

**Handbook of Hydroxyacetophenones:
Preparation and Physical Properties**

(Enlarged 2nd edition; 2-volume set)

Handbook of Hydroxyacetophenones: Preparation and Physical Properties

Enlarged 2nd edition; 2-volume set

Volume 1

by

Robert Martin

*formerly of the Institut Curie
Paris, France*

 **Springer**

Handbook of Hydroxyacetophenones: Preparation and Physical Properties

Enlarged 2nd edition; 2-volume set

Volume 2

by

Robert Martin

*formerly of the Institut Curie
Paris, France*

 **Springer**

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 1-4020-2290-5 (set)

ISBN 1-4020-2291-3 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Sold and distributed in North, Central and South America
by Springer,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Springer,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

All Rights Reserved

© 2005 Springer

No part of this work may be reproduced, stored in a retrieval system, or transmitted
in any form or by any means, electronic, mechanical, photocopying, microfilming, recording
or otherwise, without written permission from the Publisher, with the exception
of any material supplied specifically for the purpose of being entered
and executed on a computer system, for exclusive use by the purchaser of the work.

Printed in the Netherlands.

DEDICATION

To my dear Angèle, my faithful and devoted wife,
and our two mothers, Alice and Caroline, whom we are missing so much.

Robert MARTIN

CONTENTS

Short biography	ix
Foreword	xi
Acknowledgements	xiii
Introduction	1

Volume 1

MONOKETONES UNSUBSTITUTED ON THE ACETYL GROUPS

Chapter 1. Compounds derived from acetic acid	3–417
References	419
Molecular Formula Index	471
Chemical Abstracts Registry Numbers	521
Usual Names Index	545
Common Abbreviations	551

CONTENTS

Dedication page	
Short biography	
FOREWORD	ix
ACKNOWLEDGEMENTS	xi
Introduction	1

Volume 2

MONOKETONES SUBSTITUTED ON THE ACETYL GROUPS

Chapter 2. Compounds derived from halogenoacetic acids	3
2.1. <i>Compounds derived from bromoacetic acids</i>	3
2.1.1. From monobromoacetic acid	3
2.1.2. From dibromoacetic acid	27
2.1.3. From tribromoacetic acid	31
2.2. <i>Compounds derived from chloroacetic acids</i>	32
2.2.1. From monochloroacetic acid	32
2.2.2. From dichloroacetic acid	58
2.2.3. From trichloroacetic acid	64
2.3. <i>Compounds derived from fluoroacetic acids</i>	69
2.3.1. From monofluoroacetic acid	69
2.3.2. From difluoroacetic acid	70
2.3.3. From trifluoroacetic acid	71

2.4. <i>Compounds derived from iodoacetic acids</i>	93
2.4.1. <i>From monoiodoacetic acid</i>	93
2.4.2. <i>From diiodoacetic acid</i>	96
2.4.3. <i>From triiodoacetic acid</i>	96
Chapter 3. Compounds derived from aminoacetic acids	97
3.1. <i>Compounds derived from aminoacetic acid</i>	97
3.2. <i>Compounds derived from substituted aminoacetic acids</i>	101
Chapter 4. Compounds derived from alkoxyacetic acids	122
4.1. <i>Compounds derived from methoxyacetic acids</i>	122
4.2. <i>Compounds derived from phenylmethoxyacetic acids</i>	144
4.3. <i>Compounds derived from ethoxyacetic acids</i>	145
4.4. <i>Miscellaneous</i>	149
Chapter 5. Compounds derived from aryloxyacetic acids	151
5.1. <i>Compounds derived from phenoxyacetic acid</i>	151
5.2. <i>Compounds derived from substituted phenoxyacetic acids</i>	153
Chapter 6. Compounds derived from hydroxyacetic acids	167
Chapter 7. Compounds derived from acyloxy- and aroyloxyacetic acids	179
7.1. <i>Compounds derived from acetoxyacetic acids</i>	179
7.2. <i>Compounds derived from other acyloxy- and phenacyloxyacetic acids</i>	182
7.3. <i>Compounds derived from benzoyloxyacetic acids</i>	184
Chapter 8. Compounds derived from nitroacetic acids	190
Chapter 9. Compounds derived from arylacetic acids	193
9.1. <i>Compounds derived from phenylacetic acid</i>	193
9.2. <i>Compounds derived from substituted phenylacetic acids</i>	238
9.3. <i>Compounds derived from di- and triphenylacetic acids</i>	317
9.4. <i>Compounds derived from cycloalkylacetic acids</i>	319
Chapter 10. Compounds derived from S-substituted mercaptoacetic acids	322

DI- AND POLYKETONES

Chapter 11. Aromatic ketones containing only acetyl groups	335
11.1. <i>Acetyl groups located on one ring</i>	335
11.1.1. Unsubstituted acetyl groups	335
11.1.2. Diversely substituted acetyl groups	362
11.2. <i>Acetyl groups located on different rings</i>	363
11.2.1. Diphenyl derivatives	363
Symmetrical ketones	363
Asymmetrical ketones	367
11.2.2. Diphenylmethane derivatives	370
11.2.2.1. Unsubstituted acetyl groups	370
11.2.2.2. Halogenated acetyl groups	377
11.2.3. Diphenylalkanes derivatives and homologues	381
11.2.4. Diphenyl ethers and related compounds	385
11.2.5. Diphenyl sulfide derivatives and related compounds	391
11.2.5.1. Diphenyl sulfide derivatives	391
11.2.5.2. Diphenyl sulfone derivatives	393
Chapter 12. Aromatic polyketones containing at least one acetyl group and one other acyl group	397
12.1. <i>Acyl groups located on one ring</i>	397
12.1.1. Diphenyl ketone derivatives	397
12.1.2. Miscellaneous	400
12.2. <i>Acyl groups located on different rings</i>	405
12.2.1. Diphenyl ketone derivatives	405
Symmetrical ketones	405
Asymmetrical ketones	407
12.2.2. Miscellaneous	410

REFERENCES	415
MOLECULAR FORMULA INDEX	459
CHEMICAL ABSTRACTS REGISTRY NUMBERS	521
USUAL NAMES INDEX	547
COMMON ABBREVIATIONS	553

SHORT BIOGRAPHY

Robert Martin graduated as engineer from CNAM, then as doctor-engineer and doctor es sciences (Ph.D.) from Paris University. He studied with professors Léon Denivelles and Albert Kirrmann.

After having worked in the pharmaceutical industry, Robert Martin completed his career of organic chemist at a Research Laboratory of the French CNRS, located in the Curie Institute in Paris.

He has been studying the Fries reaction since 1956 without interruption. He has prepared a considerable number of aromatic hydroxyketones. A large part of these are included in the reference NMR and IR spectra collection of Sadtler (Philadelphia, USA).

His research on aromatic hydroxyketones gave rise to about forty publications between 1963 and 1992, some of them in collaboration with Mainz University (Germany) and others with Institut Curie (Paris).

In 1992, he published a review on the Fries reaction in *Organic preparations and Procedures International*. This was followed by two books dealing with aromatic hydroxyketones, published by Kluwer in 1997 and 2000.

For his various works concerning aromatic hydroxyketones he received the silver gilt medal from the Société d'Encouragement à l'Industrie Nationale in 1985.

FOREWORD

When Dr Martin asked me to write a preface to his new handbook, I was really enthusiastic. Indeed I met Dr Martin for the first time when joining the Institute Curie at the beginning of the 1990s to direct the team of medicinal chemists. At that time Dr Martin was retired from the Sanofi company but was working at the bench from early in the morning to late in the evening like a young and brilliant student. He devoted all his time and energy to make complete the description of what constitutes the subject of his published handbooks. Tireless reader of a huge number of periodicals, he collected, day after day, a large amount of data about the hydroxyacetophenones and the hydroxybenzophenones.

As a continuation of the two handbooks of both classes of compounds already published, Dr Martin now takes care of substituted hydroxyacetophenones. As these new collected compounds have been added to the unsubstituted analogs, one can say that this book constitutes an enlarged second edition of the first hydroxyacetophenone handbook. No less than 3000 molecules and 3500 references can be found in this new volume. The presentation is the same as in the first two volumes with consistent data on the synthetic route or on the natural origine of each compound, its physicochemical and spectroscopic characteristic available in the literature.

I am sure that, even at the internet era, this hanbook will be helpful for the readers concerned with the use of these compounds in all the aspects of chemistry covering pharmaceutical, agrochemical, perfume, plastics and preservatives domains or elaboration of small libraries of organic compounds for biological sceening.

Besides, consulting such a handbook is greatly facilitated by the presence of three comprehensive tables including CAS number, official nomenclature and usual names.

This will be helpful to the reader and I am sure that this book will meet with the success it deserves.

Claude Monneret
Research Director at the CNRS

ACKNOWLEDGEMENTS

I wish to express my heartfelt thanks to Dr. Pierre Demerseman who accepted me in his Laboratory at Institut Curie in 1987, and kindly revised my manuscript. I am also grateful to Dr. J.-P. Buisson, always so amiable and efficient, whose knowledge of word-processing largely contributed to the final page-setting of this work.

My thanks are also directed to Prof. Claude Monneret, formerly Head of the Chemical Department at Institut Curie, who has always been so benevolent to me. The foreword of this Handbook was also written by Prof. Claude Monneret. I most appreciate this mark of kindness.

I acknowledge as well his successor to the management of the laboratory, Dr. Jean-Claude Florent, who maintains the tradition and always welcomes me with much kindness, and all his collaborators for their warm welcome at each of my visits.

I thank my son Serge Martin for friendly advice on the English edition of this book. Moreover, Mr. Serge Martin was a constant aid to me as regards data processing.

Various friends who readily agreed to translate foreign publications are also to be acknowledged here, in particular Dr. Jean Burkhard who has been of invaluable help for translating German papers over the last 30 years. The diverse abbreviations used in ancient reviews – particularly *Chemisches Zentralblatt* – had no secrets for him. Unfortunately, he left us in 2001 at the age of 91.

In this connection, thanks are due to Mrs. Feiga Weisbuch for her precious assistance as regards Rumanian and Russian texts, Mrs. Elisabeth Matarasso-Tchiroukhine as regards German and Russian texts as well as to Miss Marie-Françoise Liachenko and Dr. Daniel Dauzonne. I wish to express my thanks to Mrs. Mireille Guyonneau and Mrs. Françoise Boucheron for their keen contribution to my bibliographic research.

Before closing, I would like to remember my dear departed. My affectionate thoughts are turned towards Prof. Léon Denivelle who transmitted to me his passion for aromatic organic chemistry in 1945, and Prof. Albert Kirmann who accepted me among his students in 1961 and was always so amiable and well-disposed whenever I went to him. I cannot mention without emotion Prof. Albert Saint-Maixen who largely communicated to me his knowledge of analytical chemistry.

I also have a personal thought towards my friends from the industry who left us too soon. I am particularly thankful to Drs. Henri Barbier, Félix Lepors and Henri Ruelleux (SPCA, Ltd.) who gave me the practical means to carry out my work on aromatic hydroxyketones. In this firm, I started my research on the Fries reaction. I also wish to acknowledge the late Dr. François Krausz who, at that time, made me benefit from his precious advice.

Robert Martin

INTRODUCTION

Acylphenols are used as starting material for an extremely large number of syntheses in organic chemistry, leading to a wide range of applications. For this reason, it seemed interesting to bring up to date the first dictionary, entitled *Handbook of Hydroxyacetophenones*, published in 1997.

All the ketones appearing in this first dictionary will also be included in the enlarged second edition entitled above. Some texts have been revised as the new informations show some interest. On top of this a large number of homologous ketones has been introduced.

However, this new (2004) version is not only an update of the former data, but 11 other ketone families have been added.

The new dictionary covers about 3000 hydroxyacetophenones, methodically classified usually under the official nomenclature of 'Ethanones' according to the International System (IUPAC) and the recommendations given in the Chemical Abstracts 'Collective Index' (CI) since 1972.

About 3500 bibliographic references are compiled in this book. Names of periodicals are abbreviated according to the Chemical Abstracts Service Source Index (CASSI). Whenever hydroxyacetophenones can be obtained from plants, sources and corresponding references are given.

For each compound described, the different protocols of synthesis are presented as well as the main physicochemical characteristics and references of spectroscopic data. Besides, the usual abbreviations are also indicated at the end of this dictionary.

For precise and quick location of an hydroxyacetophenone, you can refer either to the classification by molecular formula (*Molecular Formula Index*) or to the *Chemical Abstracts Registry Numbers* table.

A *Usual Names Index* including the current names of some hydroxyacetophenones and their precursors is also available.

Finally, a glance through any chapter of this Dictionary will inform the reader on the diverse ways of synthesizing hydroxyacetophenones. These methods can also be used to obtain hitherto unknown analogs in the related series.