

Prof. Richard Bartsch

A Tribute



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I first got to know Professor Bartsch as a typical premed student, who selected his class based upon reputation. Every lecture started with a sequential alphabetic molecule of the day. (He called it the “Sesame Street Approach”). At a time when technology would have aided a presentation of organic chemistry, Professor Bartsch continued hand drawing lecture notes, and often supplemented live during class. Never had I known a professor so in tune with the writing pace of the class, maintaining a good pace, but always watching the number of pens still writing before switching to the next slide. I still remember the introduction to cycloaddition, with the concomitant analysis of HOMO-LUMO orbitals. It was my lack of understanding that drew me to his office for help. What proceeded over the next 45 minutes was the discovery of my gap in knowledge, then a supply of 5 pages of hand drawn notes. Needless to say, I aced this part of the next exam. Dr. Bartsch changed me to a chemistry major over the course of that semester. What started as undergraduate research in his lab “to look good on my medical school application” morphed into a love of experimental science. From that point in time, I knew that chemistry was my calling and joined his group for graduate work, not as a master’s student, but as student in the Ph.D. program pushed by his guidance. I am not certain of what Professor Bartsch saw in me in those early days, but his high standards encouraged me to be the best I could, never wanting to disappoint. His standards of communication pushed me to adapt my methods: 1) to supply an

executive summary for review, then 2) update my experimental chemistry to make the best use of his time. This learned, and practiced skill has been invaluable in my professional career. By the time of my dissertation defense, during the introduction to my graduate work, two men who don't express emotion were reduced to tears. What we failed to realize until that time, was that our relationship built on chemistry had become that of surrogate father and son. To this day, we share that bond that ties and I not only consider him my mentor, but my friend. Little did I know that ten years after earning my Ph.D., I would be still studying supramolecular chemistry. Every day I go to work, I have the honor of continuing his tradition by performing the art of chemistry, that intangible quality that elevates my chemistry to a standard to which he would be proud to call me his student. The sphere of chemists is small, but whenever my journey brought me in the presence of a supramolecular chemist those awkward introductions turned to warm welcome, when I mention I studied with Professor Bartsch. It is a testament to his pedagogy, his high standards, and method of teaching that built a graduate research program designed to allow his student early success. That early success built confidence, and that confidence translated into a stable of graduates nearing 100 PhD's and masters students with a cannon of work that I have the honor of organizing into this issue. This anecdote serves not to recognize me, but to give you a personal insight into the man and his legacy. What better place to start than at the beginning.

Richard Allen Bartsch was born in Portland, Oregon in 1940. His interest in chemistry started in high school from Mr. Hogan, who transferred to Pendleton High School for just one year. He attended the Oregon State University, where he earned a B.A. in Chemistry with Honors in 1962 then a M.S. in Organic Chemistry in 1963 working with Professor John L. Kice. He continued his graduate studies at Brown University in Providence, Rhode Island, working with Professor Joseph F. Bunnett. His dissertation focused upon the mechanisms of base-promoted elimination reactions. For this research, he was awarded the Potter Prize for the best dissertation in the Department of Chemistry for 1967. After serving as acting instructor at the University of California at Santa Cruz for a year, Dr. Bartsch was a NATO Postdoctoral Fellow with Professor Sigfried Hünig at the University of Würzburg in West Germany. He then returned to his roots in the Pacific Northwest as Assistant Professor in the Department of Chemistry at Washington State University from 1968 to 1973. For 1973-1974, Dr. Bartsch was an Associate Program Administrator for The Petroleum Research Fund in Washington D.C.

In 1974, Dr. Bartsch joined the Department of Chemistry at Texas Tech University as Associate Professor, where he has built a career advancing the science of supramolecular chemistry, mechanisms of elimination reactions, and separation science. He routinely led a group composed of 12-15 graduate students and 2-3 postdocs, as well as several undergraduates performing research. In 1978, he was tenured and promoted to Professor. Starting in 1981, he became Chair, beginning a remarkable service to the Department in that capacity for 8 and ½ consecutive years. During this service, Texas Tech University recognized Dr. Bartsch's research accomplishments when he was designated a Paul Whitfield Horn Professor in 1988.

Incredibly, Professor Bartsch returned as Chair of the Department of Chemistry and Biochemistry from 1999-2005.

Professor Bartsch's excellence in teaching was recognized numerous times including by the following awards: Outstanding Professor of the Month, October, 1979, Arts and Sciences Council, Texas Tech University; AMOCO Award for Teaching Excellence, 1981, Texas Tech University; President's Academic Achievement Award, 1990, Texas Tech University; Recognition by Alpha Epsilon Delta (The Pre-Professional Health Honor Society) in 1992 as the Outstanding Professor at Texas Tech University; and election to the Texas Tech University Teaching Academy in its founding year of 1996.

Professor Bartsch's expertise in the field of supramolecular chemistry and separation science is recognized by peers for his service as Editorial Advisory Board Member, *Journal of Inclusion Phenomena and Macrocyclic Chemistry* (1986-), Editorial Board Member, *Solvent Extraction and Ion Exchange* (2002-), and the International Editorial Advisory Board Member, *Bulletin of the Korean Chemical Society* (2004-).

Design and Synthesis of Supramolecular Chelating Agents

Arguably, the modern evolution of supramolecular chemistry commenced with the landmark paper¹ by Charles J. Pedersen reporting the discovery of crown ethers. Mr. Pedersen later shared the Nobel Prize with D. J. Cram and J. M. Lehn for their pioneering work describing the preparation and applications of a variety of supramolecular compounds. While at Washington State University, Dr. Bartsch continued to advance the understanding of elimination reactions, particularly the role of base and solvent, for compounds such as 2-bromobutane.² He proposed a role of ion pairs in affecting the product distribution among 1-butene, *cis*-2-butene and *trans*-2-butene (Figure 1). To test the hypothesis required a solution that would effectively separate the ion pairs. For the chelation of the alkali metal ion of alkoxide bases, Dr. Bartsch added crown ethers (Figure 1), an elegant solution for the separation of ion pairs, and demonstrated the importance of ion pairs for these reactions. Describing the use of crown ethers to separate ion pairs to Professor H. C. Brown, a vocal proponent of one view of the mechanistic controversy, he recalls Dr. Brown saying "That is neat!"

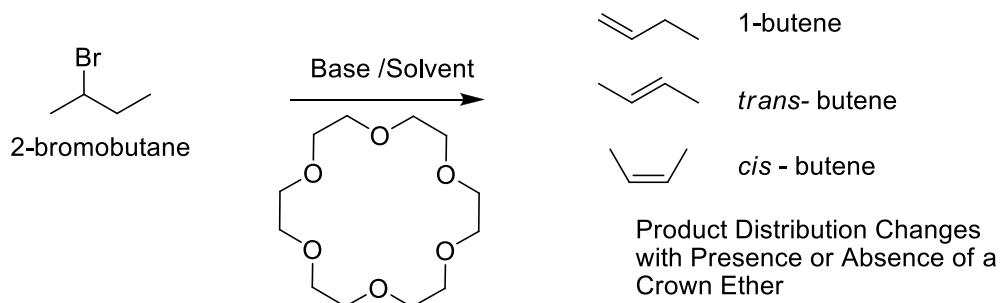


Figure 1. Role of Crown Ether-Separated Ion Pairs.

Recognizing the opportunity for not only new compounds with unique properties, but the possibility to discover science with broad based practical applications, Dr. Bartsch started contributing novel research into the synthesis of customized crown ethers with his new

appointment at Texas Tech University. Drawing upon his background in physical organic chemistry, Dick discovered crown ether complexes not only bound alkali metal ions, but also could have profound effects upon reactive species such as diazonium ions. Crown ethers were shown to stabilize aryl diazonium ions both thermally and photochemically. Recognizing the ability to enhance the binding properties demonstrated by crown ethers by incorporating tertiary binding groups, Professor Bartsch modified the traditional framework through the addition of a pendant hydroxyl functionality for further synthetic transformations. With a reactive functional group exterior to the macrocyclic ring, customized side-arms could now be added synthetically, providing a convenient route to a large number of compounds.

This elegant synthetic methodology served as the basis for large scale synthesis of *sym*-hydroxydibenzo-16-crown-5 in 100-gram batches (Figure 2). Conveniently, when a local West Texas salvage company thought they had found several drums of diethyl ether, Dr. Bartsch agreed to analyze the lot. In fact the mystery compound was bis-2-chloroethyl ether, a commercially expensive precursor often used for the synthesis of polyether compounds. The series of reactions and purifications for the preparation of this crown served as the training system for new undergraduate research coworkers for well over a decade.

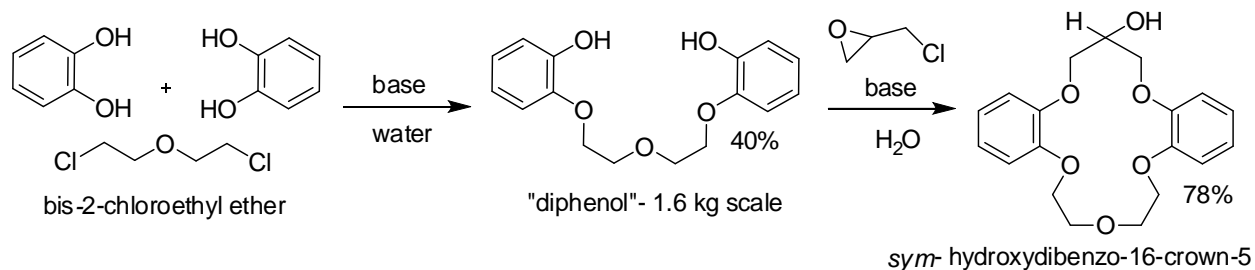


Figure 2. Large Scale Functionalized Crown Ether Synthesis.

Practical Organic Synthesis of Highly Selective Supramolecular Complexants

Part of Professor Bartsch's greatest contribution to the science of crown ethers was the demonstration of enhanced separation of alkali metal ions with proton-ionizable lariat ethers.³ He demonstrated that the inclusion of a 'built-in' counter ion enhanced separations, particularly into hydrophobic eluents or solid phase materials. When one considers the thermodynamic demand of a hydrophilic anion being transported into an organic phase, the elegance of the proton-ionizable side-arm possessing an intramolecular anion, is self evident. In fact, Dr. Bartsch's group has demonstrated highly selective complexants even during competitive conditions in 'real' world analyte streams. Interestingly, a new tunable proton ionizable group with an N-(X) sulfonyl oxyacetamide side arm varies the pK_a depending upon the electron-withdrawing nature of the X group (Figure 3). Despite the elegance of this crown ether system, synthetic access to multiple proton-ionizable groups proves quite challenging when attempting to obtain these compounds in a practical multi-gram scale. One would expect that divalent, or trivalent ions would also benefit from having the 'built-in' counter ions. As such, Dr. Bartsch's group moved to a different

scaffold, the calix[4]arenes. With four phenolic connection sites, 1-4 proton-ionizable groups can be attached. With this approach, a highly selective system for extraction of mercury(II) and of lead(II) in the presence of other metals ions has been accomplished.⁴

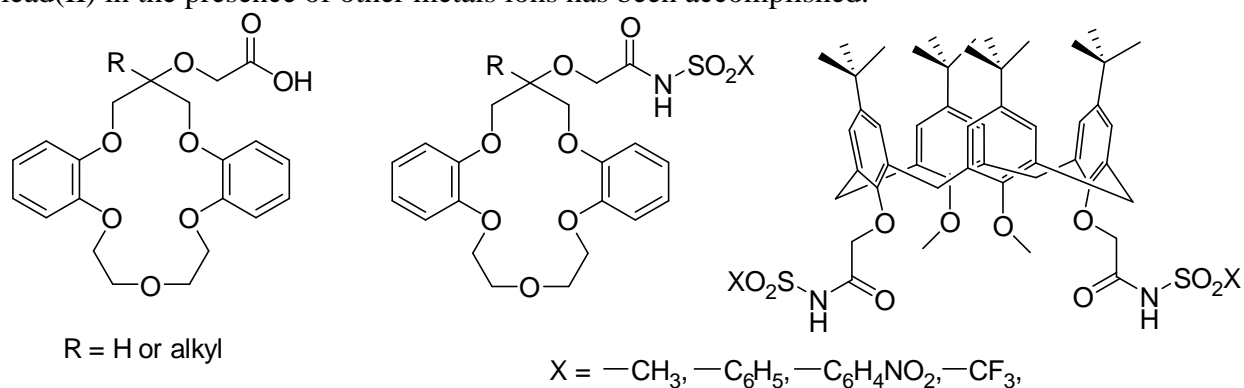


Figure 3. Highly Selective, Proton-Ionizable Supramolecular Scaffolds Designed and Synthesized by the Bartsch Research Group.

Separation Science

I don't know of a better tribute to the skill and reliability of Bartsch Research Group, than his long-term, ongoing relationships with scientists at Argonne National Laboratory, Oak Ridge National Laboratory and Los Alamos National Laboratory. For nearly two decades, Dick has contributed science in collaborative projects for separating radioactive lanthanides and actinides in highly acidic waste streams.

Dr. Bartsch has served the Separation Science and Technology Subdivision of the ACS Division of Industrial and Engineering Chemistry as Chairman-Elect-1992, Chairman-1993, Past-Chairman-1994. He was an External Review Team Member for the Nuclear Materials Technology Division (1994-2006) and then Scientific Consultant (2006-2008) at Los Alamos National Laboratory.

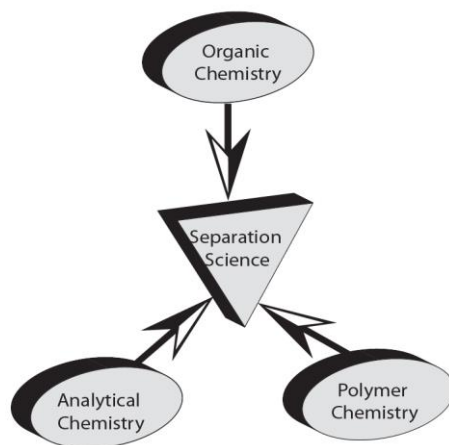


Figure 4. Combining chemical expertise for practical applications in separation science.

'Separation Science' combines organic chemistry and polymer chemistry, with analytical chemistry to achieve practical systems for 'real' world applications (Figure 4). While this tribute has focused upon Professor Bartsch's organic research, his group typically is balanced with an equal number of analytical chemistry coworkers. This unique approach to mentoring students combines the best efforts of synthetic and analytical students to generate a highly innovative and productive research engine. Dr. Bartsch's expertise with these compounds has allowed for the production of numerous practical materials, such crown ether-loaded resins, customized ion-selective electrodes, ion-selective membranes, and custom conjugates with acrylic, vinyl handles and chromophoric signaling moieties. At the time of this writing, the number of Dr. Bartsch's publications approaches 400, not including 23 reviews or monograph chapters, and 4 patents.

I know with all of Dr. Bartsch's professional success, he would gratefully acknowledge the support of his family for achieving such a distinguished career. The Bartsch legacy is not limited to chemistry, as the individual accomplishments of his family rank also are impressive. Dick and Nadine have been married since 1966, and they are blessed with two highly accomplished children, Robert and Lisa. Robert has a doctorate in Social Psychology from the University of Colorado, Boulder, and is tenured Associate Professor at the University of Houston, Clear Lake. Lisa is a CPA/MBA professional, who performs internal IT audits with a major bank. Recently, Nadine became the latest Dr. Bartsch when she received a doctorate in Counseling Psychology from Texas Tech University.

Writing this tribute has brought back many memories of Professor Bartsch. I have no doubt that many of his students would echo the sentiments and professional success inspired by Dr. Bartsch. Please join me in this celebration of Professor Richard A. Bartsch commemorating the 70th anniversary of his birth and a distinguished career in chemistry.

Robert E. Hanes, Jr., Ph. D.
Beacon Sciences, LLC
Senior Scientist
11412 Bee Cave Rd. #110
Austin, TX 78738

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