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A Tribute to Prof. William E. McEwen on the Occasion of His Seventy-Fifth Birthday

Bill McEwen celebrated his seventy-fifth birthday on 13 January 1997. Heteroatom Chemistry takes great pleasure in dedicating this and the following special issues to him on this auspicious occasion. Many chemists from around the world have prepared research articles to be placed in these special issues, honoring their distinguished colleague, and the undersigned group of associates assisting with the Journal has prepared this summary of his career and many accomplishments as its own tribute to him.

Bill received both his A.B. (1944) and Ph.D. (1947) degrees from Columbia University. Following service at the Oak Ridge Laboratory during World War II, he entered the academic world with an appointment at the University of Kansas, achieving the rank of professor in 1957. Five years later, Bill accepted a call from the University of Massachusetts in Amherst to head its Chemistry Department and to lead a newly created program of expansion. His outstanding reputation in chemistry was recognized with his being named Commonwealth Professor at Massachusetts. Bill continued as Head of Chemistry for 15 years, stepping down in 1977. The growth of the Department of Chemistry was extraordinary during this period, thanks to his leadership and wisdom. In 1990, Bill retired from the University of Massachusetts but has remained in the Chemistry Department, where he is extremely busy serving as Director of the International Council on Main Group Chemistry and as Editor of *Heteroatom Chemistry,* both of which he created.

Bill is truly a main group chemist. His early work was concerned with compounds of nitrogen, especially with Reissert compounds and alkaloids. His first article on phosphorus chemistry appeared in 1956, and he proceeded to make major contributions in phosphorus stereochemistry and reaction mechanisms. He has published several articles on compounds containing sulfur, boron, and antimony, as well as on iodonium and bromonium salts. His publication record consists of about 170 research articles and two authoritative chapters in books. In addition, he was the co-author of a popular textbook on organic chemistry and of two laboratory manuals in organic chemistry, as well as a co-editor of a two-volume work on phosphorus stereochemistry. Some of the highlights of his research accomplishments are summarized here.

From his first publication in 1949 (with R. N. Hazlett), which dealt with reactions of acylquinolinium and acylisoquinolinium salts, to his most recent publication in 1996 (with J. DeMassa), which covered one phase of the chemistry of iodonium salts, McEwen's research has concentrated to a large extent on the chemistry of 'onium salts. Of some 170 refereed articles published by McEwen et al., about 110 have revolved at least to some degree about 'onium salts. These have included reactions of phosphonium, arsonium, stibonium, oxonium, sulfonium, and bromonium salts in addition to ammonium and iodonium salts. The most significant of these studies in terms of the advancement of fundamental chemistry have been those with phosphonium salts, but the most significant in terms of commercial applications have been those with sulfonium and iodonium salts.

The first resolution of a nonheterocyclic phosphonium salt was reported by Kumli, McEwen, and VanderWerf in 1959. The first concrete evidence, based on kinetics studies, for the formation of a phosphorane intermediate in the cleavage of a quaternary phosphonium cation by the action of alkali was also reported in 1959 by Zanger, VanderWerf, and McEwen. A third communication published in that same year provided the first example of a stereospecific conversion of a phosphonium salt containing a chiral phosphorus atom to a phosphine oxide (Kumli, McEwen, and VanderWerf). Similarly, the first stereospecific Wittig reaction of a phosphonium ylide containing a chiral phosphorus atom (with formation of an optically active phosphine oxide) was reported by Blade-Font, VanderWerf, and McEwen in 1960. This also led to the correct conclusion, later verified by Horner et al., that decomposition of ordinary acyclic phosphonium hydroxides, with the benzyl anion as a leaving group, take place with inversion of the configuration of the phosphorus atom, while the Wittig reactions of the phosphonium ylides derived from these phosphonium cations occur with retention of the configuration of the phosphorus atom. After the report by Dennis and Westheimer in 1966 of the significance of pseudorotation in reactions involving phosphorane intermediates, a concept first introduced by Berry in 1960, and after much pioneering work on the detailed mechanism of the Wittig reaction by many prominent main group chemists (Wittig, Schlosser, Bestmann, Vedejs, Maryanoff, and many others), it became apparent, from the stereochemical results first reported by McEwen and VanderWerf et al., that a pseudorotation is needed before the oxaphosphetane initially formed in a typical Wittig reaction can proceed to the formation of the final products (olefin and phosphine oxide).

More recent studies of the mechanism of the Wittig reaction, some of them utilizing computational chemistry, indicate that, depending on the structures of the substrates, the presence or absence of metal salts, solvent effects, and the temperature at which the reaction is carried out, at least three different mechanisms may be operative (Ward, Mari, Baughman, Cairns, Lahti, and McEwen, 1989–1992; H. Yamataka et al., 1992–1994; K. Okuma, 1995).

Other contributions to organophosphorus stereochemistry made by McEwen et al. included studies of the decomposition of optically active quaternary phosphonium alkoxides to form hydrocarbons, phosphine oxides, and ethers with racemization of chiral phosphorus; the generation and reactions of optically active phosphines; and the reaction of optically active phosphonium ylides with nitriles and epoxides (McEwen, Parisek, Young, Wolfe, Axelrad, and Barnhardt, 1960–1967). Bill in his modesty recognizes that the contributions of other workers were more extensive than his own in these areas (Horner, Imamoto, Mislow, Ciganek, and Fluck).

Investigations of the role of O_{2p}-P, N_{2p}-P and similar interactions in heteroatom chemistry were undertaken during the period of 1971–1990. Rate data for the quaternization reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride revealed two striking effects: (1) The presence of *o*-methoxy groups in the phosphines caused a marked acceleration of the reactions. (2) The difference in the rates of reactions of triarylphosphines with benzyl chloride and *n*-butyl chloride was less than 20, probably the smallest such difference ever observed in S_N2 reactions of these halides. An explanation of these effects was offered based partly on the concept of a strong interaction, perhaps even an orbital overlap, of a pair of $2p$ electrons of an *o*-methoxy group with a $3d$ orbital (or hybrid orbital) of phosphorus in the transition state and partly on the concept that the transition state for each of the benzyl chloride reactions lies much closer to the reagents than to the products along the reaction coordinate of the energy profile diagram. Additional evidence for the postulated $2p$–$3d$ interactions was found in the UV and NMR spectra of the phosphines and the corresponding phosphonium salts. The largest effect was produced by the presence of 2,6-dimethoxyphenyl groups bonded to phosphorus. As an outgrowth of this, Prof. Masanori Wada of Tottori University has found that the presence of such groups can stabilize even some carbocations to the extent that they can exist in an aqueous medium.

In the late 1960s, Knapczyk, Lubinkowski, and McEwen discovered the photochemical generation of "instant acid" (Bronsted variety) in high quantum yield in suitable solutions of triarylsulfonium and diaryliodonium fluoroborates. The generation of acid was found to occur via the initial formation and subsequent reactions of highly reactive radical and radical–cation intermediates. Several capable and aware industrial chemists, Crivello (General Electric), Willson (IBM), and Hacker (IBM), among others, capitalized on this finding and developed important industrial processes based on these discoveries. These developments included the creation of new photoresists in the microelectronics industry, and new applications in coatings, adhesives, and inks. Among the coating applications were clear varnishes for cans, leather and vinyl coatings, abrasion resistant coatings for floor tiles, adhesive bonding agents for metals to glass, and photocuring staking compounds for mounting electronic components. A highly visible advertisement for this chemistry consists of the glitzy coatings on cans of soft drinks and beer. Large additions to the gross national products of many nations resulted from these discoveries that the National Science Foundation of the United States "bought" for about $30,000 per year in grant funds to McEwen, who is fond of advertising this as a justification for the continued funding of "small science" as against recent emphasis on the funding mainly of "big science". The discovery of the photochemical generation of "instant acid" did not arise in a vacuum. It followed numerous studies of topics such as the pyrolysis of triarylsulfonium halides, decomposition of triarylsulfonium alkoxides, substitution reactions at antimony in the tetraphenylstibonium cation, the decomposition of tetraphenylstibonium hydroxide, the crystal and molecular structures of methoxytetraphenylantimony and dimethoxytriphenylantimony, syntheses and reactions of triarylsulfonium salts, photolysis and thermolysis of pentaphenylantimony in benzene, the attack of alkoxide ions on antimony in tetraarylstibonium salts, exchange and redox reactions of diaryl sulfides with aromatic hydrocarbons, competing modes of decomposition of triarylsulfonium and diaryliodonium alkoxides, thermal decompositions of tetraarylstibonium hydroxides, and reactions of diarylbromonium salts with sodium alkoxides, all published during the period of 1965–1972.

Although the investigations on Reissert compounds would be classified as classical heterocyclic rather than heteroatom chemistry, McEwen and his co-workers devoted about 35 years, off and on, to this work. In 1955, McEwen and R. L. Cobb reported on the mechanism of the acid-catalyzed formation of aldehydes from Reissert compounds, the key feature being the involvement of mesoionic intermediates. This led in subsequent years to the utilization of such intermediates in the synthesis of several types of polycyclic heterocyclic compounds by new 1,3-dipolar addition reactions and (2 + 4) cycloaddition reactions. Both acid-catalyzed and base-catalyzed reactions of Reissert compounds were also utilized in the synthesis of alkaloids and potential medicinal agents. The synthetic utility was then expanded to the preparation and application of "open-chain Reissert compounds," including the development of Stevens-type rearrangements.

Other areas of research that have been explored by McEwen and his students have included anodic reductions brought about by the generation of unipositive magnesium and the corrosion of massive magnesium by organic radical-ions generated in such electrolysis experiments. Professor Jacob Kleinberg was the co-director of this research, and also of studies of some unique reactions of metallocenes, including radical reactions of ferrocenylcarbocations, addition of weak acids to vinylmetallocenes, and the investigation of substituent effects in the chronopotentiometric oxidation of ferrocenes.

A variety of rearrangement reactions of many different types was investigated by McEwen and his students over many years. These included studies of the Schmidt reaction, the formation of enol esters of ketones and β-ketoesters by acylation reactions in pyridine, quinoline, and isoquinoline solutions (an extension of McEwen's Ph.D. dissertation work initially carried out under the direction of Professor William von Eggers Doering at Columbia University), acid-catalyzed rearrangements of organic hydroperoxides, some novel sigmatropic rearrangements, and a new type of transmetallation/elimination reaction within a hypervalent intermediate occurring in the reaction of triphenyldimethoxystiborane with triphenyltin hydroxide.

In addition to his many research contributions previously mentioned, William McEwen has served the profession of chemistry in other important ways, most notably through extensive activity in the American Chemical Society, as a member of several journal editorial boards, and as a panel member for both the National Science Foundation and the National Institutes of Health. Perhaps his greatest service has been the creation of this journal, *Heteroatom Chemistry,* in 1989, followed shortly by his creation of the International Council on Main Group Chemistry. The success of both of these undertakings is a testament to his organizational and leadership ability. Main group chemists owe him a great debt for his pioneering efforts on their behalf. In recognition of his many years of outstanding activity in chemistry, Bill has been elected as a Fellow of the American Association for the Advancement of Science, and he has received the Outstanding Civilian Service Medal of the U.S. Department of the Army (1984) and the Chancellor's Distinguished Faculty Medal of the University of Massachusetts.

On behalf of his colleagues in main group chemistry throughout the world, we say "Many Happy Returns" on this celebration of Bill's birthday, and we look forward to many more years of his leadership in this field.

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