Professor Roberto Arturo Rossi

A Tribute

Professor Roberto Arturo Rossi was born in March 27th, 1943, in Jesús María, a small town near Córdoba city, in Argentina. He is a second generation of Italian and Spanish immigrants to study in a public university of high academic standards as is the National University of Córdoba (NUC), center of the University Reform that spread from Córdoba to other Latin American countries in 1918.

Roberto graduated as a biochemist in 1965 from the Institute of Chemical Sciences, which in 1971 turned into the Faculty of Chemical Sciences (FCS-NUC). He received his Ph.D. degree from the same institution in 1967 with honors. His thesis dealt with the chemistry of benzyne intermediates. His Ph.D. thesis adviser was Professor Héctor E. Bertorello, one of the pioneer organic chemistry professors and organizer of the Organic Chemistry Department.

In 1970, Roberto was awarded an external fellowship from CONICET, the National Research Council of Argentina, to carry out postdoctoral studies under the guidance of Professor Joseph F. Bunnett at the University of California in Santa Cruz, USA (UCSC). This stay abroad was the beginning of great many things to come.

Shortly before his arrival in Professor Bunnett’s laboratory, Bunnett and Kim had discovered that besides the up-to-then known mechanisms for substitution of aromatic halides, another pathway for substitution was possible. This route did not involve the movement of electron pairs (polar reactions), but the displacement of single electrons at a time; in other words, aromatic substitution by electron transfer. This meant that the mechanistic pathway, proposed independently by Kornblum and Russel in 1966 for the nucleophilic substitution of aliphatic halides activated by electron withdrawing groups at the α–carbon, could also be applied to the substitution of non-activated aromatic halides.
To prove the proposal and to examine its scope represented a challenge for which Roberto was prepared. Undoubtedly, his active temperament, open mind, expertise and extraordinary work capacity were key factors for a number of important findings he achieved in the field while at UCSC.

At this stage, he proved that the mechanism, named $\text{SRN}_1$ (Radical Unimolecular Nucleophilic Substitution) by Bunnett, could be initiated not only by solvated electrons from alkaline metals, as known until then, but also (and most importantly) by light. This was undoubtedly the cornerstone that would open the nowadays-powerful synthetic scope of this type of substitution. He also demonstrated the possibility, offered by the process, to achieve the formation of new C-C bonds at aromatic centers.

Roberto has always regarded Joe Bunnett with great respect as the main and most outstanding adviser of his academic life.

Roberto returned to Córdoba in 1972 with his wife, Rita Hoyos de Rossi, also a well-known chemist, and their two young children, Gabriela and Enrique. At that time he held a position as Assistant Professor at the Organic Chemistry Department of FCS-NUC, where he found an under-equipped laboratory and no funding or other supplies. However, with a T-60 NMR spectrometer and a gas chromatographic resource, kindly offered by the Biological Chemistry Department, he started the adventure to create a group in the field of Physical-Organic Chemistry which, in time, would become internationally recognized. It was a difficult task, but his academic leadership and personality attracted those that had the luck to know and work with him. One of his main teachings to his doctoral and postdoctoral students was that study, and dedication intertwined with acquired knowledge would be the mother of invention for new goals despite the limited resources available.

I met Roberto in 1973, just a few months after his return from the USA, and joined the group as a student assistant. At that time, political changes in Argentina made a serious impact on academic life in our Faculty. It was time for the staff from different academic Departments of FCS-NUC to join efforts for the benefit of the institution, a project to which Roberto was deeply involved. Shortly after his arrival, I enrolled in one of his Organic Chemistry courses, which opened up for us a new perspective to look at organic reactions and mechanisms. This whole experience convinced me to become a member of his team and I started my doctoral studies under his supervision in 1975. Antonio F. Lopez and myself were the first students to obtain our Ph.D. degrees in the group. While I was finishing, other people were incorporated, Rubén A. Alonso, Sara M. Palacios, Alicia B. Peñeño, and Ana N. Santiago, among others. To date, he has supervised numerous Ph.D. theses (seventeen, four of them in progress) and has been the adviser of postdoctoral students from other universities and of researchers from CONICET. Some of his former students remained at the Faculty as Professors. Others have become Professors at different Argentine Universities or at Research Centers of Applied and Fundamental Chemistry throughout the country and abroad.

Radical nucleophilic substitution at aromatic carbon was his first field of interest after returning to Argentina. In this area one of his main achievements was to broaden the array of
nucleophiles derived from carbon (N,N-disubstituted amides and thioamides, ketones, nitriles) and from other elements (phosphorous, sulfur, tin, arsenic, antimony, selenium, and tellurium), which opened new routes to obtain C-C and C-heteroatom bonds at sp² carbon. In the field of aromatic alkoxides and anions from aromatic amines, the preferred C-C regiochemistry was established. The stereochemistry of the radical-nucleophile coupling reaction was studied and stereoselectively achieved with chiral assisted imide enolate anions. He also searched for other approaches to initiate these chain reactions (sodium amalgam, sonication, SmI₂, and the scope of the initiation by Fe(II) salts) and to widen the spectrum of adequate solvents. Interpretation of the mechanistic studies of these systems with the aid of Molecular Orbital theory led to the elucidation of important factors governing the chemical reactivity of radical anions within different stages of the SₐRN₁ reaction. The radical-nucleophile coupling step is another part of the process he studied thoroughly as well as the importance of the intramolecular electron transfer catalysis exerted by substituents that transform unreactive systems into very reactive ones.

Roberto’s advances in the field of aliphatic substrates created a whole new strategy for nucleophilic substitutions by electron transfer. I still recall the day he came into the laboratory with the idea of: “if unactivated aromatic substrates that do not react by polar mechanism could do so by SₐRN₁, the scope could probably be extended to aliphatic compounds that are unreactive or poorly reactive by polar processes”.

1-Haloadamantanes and halotriptycenes were the first compounds to be included to the SₐRN₁ list. They were followed by neopentyl halides, cycloalkyl and bridgehead bicyclo- and polycycloalkyl halides of varying strain energy.

Nowadays, the SₐRN₁ process is recognized as a route to achieve the substitution of a wide family of substrates and nucleophiles and it is our belief that it should be definitively included in basic text books of Organic Chemistry.

Roberto is always interested in new frontiers. He was intrigued with how quantum yields of initiation could affect the global quantum yield of the whole SₐRN₁ process. Professor Alicia B. Peñénory, one of his collaborators, had the challenge to implement quantitative aspects of the photochemical project. In 2001, they finally proved that global quantum yields of substitution below unity could mean propagation chains as long as 127.

Always searching for new scope, Roberto is now actively involved in the synthetic applications of the process. His main interest relates to cyclization reactions, which have proved to be a powerful tool to obtain some natural product derivatives, the synthesis of indoles and the search for new nucleophiles and substrates. Another interesting synthetic approach recently developed by Rossi’s group is the combination of the SₐRN₁ chemistry of stannyl anions with the Stille reaction (Pd(0) catalysis), to achieve the synthesis of polyaryls substituted by electron withdrawing and electron donating groups.

He loves teaching. He has dedicated an enormous amount of effort to prepare presentations of all the courses he is in charge of, from Basic Organic Chemistry to Advanced Organic Synthesis, utilizing the liquid crystal projector, making classes very dynamic and interactive to students. It is a pleasure to attend to the group’s weekly seminars where he is always eager to
discuss new ideas and explain unexpected results. He is always willing to teach science whenever he is invited to, either in Argentine institutions located far from the main academic centers, or in Latin American and European countries. His international activities span a broad spectrum including numerous invited lectureships.

Roberto was the first Professor from the Organic Chemistry Department to look at the \( \pi \) Hückel method to interpret mechanistic aspects of experimental systems. He devotes a fair amount of time modeling his ideas on his PC with semiempirical molecular orbital packages. The Ph.D. curriculum course he taught on Molecular Orbital Theory in 1979 had a decisive influence on my future. From then on I became very much involved with the procedures of Computational Chemistry and their applications to the study of organic reactions. My associations with him in this area started in 1982, when I returned from a postdoctoral stay with Professor Michael J. S. Dewar.

In addition to his scientific pursuits, Roberto actively participates in the making of research and development policy at national level. He encouraged us to become members of the Instituto de Investigaciones Fisico Químicas de Córdoba (INFIQC), a CONICET institute for development of Physical-Chemistry in Córdoba. This participation was possible due to the vision of a group of Professors from the Physical-Chemistry and Organic Chemistry Departments of the Faculty.

He has been, and currently is on the Chemistry Committee boards of CONICET, has been involved with the National Secretary of Science and Technology, in relation to the development of the Fine Chemistry Project and with the National University of Córdoba as Secretary of Science and Technology. He was a member on the first directive board of CONICOR, the Research Council of the Province of Córdoba, created by the visionary Professor Ranwell Caputto. As member of CONICOR Roberto has had a central role in the foundation of the Applied Research Center of the Faculty (CEQUIMAP) for which he was Director, participating in different applied projects. He also had the high responsibility of being Dean of the FCS-NUC when democracy returned to the country and universities (1983-1986).

He has been Full (1983-1987) and Associate (1987-1991) Member of the Organic Chemistry Division of IUPAC. He is fully engaged with the Argentine Organic Chemistry Association, SAIQO, for which he was Chair (1986-87). Currently, Roberto is a member of numerous national and international organizations and a scientific adviser to the National Secretary of Science and Technology (SECYT). He has reached the highest research-academic position of the scientific career of CONICET, is Head of INFIQC, a scientifically-recognized institute of CONICET, and in 1989 was elected a member of the Argentine National Academy of Science.

Roberto has published over 150 research articles and reviews, among the latter a monograph of the American Chemical Society (1983) translated into Russian in 1986. He has written several chapters in different books and a recently published article in Chemical Reviews. He has also received several awards, including the Konex Award in Organic Chemistry (1983), the Bernardo Houssay Award from CONICET (1987) and The Antorchas Fellowship (1996).
Roberto’s research, along with that from other contemporary Argentine chemists, have strongly influenced the outcome of the Physical-Organic and Organic Chemistry fields in Argentina. He has played a relevant role in the foundation stage of the Faculty. His path has not been an easy one. This fact has been shared by most scientists in our country. It is not an easy task to do science in Argentina, a country in which the policy always changes. However, even today, after having received important job offers from abroad, he has decided to remain in Argentina and I know that the efforts and examples of his generation will be followed by the new ones to the benefit of the scientific future of the country.

On the home front Roberto and Rita are very fond of their grandchildren, and enjoy their visits greatly. One of Roberto’s early hobbies was the guitar interpretation of Argentine folklore music, which he still does whenever a guitar is at hand. He enjoys listening to classical music very much, watching basketball and soccer games, barbecuing, fishing in the lakes of the mountains surrounding Córdoba city and above all, doing research.

I feel highly privileged and honored to contribute to an issue of ARKIVOC dedicated to Roberto A. Rossi.

### Selected Publications of Roberto A. Rossi


2626.
42. Reactions of Trimethylstannyl Ions with Mono, Di and Trichloro Substituted Aromatic Substrates by the $S_{RN1}$ Mechanism. Corsico, E. F.; Rossi, R. A. Synlett 2000, 227.
A. B. Pierini
INFIQC- Department of Organic Chemistry
Faculty of Chemical Sciences
National University of Córdoba
Ciudad Universitaria
5000- Córdoba (Argentina)
adriana@dqo.fcq.unc.edu.ar