

Current research interests: One topic of interest focuses upon the mediated, electrocatalytic, electroreductive cyclization (ERC) of α,β -unsaturated esters onto aldehydes and ketones, and also upon mediated, electrocatalytic, electrohydrocyclization (EHC) reactions. To the best of our knowledge, we have uncovered the first examples of these processes to be conducted electrochemically, and we are excited by the prospects of being able to understand these processes at the fundamental level. Among many items under investigation, studies are presently focusing upon the role of the ligand in the electron transfer event, and upon learning how to affect these transformations enantioselectively. Studies are divided between the investigation of mechanism and the application of these powerful reactions to synthesis.

Another major area of investigation focuses upon the rearrangements of housane-derived cation radicals. We are particularly interested in further explorations of the remote regiochemical control elements that we have discovered recently, and upon applying our knowledge of these factors to the synthesis of natural products. The cation radicals are being generated in three ways, *viz.*, (1) by using triarylaminium antimony salts; (2) through the use of electrochemical mediators, once again used catalytically; and (3) by direct oxidation at the anode. Thus far, the 2nd and 3rd options have proven most effective and have lead to the cleanest and most reproducible results. In a genuine effort to reduce costs and waste, we are following up on some beautiful work that emanated from Steckhan's labs. Thus, we seek to further develop and use recyclable, polymer bound triarylamine redox reagents to affect the oxidative rearrangement chemistry and have initiated our program to accomplish these objectives.

Each of these research endeavors is making significant use of quantum mechanical calculations in an effort to understand and rationalize the detailed course of these processes, with an ultimate goal being to predict the course of as yet untried cases. In addition to our efforts at UCSB, we have teamed up with Professor Dean Tantillo of UC Davis to carry out calculations at the highest levels of theory. Here, one of our objectives is to provide a 'complete' map of the potential energy surfaces for the cation radical rearrangements. Thus far, these processes have displayed relatively flat surfaces, suggesting that dynamic effects of the nature first promulgated by Carpenter and coworkers may be playing a role.

Another area of redox chemistry that continues to attract our attention focuses upon the *in situ* generation and use of Ti(III). Special attention is currently being directed toward its application to the total synthesis of thyriferyl acetate, a marine natural product that is isolated from red algae of the genus *Laurencia*. It is a member of a larger set of structurally related bioactive compounds and displays a remarkably broad spectrum of bioactivity. It is cytotoxic to P-388 murine leukemia. More significantly, it induces rapid apoptotic cell death in a variety of human T- and B-cell lines while displaying a selective inhibition of protein serine/threonine phosphatase (PP2A), but not phosphatases PP1, 2B, and 2C. Thus, it may prove useful in correlating anticancer activity with cellular processes that are dependent upon PP2A activity.

We continue our research involving diradicals. Recently we published a full paper describing the nature of the factors that control whether a cyclopentatrimethylenemethane diradical (a TMM diyl) will preferentially undergo atom transfer cyclization (ATC) or cycloaddition. Among other topics, we described, for the first time, the effect of a Lewis acid upon the course of TMM chemistry. Startling results were obtained, showing that a Lewis acid can change entirely the course of certain reactions of TMM diyls. We are particularly interested in exploring these processes in greater detail, and are doing so at this time. In addition to achieving the assembly of synthetically useful building blocks, an objective is to build into these processes a means by which to achieve enantioselectivity.