Professor Franklin A Davis

A Tribute



DOI: http://dx.doi.org/10.3998/ark.5550190.0011.601

It is indeed a pleasure for me to write a tribute to introduce this commemorative issue of Arkivoc dedicated to Professor Franklin A. Davis on the occasion of his approaching 70th birthday and as acknowledgement of his seminal contributions to the development of organic synthesis, particularly in the area of sulfur-nitrogen chemistry and asymmetric synthesis based on this chemistry.

Franklin Davis was born in Des Moines, Iowa. He received his BS degree in 1962 from the University of Wisconsin and was awarded a PhD in organic chemistry from Syracuse University in 1966 where he worked with Donald C. Dittmer. After two years with Michael J. S. Dewar as a Welch Postdoctoral Fellow at the University of Texas he joined the faculty at Drexel University in 1968. He was the George S. Sasin Professor of Chemistry until 1995 when he joined the Chemistry Department at Temple University.

Davis's interest with sulfur-nitrogen compounds commenced at Syracuse University during his graduate studies with Donald C. Dittmer, where he was introduced to organic sulfur chemistry with the study of thiacyclobutane. He studied boron-nitrogen and boron-oxygen heterocylic compounds at the University of Texas during his post-doctoral stay with Prof. Dewar. After leaving Texas, he moved to the east coast of the United States and joined Drexel University, in Philadelphia in 1968. His early research at Drexel University was concerned with the synthesis and mechanisms of the thermal rearrangements of sulfenamides (ArS-NHAr), and

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he developed a general method for the synthesis of sulfenimines (ArS-N=CR_2, *N*-sulfenyl imines) from aromatic as well as aliphatic disulfides. These studies occurred at the dawn of a new class of compounds that were developed in Davis' laboratory, including the *N*-sulfonyloxaziridines and the sulfinimines (ArS(O)N=CR_2, N-sulfinyl imines). It was found that the selective oxidation of sulfenimines led to sulfinimines, sulfonimines and *N*-sulfonyloxaziridines. These compounds, which were unknown at that time, are now widely known as Davis' sulfinimines and Davis' oxaziridines. They are widely used in organic synthesis and have paved a new path in asymmetric oxygen-transfer reaction and in the synthesis of chiral nitrogen containing compounds. Along with the focus on *N*-sulfonyloxaziridines and sulfinimines, Davis's group has systematically investigated the synthesis of sulfenic acids (RSOH), an elusive species found in many organic and bioorganic sulfur reactions. These early studies by Davis's group are the seminal studies in this area.

The discovery of stable *N*-sulfonyloxaziridines (first example of an oxaziridine to have a substituent other than carbon or hydrogen attached to nitrogen) in Davis's group revolutionized oxygen-transfer reactions because these reagents are neutral, aprotic oxidizing reagents. In contrast to other *N*-aryl, *N*-alkyl oxaziridines, *N*-sulfonyloxaziridines were shown to oxidize nucleophilic substrates with reactivities similar to peracids. Oxidation of sulfides to sulfoxides, thiols to higher sulfur oxides, and the epoxidation of silyl enol ethers leading exclusively to α-silyloxy epoxides were established. A classic reaction with the oxaziridines from Davis's group is the α-hydroxylation of metal enolates to the α-hydroxy carbonyl functionality, a moiety found in many biologically active molecules. A plethora of publications of this particular application in the total synthesis of many biologically active compounds by leading organic chemists can be found in the literature. Davis's efforts in devising a stable oxaziridine for the transfer of oxygen in an asymmetric fashion resulted in a series of (camphorylsulfonyl)oxaziridines, synthesized by simple oxidation of corresponding camphorsulfonylimine, which can even be prepared on a large scale (>100 kg) from camphor-10-sulfonic acid. These reagents (Davis' oxaziridines) are now commercially available from Aldrich. The advent of chiral oxaziridines led to a number of asymmetric transformations including the asymmetric synthesis of sulfoxides, selenoxides, the α-hydroxylation of metal enolates, and the synthesis of enantiopure *N*-sulfinimines.

Davis' research on chiral sulfinimines, which are commercially available from Aldrich, opened a new and reliable avenue for the direct asymmetric synthesis of nitrogen-containing amine derivatives for the first time. For over one and a half decades his group has pioneered the utility of these sulfinimines in the synthesis of many amine building blocks and have demonstrated their application in the synthesis of a number of natural products. Noteworthy in this area is the enantioselective synthesis of α-amino acids, β-amino acids, α-amino aldehydes/ketones, β-amino ketones, α-amino phosphonates, aziridine carboxylates, aziridine phosphonates, 2*H*-azirine phosphonates, 2*H*-azirine carboxylates, and 2,3-diamino acids. In recent years elegant application of these building blocks in the synthesis of natural products has been the focal point of Davis' research work. The asymmetric syntheses of isoquinoline alkaloids, indolidizine alkaloids, sedridines, and most recently, the synthesis of (-)-agelastatin A,

an architecturally unique cytotoxic tetracyclic alkaloid, were accomplished by the Davis group. Besides the program on asymmetric synthesis of nitrogen containing compounds, the Davis group has also developed useful reagents for electrophilic fluorination of enolates with *N*-fluoro-*o*-benzenedisulfonimide (NFOBS), *N*-fluorobenzenesulfonimide and non-racemic *N*-fluoro-2,10-camphorsultams.

Davis has published more than 300 publications and has guided forty-one doctoral students thirty-six masters students, and twenty-seven post-doctoral associates. He has received a number of awards which include the Arthur C. Cope Scholar award of the American Chemical Society (2006), the John Scott Award from the city of Philadelphia (2006), Philadelphia Organic Chemist's Club (POCC) Award (2002), the Japan Society for the Promotion of Science Fellowship (1992), an extension for "Special Creativity" from the National Science Foundation (1990–92), the Philadelphia Section of the American Chemical Society Award (1982), and Drexel University's Research Achievement Award (1980). Davis is a member of the executive committees of the Fluorine and Organic Divisions of the American Chemical Society and served as Program Chair (1988–91) and Chair (1994) of the Organic Division.

I was fortunate to be associated with Frank Davis and to benefit from the warmth and guidance he provided. Frank demonstrates a very composed personality, is cordial to co-workers and unfailingly provides a helping hand to students. A strong family person, Frank Davis met his wife during his graduate studies. They recently celebrated their 42th year of marriage.

From the chemistry fraternity which includes his former co-workers, colleagues and friends we wish Frank Davis a happy 70th birthday!!

Dr. Kavirayani R. Prasad

Selected Publications of Professor Franklin A. Davis

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