S. K. Pradhan

S. K. Pradhan, a distinguished organic chemist, passed away at the age of 72 on 23 May 2002 in the USA following a heart attack.

Pradhan possessed one of the most incisive intellects I (SR) have ever come across. I vividly remember the first time I was witness to his remarkable analytical faculties. This was in 1963 at one of the famous Thursday evening Woodward group seminars at Harvard. On this occasion, Woodward had posed a particularly difficult problem from a piece of research that had not been published till then. The challenge was to deduce the structure of the product that would result from the given starting material under the specified reaction conditions. From his tone, it was obvious that Woodward did not expect anyone from the audience to come up with the correct solution. And no one did, until this Indian from one of the back benches, walked up to the blackboard and nonchalantly wrote the correct structure of the product! Pradhan followed this up by putting down the complex sequence of reactions that led ultimately to the end product.

Suresh Krishnarao Pradhan was born in Nagpur on 6 September 1929. After graduating from the University of London (M Sc, 1954), he joined Sir Derek Barton's group (Glasgow University and Imperial College, London) for his Ph D degree. His Ph D thesis (1958) was entitled 'Structure of limonin'. Pradhan's lifelong interest in the structure of natural products and reaction mechanisms can thus be traced to the influence of Barton early in his research career. His other major preoccupation - the chemistry of steroids - obviously stemmed from his post-doctoral association with Ringold at UCLA (1961-62), followed by a two-year stint (1962-64) at the Worcester Foundation for Experimental Biology. Between 1959 and 1961, he was at the National Chemical Laboratory, Pune. This was the period when he brought his experience with limonin to bear on the structure elucidation (in collaboration with N. S. Narasimhan and C. R. Narayanan) of the neem bitter principle, nimbin. Back in India in 1964, Pradhan spent two years at the Shivaji University, Kolhapur, and was later associated with the Regional Research Laboratory, Hyderabad (now Indian Institute of Chemical Technology) for about five years. From 1970 until his retirement in 1989, he was the Professor of Pharmaceutical Chemistry at UDCT, Mumbai.

Pradhan's research spanned four major areas: structure elucidation of natural products, stereoselective synthesis of drugs, investigation of reaction mechanisms and the discovery of new reactions. In all these efforts, he made full use of the latest developments in theoretical chemistry and analytical methods involving modern instruments.



In a significant contribution to alkaloid chemistry, Pradhan proved that atisine was a mixture of two rapidly interconverting configurational isomers. It was in his mechanistic investigations, however, that Pradhan exhibited the full power of his intellect. He was particularly interested in single-electron transfer reactions, and the application of Frontier Molecular Orbital Theory to the prediction of the product structure and stereochemistry in such reactions. For this purpose he found that the steroidal skeleton offered the ideal template. He was the first to introduce naphthalene sodium as an alternative single electron transfer reagent to generate ketyl radical-anions from ketones. This reaction was utilized to achieve the Stork reductive cyclization. The mechanism of this reaction established by Pradhan involved the novel

postulate that the radical-anion attacks the triple bond as a radical.

Pradhan next turned his attention to the mechanism of reduction of enolizable saturated ketones by alkali metal in ammonia. Taking advantage of the fact that naphthalene sodium does not reduce such ketones, Pradhan established that dianion formation is the rate-determining step in metal-ammonia reductions. He thus provided proof for the mechanism postulated earlier by Barton for this reaction. Pradhan went further: he explained the stereochemistry of such reductions by suggesting that the direction of pyramidalization of the intermediate radicalanions is governed by Frontier Molecular Orbitals. Pradhan then showed that other electron-transfer reactions were also subject to FMO control.

A new reaction discovered by Pradhan was the cyclization of 1,5-dioximes using sodium borohydride. The product is an *N*-hydroxypiperidine formed via a nitrone intermediate. The stereochemistry of the product was established by converting it to an *N*-chloro compound and studying the NMR. At UDCT, Pradhan was interested in developing asymmetric syntheses of some common drugs. An excellent example was his synthesis of the antibiotic chloramphenicol.

During his research career, Pradhan received several honours and awards. He was elected Fellow of the Indian Academy of Sciences (1986) and the Indian National Science Academy (1989). He was a member of the Board of Consulting Editors for *Tetrahedron*, *Tetrahedron Letters* and *Tetrahedron Asymmetry* from 1981.

Pradhan is survived by his wife and two daughters who live in the USA.

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