Preface

After an outstandingly successful industrial research career of some twelve-and-one-half years, Professor EUGENE G. ROCHOW joined the faculty of Harvard University where he spent the next twenty-two years. He is best known for his discovery and development of the copper-catalyzed direct synthesis of the methylchlorosilanes from methyl chloride and elemental silicon. This work was carried out while he was at the General Electric Company laboratories in Schenectady and it provided the foundation of the silicones industry. However, at Harvard he and his coworkers also have done much important research, not only in the organosilicon area, but also on other aspects of organometallic and inorganic chemistry.

Professor Rochow retired from his faculty position at Harvard in 1970, but he has remained active in chemistry. He has been a valued member of the Editorial Board of the "Journal of Organometallic Chemistry" since its beginning in 1963.

This special issue of the "Journal of Organometallic Chemistry" contains papers which are dedicated to Professor Rochow on the occasion of his 70th birthday on October 4, 1979 by some of his many friends. Some of the authors in this special issue are former coworkers of Professor Rochow; others are not. All have in common their feelings of respect and affection for him.

The Regional Editors of the "Journal of Organometallic Chemistry" are happy to join the authors of this issue in this birthday greeting to Professor Rochow and wish him many further active and productive years.

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EUGENE GEORGE ROCHOW — An Appreciation

On October 4, 1979, when Eugene G. Rochow celebrates his 70th birthday, he can look back on a distinguished career in chemistry, a career that has won him international recognition and many prestigious awards for his pioneering industrial research in organosilicon chemistry, for his far-ranging academic research and for his outstanding teaching in chemistry.

Dr. Rochow's studies in chemistry, both at the undergraduate and the graduate level, were carried out at Cornell University. During his undergraduate years he was invited to join the research seminar of Professor L.M. Dennis, a pioneer in the development of the chemistry of germanium, gallium and indium, and, shortly thereafter, he was given a place in Dennis' laboratory. Dr. Rochow's initial research experience was concerned with the electrolytic preparation of fluorine, a project that carried over into his Ph.D. research after his graduation with a B. Chem. degree in 1931.

Although his thesis research was concerned with the preparation of fluorine and with the oxyacids of fluorine, Dr. Rochow became active in organometallic research in his second graduate year. The terms of a Hechscher Research Assistantship which he had been awarded obliged him to carry out research on another project separate from his thesis work. This second research area dealt with Group III and IV chemistry: the synthesis and properties of trimethylindium and triethylthallium and the synthesis of germanium compounds for use in Hönigschmidt's determination of the atomic weight of germanium.

Of seminal importance was Dr. Rochow's association with Alfred Stock, the great German pioneer in the chemistry of molecular hydrides, who spent a year at Cornell as Baker Lecturer. During Stock's tenure at Cornell, Dr. Rochow served as his special assistant and he also drew the diagrams for Stock's famous book, "The Hydrides of Boron and Silicon", which was written while Stock was at Cornell. Thus Dr. Rochow became well acquainted with silicon chemistry in general and Stock's research in particular.

Dr. Rochow obtained his Ph.D. in 1935. A planned year of postdoctoral work with Hönigschmidt in Berlin did not materialize when the international exchange program which was to support it was cancelled by the German government. Dr. Rochow began his career with the General Electric Company in Schenectady, which was to last for twelve-and-one-half years, in the fall of 1935. Initially, he worked in ceramic chemistry, dealing there with the special materials needs of the electrical industry, but in 1938 he became active in organosilicon research. The finding that methylsilicone polymers had attractive and useful properties led to a need for a practical, industrially applicable synthesis of methylchlorosilanes. A search for such a synthesis, which soon was concentrated on a direct methyl chloride/elemental silicon approach, was crowned by success on May 10, 1940, when Dr. Rochow recorded his first successful direct reaction of gaseous methyl chloride with elemental silicon in the presence of copper. (A fascinating account of this research and, more generally, of the early days of the silicones industry and the men who were involved in its birth and development, is given in H.A. Liebhafsky's book,

"Silicones Under the Monogram", Wiley, 1978.) This discovery and the subsequent development of the process for use in large-scale production provided the foundation of the modern silicones industry. The direct synthesis, which produces the starting materials for the silicones, is practised efficiently and profitably in many countries throughout the world. Application of the direct reaction to the synthesis of phenylchlorosilanes, of methylchlorogermanes and of methyl silicate followed, and the "boom" in organosilicon chemistry was on. It has never let up!

In 1948 Dr. Rochow joined the faculty of the chemistry department of Harvard University as associate professor of chemistry (promotion to professor followed quickly). His teaching responsibilities at Harvard fell in the area of general and inorganic chemistry and while the main thrust of his research remained organometallic chemistry, with emphasis on the Group IV elements, other areas received attention as well. Projects as diverse as the use of ClF_3 as a fluorinating agent and electrode potentials in silicate melts may be noted. The direct synthesis was extended to methyltin chlorides, later to methylarsenic and methylantimony halides and to reactions of ethers with elemental silicon. More conventional organometallic reactions in solution also received considerable attention: new syntheses, new classes of compounds, properties and reactivities in solution, spectroscopic studies.

An abiding interest in the silicones and other organometallic polymers provided the motive for much of this research. Among the synthetic studies were those aimed at modification of the methylsilicones by the introduction of polar substituents onto the methyl carbon atom and those devoted to the search for stable organosilicon polymers with a silicon—nitrogen backbone. The remarkable properties of the silicones, some of which are due to low intermolecular forces in these systems, were of special interest to Dr. Rochow. The advent of low resolution (broad-line) NMR spectroscopy, with its capability of studying molecular motion, provided a new technique for investigating the silicones, and Dr. Rochow was the first to apply broad-line NMR to the study of silicone polymers. This was in the early 1950's, before commercial instruments were available, and much time and effort had to be devoted to the construction of a suitable spectrometer which then was used in studies of molecular motion in silicone and silazane polymers. The difficulties which had to be overcome in this do-it-yourself approach are recounted in Dr. Rochow's recollections of his career in chemistry, "Of Time and Carbon—Metal Bonds" (Advan. Organometal Chem., 9 (1970) 1—19).

This strong, general interest in structure and bonding could be perceived throughout Dr. Rochow's research. One sees it in his early studies of silicone polymers by electron microscopy, in collaboration with his brother Ted, at that time an electron microscopist with American Cyanamid Company, and in his application of high resolution NMR spectroscopy (with A.L. Allred) to the determination of the relative electronegativities of the Group IV elements. This interest in the determination of electronegativities led to further work which culminated in the Allred—Rochow electronegativity scale which can be found in all current textbooks of inorganic chemistry. The then newly available proton NMR technique also was used by Dr. Rochow and his coworkers in the middle to the late 1950's to study other problems of bonding and structure in organo-

silicon and organotin chemistry. Noteworthy are the studies on the structures of organotin cations, carried out with Okawara and Webster.

In the latter part of his research at Harvard, Dr. Rochow concentrated on studies of silicon—nitrogen chemistry whose ultimate aim was the development of stable and useful Si—N polymers. Although this goal was not realized, much interesting new organosilicon—nitrogen chemistry resulted from this work.

This distinguished research career has been recognized with important awards: the Baekland Medal in 1949; the S.B. Meyer Award in Ceramic Chemistry in 1956; the Perkin Medal in 1962; the American Institute of Chemists Medal in 1964; the Frederic Stanley Kipping Award in Organosilicon Chemistry of the American Chemical Society in 1965.

As a teacher Dr. Rochow also has won high marks. His Chem 1 freshman chemistry course was extremely popular. It presented chemistry to the students as it relates to everyday life (at no sacrifice of principles) long before "relevance" became an issue. None who have taken Chem 1 will forget the many instructive as well as entertaining lecture demonstrations used by Dr. Rochow not only to prove a point but also hold his audience. Life can get exciting when ethylzinc iodide is prepared right in front of you and then poured into a beaker of water! These years of brilliant teaching also have been recognized: with a Manufacturing Chemists Association Teaching Award in 1970 and the James Flack Norris Award for Excellence in Teaching of Chemistry of the Northeastern Section of the American Chemical Society in 1973.

An appreciation of Dr. Rochow would be incomplete without mentioning his books, above all his "Introduction to the Chemistry of the Silicones" (first edition, 1946; second edition, 1951), a lucid, very readable summary of the field, which appeared just when it was needed, at the beginning of this period of phenomenal growth of organosilicon chemistry. Its impact was worldwide, and it was translated into Spanish, German, French, Japanese and Russian. "The Chemistry of Organometallic Compounds", written in collaboration with Dallas T. Hurd and Richard N. Lewis and published in 1957, met the needs of the graduate level special topics course on organometallic chemistry. It was followed in 1964 by a 112 page paperback, "Organometallic Chemistry", which was aimed at the undergraduate level. Dr. Rochow's freshman teaching led to further books: "General Chemistry — A Topical Introduction" (with M.K. Wilson) in 1954, "Chemistry — Molecules That Matter" (with G. Fleck and T.R. Blackburn) in 1974, and "Modern Descriptive Chemistry" in 1977. His community of interests and scientific collaboration with his brother brought another book, "Resinography" (1976), and still another, on applications of electron microscopy to polymer science, is yet to come.

We have dealt with Eugene G. Rochow, the chemist, the teacher and the writer. We cannot forget Eugene G. Rochow, the man. His undergraduate, graduate and postdoctoral coworkers and his many friends throughout the world can speak to that point. We know him as a warm human being who is always ready to lend a sympathetic ear, always ready to give thoughtful advice and to help however he can when help is needed. Those of us who were introduced to research in the Rochow group at Harvard remember with gratitude his patience, his understanding and his encouragement, and his wry sense of humor. We learned from him not only the "how to" of research but also about

his enlightened attitudes and scientific outlook Evident in his lectures, his writings and his actions was a caring for the earth and its resources, for the environment and for humankind. His Baekland Award address, which still makes fascinating reading because it is as topical today as it was thirty years ago (see Chem. Eng. News, Vol 27, p 1510, May 23, 1949 issue for the full text) called for conservation, recycling and the use of less wasteful alternatives long before these became fashionable His address attracted much attention from the press, but for the wrong reasons The suggestion that cellulose could provide the raw material for clothing and that "we could convert pure cellulose used clothes to edible products" was selectively seized upon by the newspaper writers and cartoonists and gave them great sport The important message, unfortunately, was missed

Dr. Rochow retired from his position on the Harvard faculty in 1970, but he has by no means retired from chemistry He continued his consulting activities and his writing In fact, at least three of his books and several major chapters of the treatise, "Comprehensive Inorganic Chemistry", were written after his formal retirement We still see him at meetings His plenary lecture at the Fourth International Symposium on Organosilicon Chemistry in Moscow in 1975 was extremely provocative, calling for new, at first sight surprising and unconventional, but thermodynamically feasible approaches to the synthesis of methyl silicone monomers More recently, we recall his outstanding plenary lecture at the Fifth International Organosilicon Symposium in Karlsruhe in August 1978 which provided a very interesting, very personal account of the early days of organosilicone chemistry We are certain that his interest in science and technology in all its varied aspects will never abate!

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