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Organotin Compounds in Modern Technology

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ORGANOMETALLIC CHEMISTRY REVIEWS; including Plenary Lectures from the 3rd International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead (Dortmund, July 21st–25th, 1980)

13 D. SEYFERTH and R.B. KING (editors)
ORGANOMETALLIC CHEMISTRY REVIEWS; ANNUAL SURVEYS: SILICON – GERMANIUM – TIN – LEAD

14 R.B. KING and J.P. OLIVER (editors)
ORGANOMETALLIC CHEMISTRY REVIEWS; ANNUAL SURVEYS: SILICON – LEAD

15 O. STROUF, B. CASENSKY and V. KUBANEK
SODIUM DIHYDRIDO–BIS(2-METHOXYETHOXO)ALUMINATE (SDMA).
A Versatile Organometallic Hydride

PREFACE

In just a few decades organotin compounds have developed from being laboratory curiosities to large scale industrial chemicals. One of the first uses of organotins, and still the most important in terms of consumption, was as stabilisers for PVC. Following research into the biocidal properties of certain compounds, new avenues of application were opened, in the fields of wood preservation, crop protection and marine antifouling coatings. These uses for the most part arose out of intensive research, some of it sponsored by the International Tin Research Council and later continued in the Council's research laboratories. Today all over the world, there is a large body of research being conducted into organotin properties and many of the findings will no doubt eventually lead to further uses; a good example exists in the case of the mono-organotin compounds, which have low mammalian toxicity and are showing potential as water repellents for fabrics and building materials.

The interest in organotin chemicals is reflected in the enormous number of research papers which are published each year on this subject. There are also a number of excellent books covering the properties and general applications. When it comes to examining the industrial use of these compounds in more detail, a problem arises; this is due to the complexity of the technologies in which organotins are often used. To follow the use of organotin compounds in particular applications, one has to consult books on PVC technology, or on polyurethane polymers or wood preservation and hope to find the appropriate sections referring to the tin compounds used. When it comes to more wide-ranging topics such as agricultural chemicals or medicine it becomes even more difficult to find suitable coverage of organotin compounds.

It was in view of this, that the authors undertook the present book, in which the organotin compounds are firmly set in the context of their particular industrial usage. Basic chemistry is kept to a minimum and can be found in greater detail in other texts. Properties are only described inasmuch as they are relevant to a particular technology. What is attempted is to present an overall view of each field of application, giving as much of the specialised subject as is necessary for an understanding of the manner in which the organotin benefits the process or end use. Thus there are chapters on PVC stabilisation, polyurethane technology, wood preservation, antifouling coatings, agricultural chemicals, other biocidal uses and medical applications. Whilst not claiming by any means to be complete treatises on these subjects, it is hoped that enough information is provided to give a grasp of the subject and to allow access to more specific sources when necessary. In this respect, the extensive references are indispensable. A basic introduction to organotin compounds, with brief details of manufacture is provided in the first chapter, in order to put their subsequent use in perspective. One chapter is devoted to the mono-organotins as a newly emerging group of industrial chemicals.

A very important aspect of organotins, as with many other organometallic compounds, is their impact on the environment. In this respect, organotin compounds have an advantage in that they are ultimately degraded to harmless, inorganic forms of tin. The entry into, and subsequent fate of, organotins in the environment are considered in the final chapter, which also contains information on the toxicology of organotin compounds and some toxicity data. Illustrations have been chosen to amplify the text wherever possible.

The authors have for a number of years been engaged in developing the uses of tin chemicals in industry, particularly the organotins and over that period have visited many companies and research organisations, and also held discussions at their Institute. Much of the information has been based on these contacts, and the friendly co-operation of many firms and other organisations who use organotin chemicals in some way is gladly acknowledged here, whether for allowing facilities for visits and photography or for providing photographs or technical assistance.

In particular the authors would like to thank the following:
Dr. A. O. Christie, International Paint plc., Mr. I. D. K. Dring, British Sanitized Ltd., Mr. R. M. Leach, Osmose, Inc., U.S.A., Mr. P. G. Salmon, M and T Chemicals Ltd. The help of colleagues at the International Tin Research Institute, has also been indispensable in producing this book, notably members of Chemistry Division; also Christine Wurm, who prepared many of the drawings, Mr. K. J. Edwards and Sue Miller of the Photographic Studio, who were responsible for many of the photographs in the book.

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July, 1984

Colin J. Evans
Stephen Karpel

CONTENTS

Preface

Chapter 1 INTRODUCTION 1

Chapter 2 PVC STABILISATION 12

Chapter 1

INTRODUCTION

Organotin compounds can be defined as compounds in which at least one direct tin-carbon bond exists. The great majority of organotin compounds have tin in the IV+ oxidation state although a few are known which have tin in the II+ oxidation state. Tin-carbon bonds are in general weaker and more polar than those formed in organic compounds of carbon, silicon or germanium and organic groups attached to tin are more readily removed. This higher reactivity does not, however, imply any instability of organotin compounds under ordinary conditions.

Four series of organotin compounds are known; those with one tin-carbon bond are known as mono-organotins, those with two tin-carbon bonds are diorganotins whilst triorganotins and tetra-organotins have, respectively, three and four tin-carbon bonds. The properties of these classes of compound differ; thus whilst monoorganotins have low toxicity the triorganotins are characterised by high biocidal activity and diorganotins find use in the plastics industry as stabilisers and catalysts. The tetra-organotins have not found much commercial use to date.

The tin-carbon bond is stable to water and to atmospheric oxygen at normal temperatures and is quite stable to heat (many organotins can be distilled under reduced pressure with little decomposition). Strong acids, halogens and other electrophilic reagents readily cleave the tin-carbon bond. Tin forms predominantly covalent bonds to other elements but these bonds exhibit a high degree of ionic character, with tin usually acting as the electropositive member. Triorganotin hydroxides behave not as alcohols but more like inorganic bases, although strong bases remove the proton in certain triorganotin hydroxides since tin is amphoteric. Thus, bis(triorganotin) oxides, $(R_3Sn)_2O$, are strong bases and react with both inorganic and organic acids, forming normal salt-like but non-conducting and water-insoluble compounds. Tin doubly bonded to oxygen does not exist and diorganotin oxides, R_2SnO, are polymers, usually highly cross-linked via intermolecular tin-oxygen bonds. Unlike the halocarbons, organotin halides are reactive compounds and because of their ionic character, readily enter into metathetical substitution reactions resembling the inorganic tin halides. Unlike carbon, tin shows much less tendency to form chains of tin atoms bonded to each other. Although tin-tin bonded compounds are known (for example hexa-organoditins) the tin-tin bond is easily cleaved by oxygen, halogens and acids.

1.1 HISTORICAL DEVELOPMENT

The first organic compound of tin was prepared in 1852 by Lowig, but credit for the first comprehensive study of organotins belongs to Sir Edward Frankland (1825-1899). In 1853 he prepared "di-iodo diethylstannane" (diethyltin diiodide) and in 1859 "tetraethylstannane" (tetra-ethyltin); other compounds followed. Despite this early discovery, organotin compounds remained little more than laboratory curiosities for nearly a century.

The first commercially significant property of organotins to become recognised, was the ability of diorganotins to inhibit the degradation, under the influence of heat and UV light, of polyvinyl chloride (PVC). Diorganotin compounds were introduced as PVC stabilisers in the U.S.A. in the 1940s, in the U.K. in 1951 and in the rest of Europe and Japan in the mid-1950s. Developments in this field have been reviewed by Verity-Smith [1]. World production of organotin compounds was stated to be running at 1000-2000 tonnes by 1957, mainly for dibutyltin stabilisers for PVC. More sophisticated compounds were soon developed, in particular, thiotin compounds were shown to be extremely efficient heat stabilisers for PVC. Early in 1955, non-toxic octyltin stabilisers for PVC were discovered and following extensive testing, Government approval was obtained in the U.S.A. and elsewhere for the use of tin-stabilised PVC in food-contact applications. PVC bottles for squash and for food products were marketed in the late 1960s and represented a new outlet for octyltin compounds.

The biocidal uses of organotins stemmed from the systematic study of these compounds sponsored at the Institute for Organic Chemistry, TNO, Utrecht, by the International Tin Research Council in 1950. The research team at TNO under the leadership of Professor G.J.M. van der Kerk made important contributions to the study of the organometallic chemistry of tin, synthesising new compounds and establishing their characteristics [2-10]. In particular the powerful biocidal properties of the trialkyltin and triaryltin derivatives were established. In 1957 the German company Hoechst developed an important agricultural fungicide tradenamed "Brestan", based on triphenyltin acetate. This was particularly effective against the damaging potato blight phytophthora infestans. Subsequently in 1961 Philips-Duphar marketed a crop protectant based on triphenyltin hydroxide (which had not been covered in the earlier triphenyltin patent filed by Hoechst). By the mid-1960s world annual production of organotins had risen to around 10,000 tonnes.

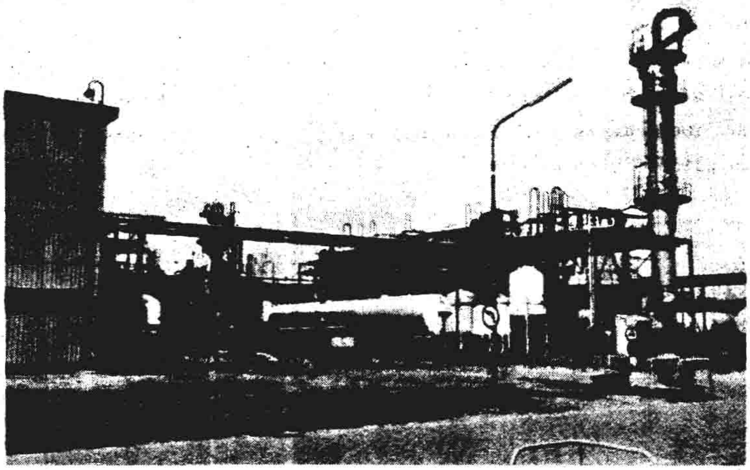

Fig. 1.1. The M & T Chemicals b.v. plant at Vlissingen-Oost, The Netherlands. Photograph courtesy: M & T Chemicals b.v.

In 1959 the seeds of another important use of organotin compounds were sewn, when the Osmose Wood Preserving Company of America began active investigation into the possibilities of organotins for wood preservation. As a result of these studies, the company marketed a commercial organotin-based wood preservative in 1960. This stimulated major developments in Europe and organotins became firmly established in the field of wood preservation over the next decade in many parts of the world. In the early 1960s organotin compounds began to find use in antifouling paint systems for ships in view of their biological activity against a wide spectrum of fouling organisms. By 1970 International Red Hand Marine Coatings had applied organotin-based coatings to some 200 vessels, representing 5 m gross tonnes of shipping. The subsequent development of more effective coatings with long-term activity has led to a marked increase in the use of organotins for antifouling systems and today this market is a growth area.

In the late 1960s the miticidal properties of tricyclohexyltin hydroxide were discovered and a commercial product based on this compound has been found extremely effective in protecting a wide range of crops and ornamentals. In the following years a number of other active organotin miticides were developed, namely bis(trineophyltin) oxide and 1-tricyclohexylstannyl - 1,2,4-triazole.

Growth of organotin usage has been considerable over the last few decades as Fig. 1.2 shows. A current estimate of consumption is over 30,000 tonnes per year. Table 1.1 lists principal uses of organotin compounds; these are discussed in depth in the remaining chapters of this book. It should be noted that three general areas of application account between them for over 95% of the total usage. These areas are: PVC stabilisers, agricultural uses and industrial biocides (in paints, timber, etc.).

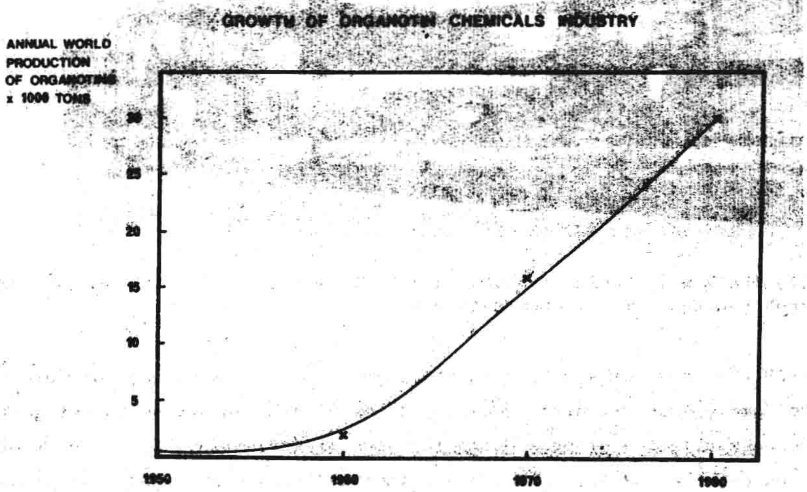

Fig. 1.2. Growth of consumption of organotin compounds.

1.2 METHODS OF MANUFACTURE

Only a brief summary is given here of the manufacturing techniques employed for organotin compounds; more detailed accounts of the chemistry [11] and the process technology [12] have been published. The principal routes are summarised in Fig. 1.3.

1.2.1 Grignard method

A very large proportion of the industrially important organotin compounds is prepared by the Grignard method:

$$SnCl_4 + 4RMgCl \rightarrow R_4Sn + 4MgCl_2$$

The route provides certain problems in control, since mixed solvent systems are needed and large volumes are involved. However, the process is very

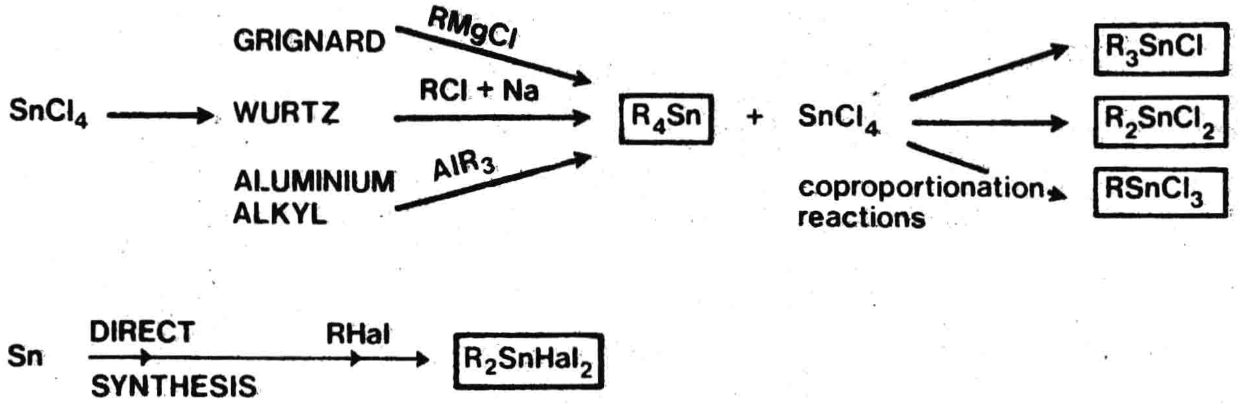

Fig. 1.3. Principal synthesis routes for producing compounds with direct tin-carbon bonds (organotins).

flexible and produces high yields; it is the only industrial method currently feasible for producing phenyltin compounds and it is also employed to produce propyl-, butyl- and octyltin compounds.

1.2.2 Wurtz synthesis

In the Wurtz synthesis, sodium is used in place of magnesium:

$$8Na + 4RCl + SnCl_4 \longrightarrow R_4Sn + 8NaCl$$

Again, large quantities of solvent are required and competing side reactions are a problem in achieving a satisfactory yield. Better results are obtained when the Wurtz synthesis is carried out with alkyltin chlorides rather than with tin tetrachloride. A starting amount of dibutyltin dichloride is first converted by the Wurtz synthesis to tetrabutyltin which then yields twice the amount of dibutyltin dichloride with tin tetrachloride. Half of the dibutyltin compound is then used to produce more tetrabutyltin for further reaction. To date the only company known to be making commercial use of this process is in the German Democratic Republic [13].

1.2.3 Aluminium alkyl route

The aluminium alkyl route to organotins has certain advantages over the other two processes, namely only a small reaction space is required, the process can be operated continuously and no solvents are needed. The method is used in F.R. Germany to produce tetra-alkyltins, particularly tetra-octyltins. Complete transfer of all the alkyl groups bound to the aluminium requires the presence of a complexing agent such as sodium chloride, ethers or tertiary amines. The alkylation to tetra-alkyltin then proceeds smoothly and completely:

$$4R_3Al + 3SnCl_4 + \underset{\text{(complexing agent)}}{4R'_2O} \longrightarrow 3R_4Sn + \underset{\text{(complex)}}{4AlCl_3 \cdot R'_2O}$$

The aluminium alkyl method is as versatile as the Grignard reaction with regard to the nature of the alkyl groups concerned.

1.2.4 Direct synthesis

Direct synthesis involves reaction between metallic tin and alkyl halide:

$$Sn + 2RHal \longrightarrow R_2SnHal_2$$