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The chemistry of functional groups
FOUNDER SAUL PATAI

Edited by
Zvi Rappoport

The chemistry of organic germanium, tin and lead compounds Volume 2

C-Ge C-Sn C-Pb

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The Chemistry of Organic Germanium, Tin and Lead Compounds. Volume 2
Edited by Zvi Rappoport

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The chemistry of
organic germanium, tin and lead compounds

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C–Ge, C–Sn, C–Pb

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Edited by

ZVI RAPPOPORT

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Dedicated to
the memory of

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and

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Foreword

The preceding volume on *The Chemistry of Organic Germanium, Tin and Lead Compounds* in 'The Chemistry of Functional Groups' series (S. Patai, Ed.) appeared in 1995. The appearance of the present two-part volume seven years later reflects the rapid growth of the field.

The book covers two types of chapters. The majority are new chapters on topics which were not covered in the previous volume. These include chapters on reaction mechanisms involving the title organic derivatives, on reactive intermediates derived from them, like cations and carbene analogs, on NMR spectra, and on gas phase and mass spectrometry of organic germanium, tin and lead derivatives. There are chapters on their alkaline and alkaline earth metal compounds, on highly reactive multiply-bonded derivatives involving the title elements and on their hypervalent compounds, their synthetic applications, biological activities, polymers, cage compounds, unsaturated three membered ring derivatives and a new germanium superacid.

The second group of chapters are updates or extensions of material included in previous chapters. These include chapters on theory, on comparison of the derivatives of the three metals, on new advances in structural and photochemistry and in substituent effects and acidity, basicity and complex formation.

The volume opens with a new historical chapter on the genesis and evolution of organic compounds of the three elements, written by one of the pioneers in the field. We hope that such a historical background adds perspectives to those working both in the field and outside it.

The contributing authors to the book come from nine countries including some from Russia and Latvia who contributed several chapters. Part of the work in the field in these countries was covered by articles in Russian which were frequently not easily available to non-Russian readers. We now have many references including *Chemical Abstract* citations which will facilitate access to these articles.

The literature coverage in the book is mostly up to mid- or late-2001.

One originally planned chapter on radical reactions was not delivered, but part of the material can be found in another, more mechanistically oriented chapter.

This and the preceding volume should be regarded as part of a larger collection of books which appeared in recent years in 'The Chemistry of Functional Groups' series and deal with the chemistry of organic derivatives of the group 14 elements (excluding carbon). These also include four parts on the chemistry of organic silicon compounds (Z. Rappoport and Y. Apeloig, Eds., Vol. 2, parts 1–3, 1998 and Vol. 3, 2001) which follow two earlier volumes (S. Patai and Z. Rappoport, Eds., 1989) and an update volume, *The Silicon-Heteroatom Bond* (1991). The 136 chapters in the ten volumes cover extensively the main aspects of the chemistry of this group in the periodic table. Some comparisons of the derivatives of these groups appear both in the present and in earlier volumes.

This book was planned to be coedited by Prof. Y. Apeloig from the Technion in Haifa, Israel, but he was elected to the presidency of his institute and was unable to proceed

with the editing beyond its early stage. I want to thank him for the effort that he invested and for his generous advice. I also want to thank the authors for their contributions.

I will be grateful to readers who draw my attention to mistakes in the present volume, or mention omissions and new topics which deserve to be included in a future volume on the chemistry of germanium, tin and lead compounds.

Jerusalem
April 2002

ZVI RAPPOPORT

The Chemistry of Functional Groups Preface to the series

The series 'The Chemistry of Functional Groups' was originally planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the preparation, properties and reactions of the functional group treated and on the effects which it exerts both in the immediate vicinity of the group in question and in the whole molecule.

A voluntary restriction on the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series and in textbooks (i.e. in books which are usually found in the chemical libraries of most universities and research institutes), should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the topic. Therefore each of the authors is asked not to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced postgraduate level.

It is realized that no plan can be devised for a volume that would give a complete coverage of the field with no overlap between chapters, while at the same time preserving the readability of the text. The Editors set themselves the goal of attaining reasonable coverage with moderate overlap, with a minimum of cross-references between the chapters. In this manner, sufficient freedom is given to the authors to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter deals with the general and theoretical aspects of the group.

(b) Chapters discuss the characterization and characteristics of the functional groups, i.e. qualitative and quantitative methods of determination including chemical and physical methods, MS, UV, IR, NMR, ESR and PES — as well as activating and directive effects exerted by the group, and its basicity, acidity and complex-forming ability.

(c) One or more chapters deal with the formation of the functional group in question, either from other groups already present in the molecule or by introducing the new group directly or indirectly. This is usually followed by a description of the synthetic uses of the group, including its reactions, transformations and rearrangements.

(d) Additional chapters deal with special topics such as electrochemistry, photochemistry, radiation chemistry, thermochemistry, syntheses and uses of isotopically labelled compounds, as well as with biochemistry, pharmacology and toxicology. Whenever applicable, unique chapters relevant only to single functional groups are also included (e.g. 'Polyethers', 'Tetraaminoethylenes' or 'Siloxanes').

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the authors and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, some volumes may be published without giving consideration to the originally planned logical order of the chapters.

Since the beginning of the Series in 1964, two main developments have occurred. The first of these is the publication of supplementary volumes which contain material relating to several kindred functional groups (Supplements A, B, C, D, E, F and S). The second ramification is the publication of a series of 'Updates', which contain in each volume selected and related chapters, reprinted in the original form in which they were published, together with an extensive updating of the subjects, if possible, by the authors of the original chapters. A complete list of all above mentioned volumes published to date will be found on the page opposite the inner title page of this book. Unfortunately, the publication of the 'Updates' has been discontinued for economic reasons.

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editors.

The publication of this series would never have been started, let alone continued, without the support of many persons in Israel and overseas, including colleagues, friends and family. The efficient and patient co-operation of staff-members of the publisher also rendered us invaluable aid. Our sincere thanks are due to all of them.

The Hebrew University
Jerusalem, Israel

SAUL PATAI
ZVI RAPPOPORT

Sadly, Saul Patai who founded 'The Chemistry of Functional Groups' series died in 1998, just after we started to work on the 100th volume of the series. As a long-term collaborator and co-editor of many volumes of the series, I undertook the editorship and I plan to continue editing the series along the same lines that served for the preceeding volumes. I hope that the continuing series will be a living memorial to its founder.

The Hebrew University
Jerusalem, Israel
June 2002

ZVI RAPPOPORT

Contents

List of abbreviations used

Ac	acetyl (MeCO)
acac	acetylacetone
Ad	adamantyl
AIBN	azoisobutyronitrile
Alk	alkyl
All	allyl
An	anisyl
Ar	aryl
Bn	benzyl
Bz	benzoyl (C_6H_5CO)
Bu	butyl (also *t*-Bu or Bu^t)
CD	circular dichroism
CI	chemical ionization
CIDNP	chemically induced dynamic nuclear polarization
CNDO	complete neglect of differential overlap
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIBAH	diisobutylaluminium hydride
DME	1,2-dimethoxyethane
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulphoxide
ee	enantiomeric excess
EI	electron impact
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance
Et	ethyl
eV	electron volt

Fc	ferrocenyl
FD	field desorption
FI	field ionization
FT	Fourier transform
Fu	furyl(OC_4H_3)
GLC	gas liquid chromatography
Hex	hexyl(C_6H_{13})
c-Hex	cyclohexyl(*c*-C_6H_{11})
HMPA	hexamethylphosphortriamide
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
i-	iso
Ip	ionization potential
IR	infrared
ICR	ion cyclotron resonance
LAH	lithium aluminium hydride
LCAO	linear combination of atomic orbitals
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
M	metal
M	parent molecule
MCPBA	*m*-chloroperbenzoic acid
Me	methyl
MNDO	modified neglect of diatomic overlap
MS	mass spectrum
n	normal
Naph	naphthyl
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NMR	nuclear magnetic resonance
Pc	phthalocyanine
Pen	pentyl(C_5H_{11})
Pip	piperidyl($C_5H_{10}N$)
Ph	phenyl
ppm	parts per million
Pr	propyl (also *i*-Pr or Pr^i)
PTC	phase transfer catalysis or phase transfer conditions
Py, Pyr	pyridyl (C_5H_4N)

R	any radical
RT	room temperature
s-	secondary
SET	single electron transfer
SOMO	singly occupied molecular orbital
t-	tertiary
TCNE	tetracyanoethylene
TFA	trifluoroacetic acid
THF	tetrahydrofuran
Thi	thienyl(SC_4H_3)
TLC	thin layer chromatography
TMEDA	tetramethylethylene diamine
TMS	trimethylsilyl or tetramethylsilane
Tol	tolyl(MeC_6H_4)
Tos or Ts	tosyl(*p*-toluenesulphonyl)
Trityl	triphenylmethyl(Ph_3C)
Xyl	xylyl($Me_2C_6H_3$)

In addition, entries in the 'List of Radical Names' in *IUPAC Nomenclature of Organic Chemistry*, 1979 Edition, Pergamon Press, Oxford, 1979, p. 305–322, will also be used in their unabbreviated forms, both in the text and in formulae instead of explicitly drawn structures.

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CHAPTER **1**

Genesis and evolution in the chemistry of organogermanium, organotin and organolead compounds

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The task of science is to induce the future from the past

Heinrich Herz

I. INTRODUCTION

Germanium, tin and lead are members of one family, called the silicon subgroup. Sometimes these elements are called mesoids as well, due both to their central position in the short version of Mendeleev's Periodic Table and to their valence shells, which occupy an intermediate place among the I–VII Group elements[1]. They can also be called the heavy elements of Group 14 of the Periodic Table.

The history of the silicon prototype of this family and its organic derivatives is elucidated in detail in the literature[2−5]. In contrast, we could not find any special accounts dealing with the history of organic germanium, tin and lead compounds. The only exception is a very brief sketch on the early history of the chemistry of organotin compounds[6]. Some scattered information on the organic compounds of germanium, tin and lead can be found in some monographs and surveys. In this chapter we try to fill the gaps in this field.

Humanity first encountered the heavy elements of Group 14 at different times; with germanium, it happened quite unusually in the middle of the 19th century. As with the discovery of the planet Neptune[7], which was first predicted by astronomers and almost immediately discovered, Mendeleev, who predicted the existence of three hitherto unknown elements, reported at the Russian Chemical Society session on December 10, 1870 on the discovery of one of these elements as follows: '. . .to my mind, the most interesting among undoubtedly missing metals will be one that belongs to Group IV and the third row of the Periodic Table, an analog of carbon. It will be a metal, following silicon, so we call it '*eca*-silicon'[8]. Moreover, Mendeleev even predicted the physical and chemical properties of the virtual element[9−12]. Having no conclusive proof of the existence of *eca*-silicon, Mendeleev himself began experimental investigations aimed at finding it in different minerals[13]. It is noteworthy that as early as 1864 Newlands[14] and Meyer[15] suggested the possible existence of an element like *eca*-silicon and predicted its atomic weight. However, Mendeleev was the first to predict properties of the element in detail.

Fifteen years later the German chemist Winkler[16,17], working at the Freiberg Academy of Mines, was able to isolate during the investigation of a recently discovered mineral argirodit (Ag_6GeS_5) a new element in its free state. Initially, Winkler wanted to