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Foreword

Professor Myron Rosenblum's contributions to organic chemistry



Professor Myron Rosenblum was born in New York in 1925. After serving in the US Army in the 87th infantry between 1943 and 1946 in Europe, he returned to the USA to study chemistry at Columbia University, where he received his BA degree in 1949. His contributions to organic and organometallic chemistry began auspiciously in 1952 when, as a graduate student working with Professor R.B. Woodward at Harvard University, he elucidated the structure of ferrocene and provided the first evidence of its aromatic character. He was awarded a PhD degree in 1954 and immediately moved to Columbia University where he stayed until 1955. This was followed by a three-year term as Assistant Professor at the Illinois Institute of Technology. Then he returned to Boston to take up a position as Assistant Professor at Brandeis University in 1958. He became Full Professor in 1966, a position he held until formally retiring in 1997. During this time he served as department chair for a year and held the Charles Breskin Professor of Chemistry chair for the last 10 years of his tenure. His retirement, however, did not

mark an end to his chemical interests but allowed him the freedom to return to the bench.

Together, we two were among a select group that had the wonderful opportunity to collaborate with him and participate in a potpourri of fascinating, inventive, and exciting chemistry. When he retired from teaching and returned to the bench, one of us (R.D.A.H.) had the good fortune to take up a postdoctoral fellowship to *literally* work alongside him. During these times we had the opportunity to observe the extraordinary insight and creativity of this remarkable man, as well as to be mentored by him in the early stages of our careers.

Myron's work with Woodward reawakened interest in the organometallic chemistry of the transition elements and set the stage for development of the modern field of organometallic chemistry, with its profound effect on current synthetic organic methodology. During the period 1955–1970, he continued to make important contributions to an understanding of the chemistry of ferrocene, especially of intra- and interannular ring effects and of the mechanism of electrophilic substitution in ferrocene. In 1964, he published his seminal book *The Iron Group Metallocenes*, detailing the progress made during the first 10 years of metallocene chemistry. His research in those early years at Brandeis also included a classic study leading to the elucidation of the mechanism of the von Richter reaction, the synthesis of dihydro-1,3,4-oxadiazinones, a new heterocyclic system, and a study of the electrocyclic thermal and photochemical decomposition of these substances, as well as a new synthesis of cyclobutadiene metal complexes from photo α -pyrones.

During the past thirty years, he has focused principally on the chemistry of organoiron complexes, and especially on the use of these as reagents and synthons in organic synthesis. In 1986, an overview of more than 60 papers published at that time in this research area was provided in a review article in this journal. This 1986 paper forms a supplement to the review of his early research progress into 'Organoiron Complexes as Potential Reagents in Organic Synthesis,' which appeared in Accounts of Chemical Research in 1974. Professor Rosenblum was one of the first to recognize the importance of organometallic chemistry in organic synthesis. His research in this area, detailing the preparation and variegated transformations of organoiron compounds, which incorporate the cyclopentadienvliron dicarbonyl group, form a coherent and important body of chemical literature. He recognized early that the cycloaddition reactions of these allyliron complexes with neutral electrophiles proceed by a stepwise mechanism in which the C_3 unit functions as a bipolar propanediyl synthon. Very shortly thereafter, he showed that these transformations could be generalized to include propargyl-, allenyl-, cyclopropyl-, and cyclopropylmethyliron complexes, thus constituting a new and general methodology for the construction of 5-7membered heterocyclic and carbocyclic systems. More recently, these reactions have been shown to provide a facile synthesis of functionalized hydroazulenes related to the guaiane and pseudoguaiane sesquiterpene family. Synthetic applications derived by elaboration of allyliron complexes through sequential electrophilic substitution and proton abstraction have been applied to short syntheses of lavandulol and red scale pheromone. His wide-ranging investigations of the chemistry of cationic iron-olefin complexes led to new and unique synthetic methodologies for the synthesis of β-lactams and α -methylene- γ -lactones and for regioselective Michael reactions. He was among the first to demonstrate redox-promoted migratory insertion in alkyliron complexes and to establish that these processes proceed with retention of configuration at the migrating center. Very early in this research, he developed the range of procedures currently used to prepare cationic iron olefin acetylene and allene complexes, and he demonstrated their high reactivity toward both carbon and heteroatomic nucleophiles. More recently, he developed the chemistry of cationic vinyl ether iron complexes and, in an extended series of papers, showed how these complexes may be made to function as stabilized vinyl cation reagents and illustrated their application in the synthesis of isopiperitone and of protolichesterinic ester. Further elaborations of this chemistry have now led to preparation of organoiron reagents that function as vinvlene dication equivalents, to methods by which these and the vinyl cation reagents may be prepared in optically active form, and to a circular dichroism quadrant rule by which the absolute configurations of these reagents may be assigned. He has very recently shown how these reagents, used in conjunction with stereoselective redox-promoted carboxylation reactions, constitute optically active 3-hydroxypropionate-2,3-dication equivalents. A strong focus on mechanistic detail and stereochemistry forms an important and unifying focus throughout all of this research.

During the past seven years, his research interests have turned increasingly toward the synthesis of metallocene polymers and oligomers in which the individual metallocene units are constrained to a face-to-face, stacked arrangement through their peri-substitution on a naphthalene spacer element. The electrical, magnetic, redox, and optical properties of these polymers has formed an important focus of his most recent research.

Myron has made many contributions to the chemical community at large, among which have been his service on the editorial boards for both The Journal of Organometallic Chemistry and Organometallics during the 1980s and the advisory board of the Petroleum Research Fund from 1981 to 1984. His keen interest in the literature and its dissemination has recently led him to set up a project that seeks to find new homes in the Third World, particularly Nigeria, for unwanted collections of scientific journals and books. His chemical career has also taken him around the world and, in 1965, he was honored with the award of a Guggenheim Fellowship that transported him and a young family to Imperial College London. This was followed by a series of visiting professorships at The Technion, Haifa (1966), The Hebrew University, Jerusalem (1973), Ben Gurion University, Beersheva (1980), and The Weizmann Institute of Science as the Meyerhoff Visiting Professor (1985).

Not only is Myron a great chemist but he is also an accomplished craftsman; together with his wife, Rachel, he plays an active part in local community craft guilds. Along with Rachel's wonderful weaving, his turned wooden bowls and hairpins enjoy 'pride of place' at the Lexington craft fairs and holiday marketplaces.

Myron may have delivered many plenary and invited lectures at academic conferences around the world, but his great love of New England and its beautiful seasons always brought him back. Indeed, he imparted some of this fondness to R.D.A.H. during his stay at Brandeis. On changeable fall or spring days he would often quote Mark Twain on the weather: "I reverently believe that the Maker who made us all makes everything in New England but the weather. I don't know who makes that, but I think it must be raw apprentices in the weather-clerk's factory who experiment and learn how, in New England, for board and clothes, and then are promoted to make weather for countries that require a good article, and will take their custom elsewhere if they don't get it." I am sure that anyone who has ever worked for or with Myron will appreciate that his inspirational scientific approach and knowledge has equipped us, his 'trainee weather-clerks', with a bountiful chemical currency that will take us far.

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