HETEROCYCLES, Vol. 80, No. 1, 2010, pp. 7 - 11. © The Japan Institute of Heterocyclic Chemistry
DOI: 10.3987/COM-09-S(S)Foreword-2

Laudatio Suzuki Akira 献呈 鈴木章 先生

> "In 1962, I was interested in the Wacker reaction... One Saturday afternoon ..., I went to a bookstore in Sapporo... and found a red and black two-tone colored book... The book was "Hydroboration" written by Professor Herbert C. Brown. ... This book changed the course of my career, ..."[1a]

Today, as we scan the ASAPs and graphical abstracts and turn the electronic pages, a constant flow of publications appear which owe their origins with the original discoveries of Professor Akira Suzuki. For over 30 years, Professor Suzuki blazed a trail of discovery in the field of his fascination - organoboron chemistry. With characteristic background preparation, thoughtful insight, and exquisite experimental execution, he provided contributions which set new trends at the outset of the very productive H.C. Brown era. Professor Suzuki's work disclosed original and versatile organoborane methodology. In retrospective analysis, it is clear that the new reactions emanating from the Hokkaido laboratories became accepted and widely used by the synthetic organic community without name and sometimes without reference, with one exception, as standard reactions for application. The outcome, as viewed from a purview of the current literature, is beyond the impact that his work has made to organic synthesis: it provided, in the mid-1970s, a shaft of light in the slightly ajar door which opened in a blazing brightness of boron chemistry and justifies the claim that B is the element for advances in chemistry as well as allied disciplines in the 21st Century.[2]

The systematic studies of numerous inorganic, organic, and organometallic chemists[3] sowed the seeds and the voluminous systematic research of H.C. Brown nurtured the practical framework of organoboron chemistry. The excellent work of D.S. Matteson[4] maintained the intense interest in B-chemistry but it was especially the findings of the transition metal catalyzed cross coupling reaction of boronic acid derivatives which now bears the Suzuki name that changed several parts of the landscape of how synthetic chemists practice their art and science.

Professor Suzuki's numerous discoveries and findings in the field with which he has had life-long fascination may be surveyed, incompletely of course, by reference to the following contributions without precise judgment of order of significance because a) they are all important as viewed from perspective of current synthetic practice and b) from advance to next advance, there is inevitable lack of predictability in terms of the value of rapidly advancing science.

In 1965, on the return flight to Japan after very successful post doctoral studies with H.C. Brown, Akira Suzuki planned his initial independent research project by consideration of the "remarkable difference between organoboranes and other organometallic compounds."[1b] This consideration as well as mechanistic insight led to the discovery of the synthesis of chain-extended ketones from reaction of trialkylboranes with α,β-unsaturated ketones. As often occurs in all areas of science, this reaction was also under study in Professor Brown's laboratories and led to a collaborative study of considerable synthetic value, the establishment that the reaction involved organoboron radical species formed by catalytic oxygen, and, amusingly, the dependence of the discovery on the presence of oxygen in Sapporo nitrogen gas and not in the Purdue high purity nitrogen. These findings stimulated work involving Cu(I)methyltrialkyborates, tetracoordinated organoborates, 1-alkynylborates, and 1-alkenylborates which provided new routes to unconjugated dienes, pure secondary amines, chain-elongated aliphatic carboxylic acids, internal alkynes, and isopropenylated cycloalkanes respectively.

In the above investigations by Akira Suzuki, rational approach and expectation, taking advantage of insight from one discovery, appreciation of fundamental facts (e.g. C-B bond strength), and, as always, the participation of the sometime friend of synthetic chemists, good fortune, led to the provision of robust synthetic methods which today may continue to be viewed as deserving greater utility.

Careful analysis led Akira Suzuki to arguably his most original contribution of the transition metal catalyzed reaction of organoboronic acid derivatives with organic electrophiles, a fundamental transformation which now bears his name. He posited that the weak carbanionic character of an organoborane which prevents this 'metal' to undergo the transmetalation step in the then accepted mechanism of the cross coupling reaction could be overcome by the use of the derived organoborates. Success followed by the development of efficient methods for the regio- and stereo-selective synthesis of (*E,E*)- and (*E,Z*)-conjugated dienes, arylated alkenes, 1,4-alkadienes, allylbenzenes and, somewhat later, products from Csp^3 -B bond coupling of R-B-9-BBN reagents with vinyl and aryl electrophiles. The latter chemistry has been pursued to advantage by others, especially by another excellent B-chemist, J. Soderquist.[5] The challenging problem of β-hydride elimination in Pd-catalyzed cross coupling to form sp^3-sp^3 bonds was also addressed by Akira Suzuki in contributions that are prognostic to the recent status of this once-defined holy grail of chemistry. Undeniably the most adaptable and convenient methodology of this type was the cross coupling of arylboronic acid derivatives with aromatic electrophiles to produce biaryls, a reaction disclosed in 1981 and under exponential growth today (a minimum of 1000 publications by SciFinder search in 2008). This method superceded the classical and random Ullmann reaction for biaryl synthesis, has been extended to heteroaromatic coupling partners in both of the boron and nucleophile combinations, and, most significantly, has been adapted in high frequency as the key process in the construction of pharmaceuticals, herbicides, natural products, and materials ranging from conducting polymers to molecular wires and liquid crystals.[6] Together with several other name reactions, the advantageous Suzuki reaction has made Ar-Ar bond formation a diversity rich and reliably applicable event for synthetic chemists.

The decisive need for stereodefined alkenyl boronic acids and halides for the above cross coupling chemistry drove the development of the regio-, stereo-, and chemo-selective haloboration reactions of alkynes, constituting the most recent area of research of Professor Suzuki. The availability of the haloboration adducts led to the development of new methods for the construction of valuable synthetic building blocks for which, as noted above in a different context, the 'underutilized' term may be also applied. From 1971, especially with his valuable student and then collaborator Norio Miyaura, now distinguished in independently established chemistry, papers flowed like mountain run-off in the Spring in all of these areas from the Hokkaido laboratories.

The achievements of Professor Akira Suzuki reflect his decisive choice of subject, establishment of deep knowledge therein, and then considerable insight and consistent dedication in execution. Although application of his discoveries to natural product synthesis abound, it is clear that his heart has been in discovery and development of synthetic methods. His chemistry is so deeply ingrained in the thinking of organic chemists that, with the exception of the cross coupling reaction, it is now used without citation, perhaps the truly identifying mark of really useful chemistry.

When one is in the presence of Akira Suzuki, three characteristics have consistently shined: his calm, yet stirring, dedication for chemistry, his steadfast respect for those that mentored him and walked with him, sometimes in identical paths, during his times of discovery, his care to provide experimental excellence, his attention to fairness and credit due for the work of others, his carefully evaluated and spoken comment of advice and guidance, and, certainly not least, his modesty and his zest for life.

Returning to the beginning citation, I have a personal somewhat parallel story: sitting in the library one evening, searching for a paper no longer remembered in *Syn. Commun.,* I turned the proverbial page and found the reaction[7] that changed my chemical life and, I add in the same breadth, the lives of organic chemists worldwide.

Before your eightieth birthday, Akira, please enjoy this special issue of *Heterocycles,* dedicated to your multifaceted contributions to organoboron chemistry whose impact to organic synthesis is only in early evolutionary stages.

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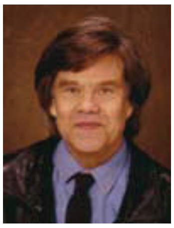

Victor Snieckus was born in Kaunas, Lithuania in 1937 and spent his childhood in Germany during World War II. He received the B.Sc. degree at the University of Alberta (1959) where he was strongly influenced by R. Sandin. After graduate work at the University of California, Berkeley (M.Sc. with D.S. Noyce) and Oregon (Ph.D. with V. Boekelheide), he returned to Canada for a postdoctoral year with O.E. Edwards at NSERC, and then joined the faculty at the University of Waterloo in 1966. He held the Monsanto/NRC Industrial Research Chair until 1998 when he accepted the Bader Chair in Organic Chemistry at Queen's University.

Recent awards include the Order of Grand Duke Gediminas by the President of Lithuania (2004), Givaudan/Karrer Medal, University of Zurich (2008); International Society of Heterocyclic Chemistry, Honorary Lecturer (2009); Central European Novartis Lecturer, Prague, Budapest, Bratislava (2009), Fellow, American Chemical Society (one of two non-Americans) (2009), Honoris causa, Tallinn Technical University, Estonia (country of his Mother) (2009).

He is the author and coauthor of 352 publications and 9 patents. His current research interests focus on new synthetic methodology and strategy; construction of bioactive molecules, natural products and man-made materials; the Directed ortho and remote Metalation reactions (DoM, DreM); Aromatic carbanion chemistry; transition metal catalyzed coupling reactions, with emphasis on the Suzuki reaction; axially chiral biaryl and planar chiral ferrocene ligands for asymmetric organometallic catalysis; discovery and development of new methods for medicinal and process chemistry application.