Professor Giuseppe Bartoli

A Tribute

It is a real pleasure for me to write a tribute to Professor Giuseppe Bartoli on the occasion of his approaching 65th birthday. From the day of our first meeting in 1976, at the University of Bologna, I have considered him as a role model, a source of inspiration and a genuine asset to my profession. Now that I am a long way from Bologna, I miss the long games of "tressette" (an Italian game with cards) during lunch break and discussions on chemistry. Professor Bartoli has certainly reached an eminent position among present day scientists, as I aim to demonstrate by writing these brief notes about the areas in which he has achieved distinction.

Giuseppe "Pino" Bartoli was born in Rottofreno, on May 25, 1941. He was awarded his degree in Industrial Chemistry from the University of Bologna in 1967. Then, following his first mentor, Professor Todesco, at the University of Bari, he started his academic career as Assistant Professor of Organic Chemistry in 1968. There, he met a young colleague, Marcella Bosco, the woman who would become his wife, the mother of their daughter Francesca, but chiefly the harshest critic of his chemical work. He moved in 1976 to the University of Bologna, where he became Associate Professor of Organic Chemistry in 1980, and then to the University of Camerino in 1986, as Full Professor. In 1993 he finally came back to Bologna, where his family continued living from 1975. He is currently Professor of Organic Chemistry at the Faculty of Industrial Chemistry, at the same institute where he took his first steps as student and researcher.

From 1999 to 2001, he was a member of the Board of Directors of the Division of Organic Chemistry of the Italian Chemical Society (SCI). He has held the position of Head of the Department of Organic Chemistry 'A. Mangini', at the University of Bologna, since November 2001. He is the author of over 160 papers in the most important international journals dealing with his research interests.

Professor Bartoli's scientific career began with studies on free energy relationships. He demonstrated that differences in reactivity, expressed by rate constants for the attack of nucleophiles at aromatic sites in S_NAr reactions as the polarizability of nucleophile was varied, depended linearly on the polarizability of the nucleofuge for a fixed substrate framework. As a further development, he also proposed a relationship, which separated the contribution of basicity and polarizability of nucleophile, nucleofuge and substrate framework.

Then, during his studies on S_NAr reactions, he discovered that the reaction of Grignard reagents with nitroarenes was a very useful synthetic tool. He rationalised the mechanism on the basis of a SET pathway, where the geometry of the alkyl radical influences the site of collapse on the nitroarene radical anion viz: alkyl radicals on the ring, allyl radicals on the nitrogen atom and vinyl radicals on the oxygen atom. Taking these observations into account, Professor Bartoli showed that the alkyl Grignard reaction behaved as a process analogous to the Friedel-Crafts reaction proceeding with reversed polarity. Contemporarily but independently from Prof. Makosza's work on VNS Prof. Bartoli devised the best reagents for oxidizing, dehydrating and reducing unstable nitronate-adduct intermediates. The attack of vinyl Grignard reagents on the oxygen atom of nitroarene radical anions led to an indole synthesis now named "*Bartoli indole synthesis*" in many textbooks monographs and papers. This *de novo* construction of the indole ring is now one of the most widely used syntheses of 7-substituted indoles.

A laboratory accident moved Prof. Bartoli's chemical interests from nitroarenes to dianions of enamino ketones, and now Bartoli's rules for the regioselective alkylation of enamino ketone dianions are cornerstones in this field. The chance to selectively alkylate the α or γ-position of an enaminone moiety allowed the synthesis of many heterocyclic systems, such as pyridine, pyrimidine, pyranones and furans. Moreover the alkyl group on the nitrogen atom was used as a chiral auxiliary for enantioselective alkylation of the γ-position.

In the early 90's, Prof. Bartoli's interest moved towards cerium-mediated organic chemistry. First, he was fascinated by the chemistry of organocerium reagents in addition to easily enolizable electrophiles. Then he discovered that cerium was not a chelating metal and he stated the rules for the stereoselective reduction of functionalised ketones in the presence of a Lewis acid promoter. Reductions with chelating agents, such as titanium tetrachloride, and with non-chelating agents, such as cerium trichloride, proceed through a cyclic or a Felkin-Ahn transition state respectively, leading to opposite stereochemical outcomes. Prof. Bartoli found that the complex formed by cerium (III) chloride and sodium iodide showed strong Lewis acid character. These reagents are cheap, non-toxic and water tolerant, so all the protocols they are involved in are environmentally benign, in contrast to more common, but non-water tolerant and toxic Lewis acid reagents. Due to these characteristics, $CeCl_3$/NaI system has rapidly become a widely employed catalytic system.These discoveries prompted Prof. Bartoli to leave organometallic chemistry and to focus mainly mainly on stereo and enantioselective Lewis-acid-catalysed reactions with magnesium and zinc perchlorates the ultimate topic of his research work.

The contributors to this issue are colleagues and friends who would like to join me in wishing him "ad multos annos"

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Selected publications of Prof. Bartoli

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