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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

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GENERAL INTRODUCTION

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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*

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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 E. L. 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*

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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

★

CONTRIBUTORS TO THIS VOLUME

H. R. V. ARNSTEIN, D.SC., A.R.C.S., D.I.C.
National Institute for Medical Research, Mill Hill, London, N.W.7

D. V. BANTHORPE, PH.D.,
Department of Chemistry, University College, London, W.C.1

Professor R. BELCHER, PH.D., D.SC., F.INST.F., F.R.I.C.
Department of Chemistry, University of Birmingham

K. I. BEYNON, B.SC., PH.D.,
Woodstock Agricultural Research Centre, Shell Research Ltd., Sittingbourne, Kent

W. BYERS BROWN, M.SC.,
Theoretical Chemistry Institute, University of Wisconsin, Madison 6, Wis., U.S.A.

ISOBEL G. M. CAMPBELL, B.SC., PH.D.,
Department of Chemistry, University of Southampton

J. D. DOWNER, PH.D., D.I.C., A.R.I.C.,
Thornton Research Centre, Chester

R. E. FAIRBAIRN, B.SC., PH.D., F.R.I.C.,
Dyestuffs Division, I.C.I. Ltd., Hexagon House, Blackley, Manchester 9

R. F. GARWOOD, B.SC., PH.D., A.R.I.C.,
Department of Chemistry, Queen Mary College, London, E.C.1

Professor D. H. HEY, PH.D., D.SC., F.R.S., F.R.I.C.,
Department of Chemistry, King's College, London, W.C.2

ALISON M. G. MACDONALD, M.SC., PH.D., A.R.I.C.,
Department of Chemistry, University of Birmingham

Professor W. K. R. MUSGRAVE, PH.D., D.SC.,
Department of Chemistry, University of Durham

J. E. PAGE, PH.D., D.SC., F.R.I.C.,
Glaxo Laboratories, Greenford, Middx.

E. H. RODD, D.SC., F.C.G.I., D.I.C., F.R.I.C.,
Limpley Stoke, Bath

Professor H. D. SPRINGALL, M.A., B.SC., D.PHIL., F.R.I.C.,
Department of Chemistry, University of Keele

W. I. STEPHEN, B.SC., PH.D., A.R.I.C.,
Department of Chemistry, University of Birmingham

D. F. STYLES, A.M.C.T., A.I.I.N.F.S.C.,
Dyestuffs Division, I.C.I. Ltd., Hexagon House, Blackley, Manchester 9

W. A. WATERS, M.A., PH.D., SC.D., F.R.S., F.R.I.C.,
Dyson Perrin's Laboratory, Oxford

A. F. WELLS, M.A., SC.D.,
Dyestuffs Division, I.C.I. Ltd., Hexagon House, Blackley, Manchester 9

PREFACE TO VOLUME I

THE first volume of *Rodd's "Chemistry of Carbon Compounds"*, or simply "*Rodd*", as it is more usually called, appeared in 1951. In his preface, Dr. Rodd mentioned that "as editor he undertook a task the magnitude of which he hardly grasped". The task was indeed a formidable one and he was to devote himself wholeheartedly to it for a further ten years. Meanwhile, he had the satisfaction of seeing the project come to fruition, and the book become accepted as the most comprehensive, modern text-book of factual organic chemistry. The early volumes of the original edition were written just after World War II when the great upsurge in the publication of scientific information was becoming apparent. Ever since then the output of new factual and theoretical information on organic chemistry has continued to increase and shows no sign of slackening. It was clear that a new, revised edition of the book was required, a view which has been amply confirmed as the revised chapters have come forward.

Volume I of this new edition, dealing with aliphatic compounds, follows, in the main, the original framework based on the *Richter* classification, since, even with its imperfections, this is still regarded as being the most satisfactory for a book of this kind. Many of the chapters are therefore similar in scope to the corresponding ones in the original edition. Some modifications have, however, been introduced to overcome the most obvious defects. Thus a change has been made in dealing with the so-called "non-functional" groups of substituents, the halogens, nitroso, nitro, azo and azoxy. In all these cases, on the *Richter* classification the poly-substituted derivatives of the hydrocarbons are fragmented and their descriptions dispersed throughout various chapters; according to their structure di-substituted derivatives appear as derivatives of glycols or aldehydes and ketones, tri-substituted derivatives as those of glycolic aldehyde, glycerol or formic acid, and tetra-substituted methanes as derivatives of carbonic acid. In order to avoid this fragmentation all the main types of halogeno-substituted hydrocarbons are now described in Chapter 3, and the mono- and poly-nitroalkanes, etc. in Chapter 6; halohydrins and nitroalkanols are described under monohydric alcohols, halogenocarboxylic acids under carboxylic acids, etc., as if they were mono-functional compounds.

A further change has been made in the classification of carbon monoxide,

isocyanides and fulminic acid, which are no longer regarded as derivatives of formic acid, but are classified in Chapter 10 as derivatives of divalent carbon, while carbonic acid and its derivatives are described in Chapter 11 as being relatively simple derivatives of methane rather than as dihydroxy-carbonyl compounds intermediate between aldehydo- and keto-acids and dicarboxylic acids in the original classification. In all other cases where there are two or more functional groups, in the usually accepted sense, the original classification is maintained. In this classification all compounds except those mentioned above are related to mono-, di-, tri- etc. -hydric alcohols. Amines are regarded as generically related to alcohols by replacement of the hydroxyl group by the amino group and consequently follow them. In the same way thiols are derived from alcohols, the hydroxyl group being replaced by the thiol group, whilst sulfoxides, sulphones and sulphonic acids follow in that order as oxidation products of the parent thiol.

Remembering that, by a somewhat broad extension of definitions, all aliphatic compounds other than the hydrocarbons and the non-functional derivatives mentioned above (although these may be included if the extension is stretched far enough) are regarded as derived from the alcohols and their oxidation products, the reader will have little difficulty in finding his way about the volumes.

Two other changes should be noticed; the Chapter on Synthetic Macromolecules and Rubber, originally in Vol. II, is now brought forward to its more logical position in Vol. I, and the original chapter on Proteins is missing. The basic chemistry is discussed in the chapter on amino-acids and, since the detailed descriptive matter forms part of the original Vol. V, it was considered more appropriate to defer the revision of this chapter to the final volume.

In the last fifteen years the tendency for the organic chemist to make use of the work and techniques of the physicist and physical chemist, in his own particular problems, and for the theoretical organic chemist to take advantage of ideas developed in the fields of mathematics and physics, especially atomic physics, has become more and more marked. This is reflected in the introductory essays on the more important techniques and physical methods of investigation now used quite generally by organic chemists. All these essays have needed to be rewritten; some, especially those on analysis, spectroscopy, stereochemistry and reaction mechanisms, are considerably extended and two additional essays on the use of isotopes in organic chemistry, and on the wave mechanics of carbon compounds, are now included.

In revising the various chapters of the book the aim has been to bring the subject matter up to date and the nomenclature into line with the rules

laid down by the International Union of Pure and Applied Chemistry (IUPAC), so that the book shall continue to serve as a work of reference for the accumulated factual knowledge of organic chemistry and to give guidance to original sources and other literature for details beyond its scope. In the latter connection particular care has been taken to refer to the extensive literature now existing in the form of review articles and monographs. As in the original edition, the subject matter is mainly descriptive but more attention is of necessity now given to important physical chemical, structural and mechanistic aspects of the various classes of compounds.

Acknowledgement is made in the appropriate places for permission to reproduce drawings and diagrams published elsewhere. Such permission has been kindly given by The Chemical Society, London, The Royal Society of London, The Royal Institute of Chemistry, London, The Optical Society of America, The Cornell University Press, New York, and Messrs. Longmans, Green and Co., to whom the publishers express their grateful thanks. The editor also wishes to acknowledge with gratitude the help and encouragement he has had from the members of the Advisory Board, LORD TODD, Sir JAMES COOK, Sir EWART JONES, Sir ROBERT ROBINSON, Professor R. N. HASZELDINE, Professor R. D. HAWORTH, Professor E. L. HIRST, and especially, his colleague over many years Dr. E. H. RODD, who continues to act in a very practical sense as the "father" of the present edition and whose training in editorship and advice on innumerable matters have been invaluable. Finally, a word of thanks is due to the willing band of contributors, who have given freely of their time and knowledge, and have at all times been most co-operative and to Mr. E. B. ROBINSON, M.Sc, A.R.I.C., for help in proof-reading.

S. COFFEY

February, 1964

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 μ C	curie, millicurie and microcurie
conc.	concentrated
crit.	critical
D	Debye unit, 1×10^{-18} e.s.u.
<i>D</i>	dissociation energy
<i>D</i>	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
ErcB	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
<i>L</i>	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
<i>n</i>	normal; refractive index; principal quantum number
<i>o</i>	ortho-
<i>P</i>	polarisation; probability; orbital state
Pr	propyl
Ph	phenyl
<i>p</i>	<i>para</i> -; orbital
<i>R</i>	clockwise configuration
<i>S</i>	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
<i>s</i>	symmetrical; orbital
<i>sec</i>	secondary
soln.	solution
<i>T</i>	absolute temperature
Tosyl	<i>p</i> -toluenesulphonyl
Trityl	triphenylmethyl
<i>t</i>	time
temp.	temperature (in degrees centigrade)
<i>tert</i>	tertiary
<i>U</i>	potential energy
<i>v</i>	velocity
α	optical rotation (in water unless otherwise stated)
[α]	specific optical rotation
α_A	atomic susceptibility
α_E	electronic susceptibility
ϵ	dielectric constant; extinction coefficient
μ	microns (10^{-4} cm); dipole moment; magnetic moment
μ_B	Bohr magneton
λ	wavelength
ν	frequency; wave number
χ, χ_d, χ_μ	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.

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ALIPHATIC COMPOUNDS

Chapter 1. The Saturated or Paraffin Hydrocarbons. Alkanes

by J. D. DOWNER and K. I. BEYNON

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- Vol. IC Di-, Tri- and Tetra-hydric Alcohols; Their Oxidation Products and Derivatives
- Vol. ID Penta- and Higher Poly-hydric Alcohols; Their Oxidation Products and Derivatives; Saccharides
- Vol. IE Enzymes; Macromolecules; Cumulative Index Vols. IA–IE