasic acids such as adipic, pimelic and suberic acid, *cyclic* ketones are produced.

(3) Aldehydes and ketones are obtained by direct addition of water to acetylenic hydrocarbons in the presence of a mercury salt as catalyst (see Vol. IA, p. 457).

(4) Alkyl hypochlorites, obtained from the alcohols by the action of chlorine and alkali, decompose under suitable conditions of light and temperature to yield aldehydes or ketones and hydrogen chloride. The hypochlorites of tertiary alcohols yield ketones and alkyl chlorides (*F. D. Chattaway and O. G. Backeberg, J. chem. Soc., 1923, 123, 2999*):



## 2. Saturated aldehydes

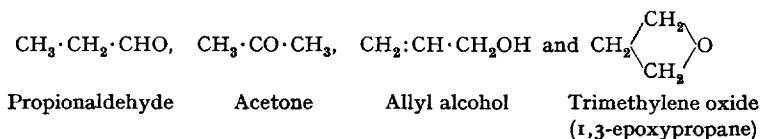
### (a) Aldehydes, alkanals, $\text{C}_n\text{H}_{2n+1}\cdot\text{CHO}$

The homologous aldehydes show in their properties a gradation similar to that of the alcohols. The lower members are gaseous or volatile liquids, soluble in water, and have a characteristic odour, but the higher are solids, insoluble in water. In general, they are less soluble in water and more volatile than the alcohols. Chemically, they are neutral substances. Their reactivity places them amongst the most important synthetic reagents.

*Nomenclature and isomerism.* Empirically, the aldehydes are distinguished from the alcohols by possessing two atoms less of hydrogen—hence their name, suggested by Liebig (from *Alcohol dehydrogenatus*).

The common name of an aldehyde is derived from that of the acid of the same number of carbon atoms to which it gives rise on oxidation *e.g.* acetaldehyde from acetic acid. In the Geneva nomenclature, now adopted by the I.U.P.A.C., the names of the aldehydes are formed from the corresponding saturated hydrocarbons by substituting the final "e" by the suffix al; thus acetaldehyde,  $\text{CH}_3\cdot\text{CHO}$  is ethanal. The systematic numbering starts from the CHO group; *e.g.*  $(\text{CH}_3)_2\text{CH}\cdot\text{CHO}$  is 2-methylpropanal.

The number of isomeric aldehydes of definite carbon content equals the number of possible primary alcohols having the same carbon content. The aldehydes are isomeric with the ketones, the ethylenic alcohols and the anhydrides of the ethylene glycol series, containing an equal number of carbon atoms; thus the following are isomeric:



(i) *Formation and preparation*

(1) *By the oxidation of primary alcohols*, whereby the  $\text{CH}_2 \cdot \text{OH}$  is converted into the CHO group, e.g. by potassium dichromate and dilute sulphuric acid or by atmospheric oxygen in the presence of a catalyst (*R. R. Davies and H. H. Hodgson*, J. chem. Soc., 1943, 282).

When chlorine is used as an oxidising agent, the aldehyde is first formed, but chlorination of the alkyl group follows.

The main by-products in the oxidation of primary alcohols to aldehydes are carboxylic acids which may become esterified during the reaction. Volatile aldehydes should therefore be removed by distillation as formed (*Org. Synth.*, 1932, 12, 64).

Aldehydes may be prepared by a modification of the Oppenauer method of oxidation (Vol. IB, p. 14) (*A. Lauchenauer and H. Schinz*, *Helv.*, 1949, 32, 1265).

*tert*-Butyl chromate is a fairly specific reagent for the oxidation of primary alcohols to aldehydes (*R. V. Oppenauer and H. Oberrauch*, *Anales Asoc. quim. argentina*, 1949, 37, 246).

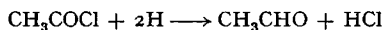
(2) *By direct decomposition (dehydrogenation) of a primary alcohol* by passing alcohol vapours through a red-hot tube or better over finely divided copper at 200–250° (*W. Ipatiew*, *Ber.*, 1903, 36, 1990; *P. Sabatier and J. B. Senderens*, *Compt. rend.*, 1903, 136, 738; *L. Bouveault*, *Bull. Soc. chim. Fr.*, 1908, [iv], 4, 119; *H. Adkins et al.*, *J. Amer. chem. Soc.*, 1933, 55, 2992; *R. E. Dunbar and M. R. Arnold*, *J. org. Chem.*, 1945, 10, 501).

Dehydrogenation can also be effected by heating with Raney nickel. In the case of optically active alcohols, such as 2-methylbutan-1-ol, this can occur without loss of optical activity (*E. J. Badin and E. Pacsu*, *J. Amer. chem. Soc.*, 1944, 66, 1963).

(3) *By heating the calcium salts of fatty acids with calcium formate* (*F. Krafft*, *Ber.*, 1880, 13, 1413).

(4) *By the reduction of acid chlorides* by sodium in moist ether (*W. H. Perkin jun. and J. J. Sudborough*, *Proc. chem. Soc.*, 1894, 10, 216) or prefer-

ably by hydrogenation in the presence of a poisoned palladium-barium sulphate catalyst (*K. W. Rosenmund*, Ber., 1918, 51, 585; *E. Mosettig* and *R. Mozingo*, Org. Reactions, 1948, 4, 362),

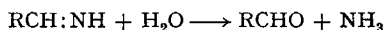
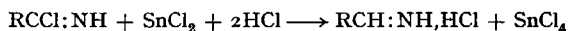
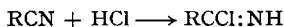


or by lithium tri-*tert*-butoxyaluminumhydride at  $-70^\circ$ ; at  $0^\circ$  the aldehydes, are themselves reduced further (*H. C. Brown* and *R. F. McFarlin*, J. Amer. chem. Soc., 1958, 80, 5372).

(5) *By the reduction of carboxylic acids with sodium amalgam* (*Davies* and *Hodgson*, J. Soc. chem. Ind., 1943, 62, 128).

(6) *From alkyl cyanides.* (a) By way of their iminochlorides.

The cyanide is added to a solution of stannous chloride in ether saturated with hydrogen chloride. The product is hydrolysed by warm water to the aldehyde, which is extracted with a solvent or steam-distilled. The yields are very good with the higher cyanides (*H. Stephen*, J. chem. Soc., 1925, 127, 1874; *Mosettig*, Org. Reactions, 1954, 8, 246):



(b) By catalytic hydrogenation in the presence of semicarbazide (*H. Plieninger* and *G. Werst*, Ber., 1955, 88, 1956).

(c) By reduction with lithium triethoxyaluminumhydride (*Brown*, *C. J. Shoaf* and *C. P. Garg*, Tetrahedron Letters, 1959, 3, 9), lithium trimethylborohydride (*A. Khuri*, Diss. Abs., 1960, 21, 55) or lithium aluminium hydride (*Mosettig*, *loc. cit.* p. 252).

(7) *By reduction of a N,N-disubstituted amide* derived from *N*-methylaniline (*F. Weygand et al.*, Angew. Chem., 1953, 65, 525; *S. S. Nigam* and *B. C. L. Weedon*, J. chem. Soc., 1957, 3320), ethyleneimine (*Brown* and *A. Tsukamoto*, J. Amer. chem. Soc., 1961, 83, 2016) or a pyrazole (*W. Ried* and *F. J. Königstein*, Angew. Chem., 1958, 70, 165), with lithium aluminium hydride. Alternatively, the *N,N*-dimethylamide may be reduced with lithium diethoxyaluminumhydride (*Brown* and *A. Tsukamoto*, J. Amer. chem. Soc., 1959, 81, 502). Reduction of substituted amides to aldehydes by alkali metals in liquid ammonia is also possible (*A. J. Birch*, *J. Cymerman-Craig* and *M. Slaytor*, Chem. and Ind., 1954, 1559; Australian J. Chem., 1955, 8, 512).

(8) *By the hydrolysis of Reissert's compounds* ( $\alpha$ -acyl- $\gamma$ , $\delta$ -dihydroquinaldonitriles); this provides an indirect method for the conversion of carboxylic

acids into aldehydes (*J. M. Grosheintz and H. O. L. Fischer*, J. Amer. chem. Soc., 1941, 63, 2021; *Mosettig, loc. cit.* p. 220).

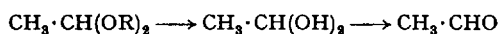
(9) *By the alkaline decomposition of benzenesulphonacylhydrazides* (*M. Sprecher, M. Feldkimel and M. Wilchek*, J. org. Chem., 1961, 26, 3664).

(10) *By hydrolysis of some of their derivatives*; this method is of practical importance.

(a) From aldehyde-ammonia and aldehyde-bisulphite compounds (see pp. 40, 31); from oximes and hydrazones (pp. 45, 47).

(b) From alkylidene dihalides, e.g.  $\text{CH}_3 \cdot \text{CHCl}_2$  by heating them with water and a base such as lead oxide.

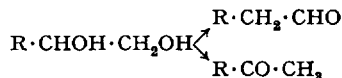
(c) From acetals and alkylidene diacetates, by dilute acids or (in the latter case) alkalis:



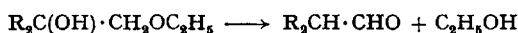
(11) *From  $\alpha\beta$ -glycols or their ethers*, containing at least one primary alcoholic group, by loss of water or alcohol, or from the corresponding ethylene oxide, by molecular rearrangement.

(a) Ethylene glycol yields acetaldehyde when heated with dilute sulphuric acid (*K. Krassusky*, J. Soc. phys.-chem. russe, 1902, 34, 537, 556).

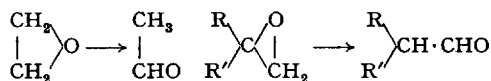
(b) Primary-secondary glycols under the same conditions yield a mixture of aldehyde and ketone:



(c) Primary-tertiary ethylene glycols yield aldehydes when heated with anhydrous formic or oxalic acid (*A. Béhal and M. Sommelet*, Compt. rend., 1904, 138, 89); the ethers  $\text{R}_2\text{C}(\text{OH}) \cdot \text{CH}_2\text{OR}$  react particularly easily (*R. A. Barnes and W. M. Budde*, J. Amer. chem. Soc., 1946, 68, 2339):



(d) Ethylene oxide and its homologues, especially the primary-tertiary compounds, undergo rearrangement when heated with alumina (*W. Ipatiew and W. Leontowitsch*, Ber., 1903, 36, 2016) or on boiling with dilute acid (*J. von Braun, ibid.*, 1923, 56, 2178; *Barnes and Budde, loc. cit.*):



(12) *From sodium salts of primary nitroparaffins*, which yield aldehydes and