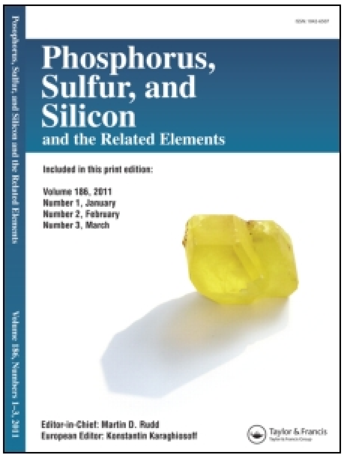

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A review of: "CATALYZED DIRECT REACTIONS OF SILICON. Edited by K. M. Lewis, Union Carbide Corporation, Tarrytown, NY, USA and D. G. Rethwisch, University of Iowa, Iowa City, IA, USA; Studies in Organic Chemistry, Volume 49, © 1993, 664 pages Hardbound, Price: DFI 465. (US $265.75), ISBN 0-444-81715-8."

Donald L. Bailey; Eugene G. Rochow

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Book Review

The following book review is comprised of the Foreword and Preface to the above titled book followed by a listing of the book contents.

CATALYZED DIRECT REACTIONS OF SILICON.* Edited by K. M. Lewis, Union Carbide Corporation, Tarrytown, NY, USA and D. G. Rethwisch, University of Iowa, Iowa City, IA, USA; Studies in Organic Chemistry, Volume 49, © 1993, 664 pages Hardbound, Price: Dfl 465. (US $265.75), ISBN 0-444-81715-8.

FOREWORD

Economical processes for the formation of carbon-silicon bonds are of the utmost importance in the manufacture of silicone polymers and organosilicon compounds. Although silicon is abundantly found in the form of silica and silicate minerals there is little evidence that organosilicon compounds occur in nature. Historically, the synthetic methods used to prepare the first organic compounds of silicon were found to be laborious and commercially unattractive. The more successful utilized organometallic reagents such as diethyl zinc in reactions with silicon tetrachloride and ethyl silicate to obtain these compounds (Friedel, Crafts and Ladenburg, 1863–1871 [*sic*]). Important advances in the synthesis of organosilanes were made by F. S. Kipping who made extensive use of Grignard reagents (organomagnesium halides) to replace groups in chlorosilanes and silicon esters with hydrocarbon substituents. While this work provided a basis for the modern chemistry of organosilanes it did not recognize the valuable properties of silicones and did little, processwise, to advance the commercial production of organosilicon chemicals.

The advent of World War II brought with it the observation that silicone polymers had unusual thermal stability along with a number of other properties of interest in a wide variety of applications. Simultaneously, it stimulated research on more practical processes for their production. The discovery by E. G. Rochow in 1945 that organosilicon halides could be produced by a "Direct Synthesis" from silicon and methyl chloride, in the presence of a copper catalyst, revolutionized the growth of the silicones industry. Subsequent studies, mostly carried out by industrial research laboratories and in many cases unpublished, have resulted in a broad, practical technology for Direct Reactions based on silicon. One book, currently out-of-print, has been published on the subject, "ORGANOHALOSILANES: Precursor to Silicones" by R. J. H. Voorhoeve (Elsevier, 1967). The bulk of other

*The book may be obtained from: Elsevier Science Publishers, P.O. Box 211, 1000 AE Amsterdam, The Netherlands, FAX (Amsterdam) (0) 20 5803-705, Telephone (Amsterdam) (0) 20 5803-753, Telex 18582 espa nl; In the USA & Canada: Elsevier Science Publishing Co., Inc., P. O. Box 945, Madison Square Station, New York, NY 10160-0757, FAX (New York) 212-633-3380, Telephone (New York) 212-989-5800, Telex 420643 aeppui.

The following contains the Foreword and Preface to Elsevier's Catalyzed Direct Reactions of Silicon. *Permission to reprint this excerpt granted by the publishers.*

information can be found primarily by reading the patent literature. References concerning recent research on theoretical aspects of the Direct Reaction are rare.

Considering the scarcity of authoritative articles since Voorhoeve's book, it is the purpose of this monograph to present state-of-the-art information on Direct Reactions of silicon and their silane products. The latest published data on commercial production of silicon and silanes, catalysis, catalyst promoters, kinetics, fluidized bed technology, surface analytical techniques and possible reaction mechanisms are among the topics covered. It is expected that the recent progress made will interest a broad range of scientists, including organic and organometallic chemists, material and polymer scientists, chemists and chemical engineers concerned with catalytic gas-solid reactions and semiconductor processes. The monograph does not provide a comprehensive survey of all of the Direct Reactions of silicon nor is it intended to do so. Significantly, major emphasis is given to recent technology pertaining to methylchlorosilanes with scant attention being paid to ethyl chloride, phenyl chloride, or other alkyl halides known to undergo Direct Reactions with silicon. This reflects the relative importance of methylsilicones in industrial applications. (It also demonstrates the bias towards practicality of research carried out by industry.) Even so, the methylchlorosilanes technology has important implications for other Direct Reactions in terms of catalysis, raw material specifications and reaction conditions. Hopefully, the field of Direct Reactions between hydrocarbon halides and silicon will be studied more broadly in future work, perhaps in academic circles with less concern for immediate commercial exploitation.

In popular usage, the term "Direct Process" has generally meant those reactions of silicon which result in the formation of silanes containing carbon-silicon bonds. This monograph uses a broader interpretation of the term and has expanded it to include reactions of silicon with hydrogen chloride and amines. As a consequence, just as there are Direct Processes for producing alkyl- and arylchlorosilanes, there are also Direct Processes for producing chlorosilanes, alkoxysilanes, alkyl silicates, aminosilanes, etc., from silicon. The silanes obtained from such processes have considerable importance, not only to the silicones industry, but also in electronic applications. By the now well-known platinum catalyzed addition of unsaturated organic compounds (e.g. olefins) to silane monomers containing silicon-hydrogen bonds a large number of useful organosilane monomers and polymers can be prepared. Similarly, hydrochlorosilanes have proven invaluable in the manufacture of ultra-pure silicon essential in making semiconductor devices. While still in the research and development stage, the preparation of tris(dimethylamino)silane by the copper catalyzed reactions of dimethylamine with silicon is particularly intriguing. This represents the first practical approach to synthesizing distillable silanes containing nitrogen bonded to silicon. Assuming that the appropriate supporting technology can be developed, tris(dimethylamino)silane is an attractive precursor to high purity silicon nitride, organofunctional silanes and many other types of aminosilanes. Drs. Kanner, Quirk and others at Union Carbide have already obtained a number of patents covering these technologies.

It should be evident to the reader that although many of the Direct Processes for producing silicon chemicals have been studied in great detail there are still a number of fruitful areas available for further research. To illustrate a few: Dichlorosilane is obtained from hydrogen chloride and silicon Direct Reaction but the major products are trichlorosilane and silicon tetrachloride; what catalysts and conditions are necessary to optimize its production? Reactions of alcohols with silicon have received little attention, except in the manufacture of alkyl silicates; can these reactions be used to efficiently prepare triethoxysilane or other useful alkoxysilane intermediates? Future growth in silicone chemicals and related fields will be determined, in part, by technical advances on catalyzed Direct Reactions of silicon. By making the latest information available in a published volume, Drs. Lewis and Rethwisch are encouraging readers to carry out research in this important area of chemistry and to contribute to its further development.

Traverse City, Michigan 49684 Donald L. Bailey

PREFACE

As silicone historian Herman Liebhafsky has written, "The most important single experiment and the best single day's work in the history of the silicone industry" was the first successfully-demonstrated, proven, recorded and witnessed synthesis of methyl silicone from methylchlorosilanes/produced by the Direct Reaction of methyl chloride with catalysed silicon. The date was May 10th, 1940.

Over the intervening 49 years, enormous effort has been devoted to the study of the Direct Reaction of organic compounds with elementary (or "metallic") silicon, and the rewards have been equally enormous, both in scientific and industrial terms. Accessibility of the methylchlorosilanes from such a reaction has led to a flourishing worldwide silicones industry, the owners of which have wisely plowed back a substantial part of earnings for further study of such reactions. At the same time, the intriguing idea of other inorganic organic polymers derived from common metals and metalloids has caught the interest of many other research chemists in academic and government laboratories, leading to a great outpouring of experimental results which contribute to our understanding and application of these Direct Syntheses.

Unfortunately, the resulting thousands of publications have mostly remained scattered throughout the world's chemical and patent literature, in many languages. Now comes an ambitious effort by Drs. Lewis and Rethwisch to produce a current overview of the Direct Synthesis in its many manifestations, not in the form of a compendium of the past literature but in terms of present-day understanding and practice. Their book fills a long-felt need, and will give both young researches and experienced practitioners a look at where we stand today.

The editors and authors have their own commendable scheme of organizing this book, but to this writer (who now sees things in an historical and educational light) the contents group themselves into six natural headings:

1. Elemental Silicon, its production and analysis, and the standards of purity.
2. The catalyst or catalysts: selection, preparation and promotion.
3. The reaction itself: conditions, control, kinetics and mechanism.
4. Equipment for carrying out the reaction on a laboratory and an industrial scale.
5. The analysis of the products and the disposal of waste, and
6. The broadening of the Direct Reaction to other inorganic and organic reactants, notably the hydrogen halides and various alcohols and amines.

To this writer, item (6) remains the most important and intriguing aspect. After extending the Direct Reaction to germanium and tin, and encouraging Ludwig Maier and others to extend it to the elements of Group V, he is still curious about other possibilities of theoretical and practical interest. The ultimate example of this still mysterious unknown territory is the possibility of bringing about the reaction of dimethyl ether with catalysed silicon, for there we have all the elements necessary for methyl silicone and in the right proportions. Such a synthesis would involve no extraneous elements and no halogen corrosion, nor any disposal problem. Yet nobody so far has been able to twist the arm of the Direct Reaction in just the right way to achieve this highly desirable end. Perhaps some students or ambitious junior staff member will read this book and be inspired by it to start off on an original direction of research, leading to success. We all hope so!

Fort Myers, Florida Eugene G. Rochow

Contents: 1. Commercial production of silanes by the direct synthesis (B. Kanner, K. M. Lewis). 2. Production of silicon for the methyl chloride direct synthesis (J. H. Downing *et al.*). 3. Quality criteria for silicon used for organo-silicon industry (H. M. Rong *et al.*). 4. Some considerations of the direct synthesis of methylchlorosilanes (W. F. Banholzer *et al.*). 5. Selection of copper formate catalysts for the direct synthesis of methylchlorosilanes (K. M. Lewis *et al.*). 6. Catalyst preparation for the direct synthesis of methylchlorosilanes: practical, theoretical, and reactor design considerations (L. K. Doraiswamy, A. N. Gokarn). 7. Kinetics of the methyl chloride-silicon direct reaction (I. R. Moore, J. A. Nelson). 8. Gas chromatogaphic analysis of methylchlorosilanes produced by the direct reaction (L. G. Hawkins). 9. Gas chromatographic analysis in the manufacture of chlorosilanes (H. Rotzsche *et al.*). 10. In-line Fourier transform infrared spectroscopic analysis of methylchlorosilanes produced by the direct reaction (H. B. Friedrich *et al.*). 11. Copper-catalyzed etching of silicon (J. A. Mucha *et al.*). 12. Model reaction studies of the direct synthesis of methylchlorosilanes (K. A. Magrini *et al.*). 13. Selective formation of dimethylchlorosilane on Si surfaces (K. A. Magrini, J. L. Falconer). 14. Effects of promoters on the catalytic synthesis of methylchlorosilanes (L. D. Gasper-Galvin *et al.*). 15. Chemisorption and catalytic activity of Cu and Ag atoms on Si(111) surfaces (S. H. Chou *et al.*). 16. Surface-chemical studies of the mechanism of the direct synthesis of methylchlorosilanes (K. M. Lewis *et al.*). 17. Direct synthesis of chlorosilanes and silane (W. C. Breneman). 18. By-products from waste treatment for a bench scale trichlorosilane/tetrachlorosilane direct process (J. A. Cervantes *et al.*). 19. Mathematical modelling of diffusion and microkinetics in direct reactions of silicon and in the processing of electronic components (S. S. E. H. Elnashaie). 20. Copper-catalyzed reaction of dimethylamine with silicon (K. M. Lewis *et al.*). Author index. Subject index.