Myths and Models in Physical Organic Chemistry: Mills-Nixon; CIP, Through-Bond Coupling; Polar Pi-Effects

Physical Organic chemists place a priority on simple models for abstracting structure/physical property relationships in Organic chemistry that promote our understanding the energetics and mechanistic conformational, mechanistic and stereochemical phenomena. Despite the basic tenet that resistance to refutation is the gold standard for acceptance of a model, the success of a model at forecasting phenomenological outcomes becomes more and more the modern basis for support of its continued application. This effect can be seen as stemming from the move toward career success metrics based on citation and cult of personality. Consequently, untenable corollaries to a successful model may be hard to dispel from the literature because the attractiveness of such mythology draws in a community of believers who seek to find and prove rather than disprove, which create a self-fulfilling cycle. Four such cases in Physical Organic chemistry will be discussed: Mills-Nixon; CIP, Through-Bond Coupling; Polar Pi-Effects. In each case, a basic model had been previously developed to explain a Physical Organic chemistry phenomenon and this prior model had served the community well. It was the extension of the model to a supposed "analogous" situation, which we believe proves to be untenable. Thus, in every case there is no basis for continued propagation of the theory; nonetheless Organic chemists persist in applying the model.