Angewandte Chemie

Roland Köster (1924–2009)

On June 12th, 2009, boron chemistry lost one of its pioneers. For more than 40 years Roland Köster had developed and shaped many facets of organoboron chemistry; in this area he was certainly the leading and driving force in Germany and without doubt he was among the world's absolute authorities. After his Abitur in 1942, state labor service, military service, and captivity as a prisoner of war, he began his chemistry studies in Heidelberg in 1946, where he gained his doctorate in organic chemistry in 1951 for work on tannins with Otto Theodor Schmidt. His first professional position brought Köster to Karl Ziegler at the Max-Planck-Institut für Kohlenforschung in Mülheim, to what was for him a totally new, experimentally unfamiliar, yet fascinating topic. Initially he followed the work of Ziegler in organoaluminum chemistry, but he soon turned his attention to the element boron, which in the 1950s had received little attention in both organic and organometallic chemistry.

Based on the work of Ziegler, Köster used the now readily available aluminum alkyls for the simple and fruitful synthesis of trialkyl boranes, especially triethylborane BEt_3 (e.g. from $AlEt_3$ and KBF_4), which later became one of his standard reagents. With the trialkyl boranes he rapidly found analogies to the chemistry of the aluminum alkyls, and in the years that followed he exploited the thermal instability of many trialkyl boranes for their rearrangement, isomerization, and cyclization and to obtain reactive, preparatively extremely useful mixtures of different alkyl diboranes. At the same time, Köster had optimized routes for the synthesis of diborane (B_2H_6) on a large scale, and he was thus able to conduct in-depth studies of the synthetic potential of simple boron–hydrogen compounds.

The well-known hydroboration was developed not only by H. C. Brown but also in parallel by Roland Köster, although the two scientists followed quite different pathways. Whereas the Brown hydroboration reagents are used mostly in the presence of donor solvents such as tetrahydrofuran or dimethylsulfide, the Köster technique avoided such solvents. Naturally there were overlaps in the results of the two groups. Noteworthy is the dimeric 9-borabicyclo[3.3.1]nonane, abbreviated 9-BBN, perhaps the most well-known hydroboration reagent, which had been described by Köster as early as 1960[1] and was first promoted by H. C. Brown in 1968 as useful for further syntheses.

The Köster concept of alkyl diboranes (for which he coined the term "hydride bath") was less convenient than that of Brown but nevertheless opened up pathways to novel organoboranes whose formation, structure, and properties were not readily predictable. Two carboranes from the 1960s serve as examples here. At that time, carborane chemistry began its first steep ascent in the USA, based on the polyboranes B_5H_9 and $B_{10}H_{14}$ that were abundantly available there. Painful limitations were revealed in the preparation of 1,5-dicarba-*closo*-pentaborane(5) $C_2B_3H_5$ and 2,3,4,5-tetracarba-*nido*-hexaborane(6) $C_2B_4H_6$, which were only obtained in traces and the syntheses of which were poorly reproducible. In contrast, Köster was successful in the synthesis of large amounts and high yields of the corresponding surprisingly stable peralkylated derivatives. The "nonclassical" $C_2B_3R_5$ can be transformed in two steps into its "classical" dimer, the peralkylated hexaboraadamantane $C_4B_6R_{10}$, which depending on the residues R rearranges in a rapid or slow irreversible valence isomerization into a "nonclassical" peralkylated tetracarba-nido-decaborane(10).[2]

Much of Köster's work with triethylborane was ground-breaking. The activation of BEt_3 with pivalic acid as catalyst allowed, through the generation of ethane, the simple quantitative determination of acidic element−H functions and the reliable preparation of anhydrous salts. The gentle alkyl borylation of sugars with subsequent chromatographic separation and the borylation of starch were also successful with this principle.

The reaction of alkynyl triorganoborates with electrophiles discovered in cooperation with Paul Binger has become a carboboration reaction used world-wide. From it, Köster developed a fascinating chemistry of alkenyl boranes, the potential of which is far from exhausted. He prepared a number of cyclic heterodienes containing the C=C−B−X unit (X = C, N, P, O, S, Se) and vigorously investigated their behavior as ligands in transition-metal complexes. This chemistry stood at the center of his active research, particularly during the 1980s and 1990s.

The scientific life's work of Roland Köster is inseparably associated with the publication of three comprehensive volumes of "*Houben-Weyl Methoden der Organischen Chemie*".[3] The desire to bring order clearly, accurately, systematically, and consistently to as many aspects of organoborane chemistry as possible occupied him from the beginning and ultimately prompted him to produce a work which even today, 25 years after the appearance of the last volume, has lost nothing on quality and topicality. These three volumes contain a considerable amount of well-ordered information on organoboron chemistry, which is often difficult or even impossible to bring to light by modern computer-assisted literature searches. Even after the appearance of this opus, Roland Köster continued this work with the talent and dynamic energy he had brought to his research. He recognized early on that interaction between as perfect

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as possible analysis and synthesis, as well as later between theory and synthesis, is essential. In this endeavor, he not only took advantage of the perfect infrastructure of his institute as early as the 1950s, but moreover sought successful cooperation with other scientists.

In 1969 Roland Köster was elected Scientific Member of the Max Planck Institute, proved successful as a teacher at the University of Vienna, were he was appointed adjunct professor in 1978 and supervised numerous postgraduate students. Even after his retirement in 1992 his scientific interests remained undiminished. In addition to his basic research, as a scientist he was always interested in applications, which led to his involvement in more than 150 patents.

Roland Köster was a sociable, astute, and humorous person, always anxious to exchange scientific experiences and to foster good relationships. Boron chemistry in Germany is indebted to him not only for his excellent scientific achievement but also for the initiative of promoting the interchange of ideas in this area of chemistry throughout the generations. He was one of the founders of the Deutsche Borchemiker-Treffen (German Boron Chemists' Meeting), which for a good forty years has served young scientists as a forum for problem solving.

Roland Köster spent the latter years of his retirement in Heidelberg, in the town of his childhood and his studies. Roland Köster's life was fulfilled, scientifically and privately. He is survived by his wife Doris, four children, and five grandchildren.

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[3] *Houben-Weyl Methoden der Organischen Chemie, Organobor-Verbindungen I, II, III* (Ed.: R. Köster), Thieme, Stuttgart, **1982**, **1983**, **1984**.

DOI: 10.1002/anie.200904401