

Dilip Kumar Banerjee (1912–1993)

An obituary by M. V. Bhatt

Dilip Kumar Banerjee's name is closely associated with steroid synthesis in India. To some extent, his eminence in this field has overshadowed his contributions to other areas like reaction mechanisms and synthesis of non-steroidal compounds.

Broadly, the three decades 1930–1960 could be considered the golden age of steroids. The structural work of Wieland (1927)*, Windaus (1928)*, Butenandt (1939)* and Ruzicka (1939)* had opened up the field for synthesis. Researches of Kendall (1939)** and Reichstein (1939)** on the medical application of corticosteroids further whetted interest in this area. The synthetic challenges involved in a total synthesis were formidable. To synthesize a non-aromatic steroid, like the much-maligned cholesterol in the laboratory, could involve wading through a welter of 255 unwanted isomers, and a synthetic sequence of as many as about 20 steps. It was a real *ultima Thule* of organic chemistry.

These challenges attracted many outstanding chemists to this area, as never before or since. New reactions were developed (Diels and Alder 1950)*, and new methodologies (Robinson, 1947*), and new concepts were born (Barton, Conformation of the steroidal nucleus) (1950, 1969)*. By 1960, every important non-aromatic steroid had been synthesized by two or three different groups. Work of Robinson (1946, 1951), Woodward (1951, 1965*), Johnson (1952, 1956), Bachmann (1940), Stork (1947, 1954), Sarett (1946, 1952), Wilds (1950, 1953), Djerassi (1953) and Torgov (1961) not only changed the picture of steroid synthesis but also changed the organic chemical practices substantially.

Banerjee joined the Department of Organic Chemistry, Indian Institute of Science, Bangalore as its head in 1954, a position he held till 1971. However, his association with the Department and the Institute continued till 1975. During

1971–1972 he was the Director of the Institute and was later Honorary Professor. The line of work he initiated in the Department was the stereoselective synthesis of steroids. This area had attracted him from the early days of his D Sc (Calcutta, 1941) research work. His association with W. S. Johnson at Wisconsin (1947–1949) had sharpened his interest in the area of steroids. With Johnson he had published an important paper on the synthesis of estrone and its isomers (1952)—the second synthesis of the hormone.

In one of his early papers from



Bangalore (1956), (perhaps one of his most cited), he described the first stereospecific synthesis of dl equilenin methyl ether (2 asymmetric centres). More importantly, the paper described an efficient and *practical* synthesis of two BCD ring synthons having the correct CD ring junction *trans* stereochemistry prevalent in natural steroids. These synthons were meant to be used for grafting the four carbon framework to build the A ring and yield either testosterone or its 19 nor-analogue. Although this work represented the third synthesis of the equilenin molecule,

it was the only one to describe a method for control of stereochemistry at the CD ring junction. Banerjee's synthesis involved building the D ring by a method involving serendipitous discovery described by Johnson, Peterson and Gutsche (1945). Whereas these authors could get a mixture of 63% *trans* and 33% *cis* CD ring junction products, Banerjee modification gave exclusively stereospecific CD *trans* ring junction. A French firm promptly used Banerjee synthons as the basis for their manufacture of a number of biologically active steroids.

A stereoselective synthesis of dl estrone (1961), synthesis of dl 8-isotestosterone (1960, 1964) and of dl testosterone and its, 9, 11-dehydro derivative are some of his notable contributions. Synthesis of steroids did not cease to fascinate him till the end. He has published over 50 papers on steroids and related topics. As late as 1984, thirteen years after his formal retirement, he published a paper on 11- α -cyano-D-homo-equilenin methyl ether.

Valerenone, a non-isoprenoid ketone, and α -selinene, a sesquiterpene are two compounds on whose synthesis he has reported. Synthesis of degradation products of bile acids like Wieland's tricarboxylic acid, and of C-11 acid, the degradation product of abietic acid, were some of his other synthetic goals.

Two of his investigations on reaction mechanisms need mention. The cyclization behaviour of diethyl- β -ethoxy-carbonyl pimelate mediated by different carbanion-generating agents gave different products. The cause of these disparate results was carefully delineated by an incisive investigation. The cause of the anomalous UV absorption spectrum with maximum 247 nm of some dicyanoesters was shown to be arising out of involvement of tautomerism between cyanoesters and ketimines.

For a person trained in the classical methods of organic chemistry, which were limited to the use of degradation and synthesis (as a tool), he used in his

* indicates the year of award of Nobel Prize in Chemistry and ** indicates that the field was medicine and physiology.

work, many of the physical methods of structure determination as they became available, viz. UV, IR, NMR, X-ray crystallographic analysis and ORD. He was very receptive to new ideas, except when they concerned his deeply held perceptions. He did not rate formal teaching highly. His view was that organic chemistry has to be taught and learnt through laboratory experience. As a collaborator, he was more than fair in giving credit and was very generous in appreciating his students and younger colleagues. During his stewardship of

the Department a number of independent papers were published by students and post-doctoral workers. Banerjee was a highly principled person, a dedicated research worker and a careful investigator throughout his career. No other synthetic chemist before him from this country had displayed the tactical ability to push through a synthesis of over 15 steps.

He was a deeply religious person. The great monastic tradition of this country and Advaita attracted him deeply.

Banerjee has published over one

hundred papers and patents. He was elected to the Indian Academy of Sciences (1957) and the Indian National Science Academy (1961). Among the numerous honours he received, should be mentioned the T. R. Seshadri 70th Birthday Commemoration Medal, P. C. Ray Memorial Medal and lectureship and J. C. Ghosh Medal and lectureship.

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MEETINGS/SYMPOSIA/SEMINARS

Workshop on Information Management for the Medicinal and Aromatic Plants Industry

Place: New Delhi
Date: 12-14 October 1993

The workshop envisages interaction, coordination and exchange of information among the researchers, entrepreneurs, crude drug dealers, cultivators, Government agencies and others interested in medicinal and aromatic plants. The workshop will focus on the potential of several emerging areas such as demand and availability, standardization, drug development, etc. The workshop will provide a common platform for all those involved in various facets of medicinal and aromatic plants industry to discuss the flow of information in a Lab-to-Land and Land-to-Lab network.

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DAE's Second Biennial 'Trombay Symposium on Radiation and Photochemistry' (TSRP-94)

Place: Bombay
Date: 17-21 January 1994

The topics to be covered include: Ultrafast processes such as dynamics of electron solvation, geminate recombination. Charge, electron and energy transfer processes. Excited states, ionic intermediates and free radicals in the gaseous, condensed and organized media. Multiphoton excitation and ionization. Selectivity and vibrational photochemistry. Chemistry and spectroscopy in molecular beams and supersonic jets. Biomimetic chemistry. Chemical lasers. Chemical aspects of radiation damage. Technological and biomedical applications of radiation and photochemistry.

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