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CONGRATULATIONS ON YOUR 80-YEARS BIRTHDAY TO PROFESSOR AKIRA SUZUKI

Rare chemists are so world-famed as Professor Akira Suzuki. Every organic chemistry student knows the Suzuki cross-coupling reaction (it is also called Suzuki reaction or Suzuki-Miyaura coupling) and most of them can draw mechanism of the transformation. Nowadays Suzuki coupling is popular like Diels-Alder cycloaddition or Grignard reaction at that time. It is really impossible to find any issue of journal on organic or organometallic chemistry that wouldn't contain the article on the Suzuki reaction. Hundreds of papers are reported to the syntheses of various substances including many natural compounds via the reaction.

This palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halids discovered in 1979 (N. Miyaura, A. Suzuki, *J. Chem. Soc., Chem. Commun.*, **1979**, 866; N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Letters*, **1979**, 3437) has become classic method for generating carbon-carbon bonds. Recent catalyst and protocol developments have broadened the possible applications of the reaction enormously so that the scope of the reaction partners includes alkyls, alkenyls, alkynyls and aryls. As the boron reagents, arylboron, potassium trifluoroborates and alkylboron derivatives can be employed. The Suzuki coupling offers several additional advantages such as being largely unaffected by the presence of water, tolerating a broad range of functional groups, and proceeding generally regio- and steroselectively. It is important that the inorganic by-products are non-toxic and easily removed from the reaction mixture thereby making the coupling suitable not only for laboratories but also for industrial processes. Reaction transformations include also: the use of green media such as water, ethanol, poly(ethyleneglycol), supercritical carbon dioxide, ionic liquids, and solvent-free etc; the design of recoverable and reusable polymer-supported catalysts and entrapment or intercalation of metal species; and the search of the novel synthetic methodologies involving ultrasound irradiation, microwave heating technique, and continuous flow processes with using a microencapsulated palladium catalyst.

The Suzuki coupling is now a standard reaction and numerous relatively simple and very complex molecules were constructed using it, see: A. Suzuki, in *Organoboranes in Organic Syntheses*, Hokkaido University, Japan, 2004; A. Suzuki, H.C. Brown, *Organic Synthesis via Boranes. Vol 3. Suzuki Coupling,* Aldrich Chem. Co, Inc, Milwankee, 2003; N. Miyaura, *Cross-Coupling Reactions: A Practical Guide*, Springer, New York, 2002; N. Miyaura, A. Suzuki, *Chem Rev.*, **1995**, *95*, 2457; N. Miyaura, Y. Yamamoto, in *Comprehensive Organomrtallic Chemistry III*, R.H. Crabtree, D.M.P. Mingos, Eds.; Elsevier: Oxford, 2007, Vol. 9, p. 146.; H. Doucet, *Eur. J. Org. Chem.*, **2008**, 2013.

Not only with coupling reaction has become Akira Suzuki famous. He is one of the best world expert on organoboron chemistry. He started to work in this field (stereochemistry of hydroboration reaction) under Prof. Herbert C. Brown at Purdue University (USA) as a post doctoral research fellow (1963-1965). Returning to Sapporo, Japan, in 1965 he began studying properties of organoboranes. In 60-70th, the leading world boron groups investigated a great deal of triorganoborane chemistry, and Akira's team was not an exception. In his research group at the Hokkaido University, a number of significant novel reactions have been discovered and it was demonstrated that organoboranes are powerful and versatile reagents for organic synthesis. Akira himself typified other works of his group in the following:

- oxygen-induced organoborane reactions,
- synthesis via copper(I) methyltrialkylborates,
- synthesis via 1-alkenyl- and 1-alkynylborates,
- haloboration and thioboration of alkynes,
- electrochemical reactions of organoboranes.

A. Suzuki's works are of particular originality and creativity that open up new lines for us, always new ways of thinking and rushes of inspiration. Suzuki team fellows not only elaborate the new approaches for organic synthesis but they are able to use all the rich methods of the modern organic chemistry and catalysis.

In cooperation with Purdue group, a series of important radical reactions proceeding only in the presence of oxygen was discovered. It was demonstrated that oxygen initiates spontaneous 1,4-addition of trialkylboranes to numerous α,β-unsaturated carbonyl compounds including methyl vinyl ketone, methyl isopropyl ketone, acetylacetylene, vinyloxirane, 3,4-epoxy-1-butyne, and crotonaldimine. 1,6-Addition to 1-acyl-2-vinylcyclopropane as well as radical 1,2-addition of triorganoboranes to monomeric formaldehyde were also found. The latter reaction, in combination with hydroboration, presents a promising route for the one-carbon homologation of olefins.

At the end of 70th, A. Suzuki, N. Miyaura and co-workers have successfully exploited copper(I) tetraorganoborates and lithium alkynyl(trialkyl)borates. In the result, series of excellent approaches to acetylene, alkene, and allene derivatives have been worked out.

The Suzuki's pioneer works on electrochemical transformations of trialkylboranes present an important contribution to "green chemistry". Thus, it was demonstrated that electrolysis of trialkylboranes R_3B can be successfully used for the preparation of higher hydrocarbons R-R, methyl ethers ROMe or alkyl acetates MeCOOR. Electrochemical reactions of trialkylboranes with substrates having acidic hydrogen such as acetonitrile, nitromethane, 1-alkynes, piperidines, and ethyl phenylacetate proceed smoothly to provide convenient approaches to nitriles, nitroalkanes, internal alkynes, N-alkylpiperidines,and ethyl 2-alkylphenylacetates.

Haloboration of alkynes was not discovered in Japan, but it was Sapporo group where excellent methodologies based on this addition reaction have been developed. A. Suzuki, S. Hara, and co-workers have demonstrated that haloboration of 1-alkynes proceeds via the Markovnikov *syn*-addition of the B-Hal fragment (Hal = Cl, Br, J) to the triple bond furnishing the corresponding *Z*-2-halo-1-alkenylboranes and the order of the haloborane reactivity is following: 9-J-9-BBN, $BBr_3 > BCl_3 >$ 9-Br-9-BBN >> 9-Cl-9-BBN. In the case of acetylene itself, the reaction with BBr_3 gives rise to (*E*)-(2-bromoethenyl)dibromoborane, probably via initial *syn*-addition followed by (*Z*)→(*E*) quantitative isomerization. The haloboration products contain three functionalities (boron, halogen and the C=C bond) and all three were skilfully exploited to a creation of a novel branch of fundamental organic chemistry. As the result, excellent ways to various 2-halo- and 1,2-dihalo-1-alkenes, 1,3-dienes and enynes, unsaturated and polyene ketones, esters, amides, δ-keto esters, and many other compounds were worked out. The methodologies developed were utilized for the preparation of prostaglandine B_1, nerolidol, S(-)- and R(-)-ipsenols, sex pheromone of the bark beetle as well as a mosquito attractant pheromone. I would like to mention here the preparation of 2-bromoallylboranes via 1,2-bromoboration of allene with BBr_3 and their application as allylborating reagents.

The reaction of organoboranes with organic azides discovered in early 70th presents a rapid route to secondary amines and Akira's Sapporo team was the first who paved the way at this point. A number of ethyl(alkyl)- and ethyl(phenyl)amines were obtained by the interaction of triethylborane and alkyl or phenyl azides.

In connection with the recent enthusiasm for "click chemistry", a convenient way to alkyl- and cycloalkyl azides based on the interaction of trialkylboranes with iron azide in the presence of hydrogen peroxide should be mentioned

In addition, Prof. A. Suzuki has published seventy useful papers not connected with boron chemistry. He studied also carbonylation and other reactions of various organic compounds in super acid media, chemistry of naphtalenes and phenathrene derivatives, aconite bases, and other problems.

Professor Akira Suzuki is not only an excellent scientist but also a wise teacher and a very good human being. My first meeting with Akira had been happened in Moscow in 1971 at the organometallic congress and this was the beginning of our friendship which has continued until this day. Instantly I noticed his self-discipline, preciseness, and nobility. In 1987 at IMEBORON-VI in Bechyne near Tabor (Former Czechoslovakia), I met him again. At that time both of us were inveterate smokers, and during the session breaks we founded an appropriate corner, he smoked my Russian cigarette and I his Japanese, and we spoke a great deal of chemistry, politics, life and death, about everything else. We understood each other perfectly, we had similar views on many things. I was delighted with his good humor and his original approaches to organic chemistry. With the great pleasure, I remember conferences in Torun

(Poland, 1990), on the ship Moscow-Kostroma-Plyos (Russia, 1993), and visiting Sapporo in the autumn of 1993 particularly. Akira and his wife Yoko were cordial hosts. They gladly showed beauties of Hokkaido (marvelous journey around Sapporo by his car with the right wheel) and Japanese traditions; they laughed amicable at my first attempts to eat with chopsticks. I spent several hours in their daughter family and played with his granddaughter. In May of the same year in Moscow Yoko and Akira played with my little grandson. Now our grandchildren are quite adults.

Being the Vice-President of the Chemical Society of Japan, A. Suzuki has provided the libraries of the Moscow University as well as Zelinsky and Nesmeyanov Institutes in 90th with journals *Chemistry Letters* and *Bulletin of the Chemical Society of Japan.* Here I wish once more to express the great gratitude for this “king gift”.

Akira’s works present very important sections of many books and reviews dealing with the application of boron derivatives in synthesis. He has delivered many plenary and invited lectures at academic conferences around the world. He is a happy “Chemical father and grandfather”. Several his former students have become distinguished scientists and university professors.

In chemistry of 20th century, the Suzuki’s name is settled down in one line with Grignard’s, Diels’ and Alder’s, Wittig’s, Cope’s and few other names. The scientists mentioned are different, but each enriched Chemistry greatly. And in 21st century Suzuki cross-coupling (Suzuki-Miyaura coupling) will be one of the most important, useful, and attractive reactions.

This issue of HETEROCYCLES is dedicated to Professor Akira Suzuki on occasion of his 80-years birthday and it is only small mite of our profound respect to this Great Chemist for his contribution to science. His activity is not exhausted.

My dearest Akira-sama,
I wish you good health and continuous scientific teaching activity, be happy, be happy with Yoko and your daughter’s families.

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Yurii N. Bubnov was born in 1934 in Rostov the Great (200 km North of Moscow, Russia). He graduated from Moscow State University, Faculty of Chemistry in 1957, received Ph.D. in 1961 from Zelinsky Institute of Organic Chemistry of Academy of Science of the USSR under the direction of Professor Boris Mikhailov and Doctor of Sciences Degree (organic chemistry) in 1983 from the same Institute (Habilitation: “Allylic boranes in Organic Synthesis”). Professor (1991), Full member of Russian Academy of Sciences (RAS, 2000), Director of Nesmeyanov Institute of organoelement compounds of RAS since 1996. Scientific interests: chemistry of organoboron compounds (unsaturated, cyclic, and cage derivatives), their application to multipurpose organic synthesis, including alkaloids, pheromons and other natural substances; borotropy and conformational analysis.