This review paper dealt with the use of anionic or neutral nucleophiles to replace substituents in the vinyl position. It categorized the vinyl substitutions by mechanistic routes, paying special attention to the bimolecular route. Some areas, for example, the stereochemistry and the element effect, were discussed in more detail than others. [The SC14 indicates that this paper has been cited in over 220 publications.]

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When I finished my PhD work, I coauthored a review on nucleophilic reactions on carbon-carbon double bonds,1 17 percent of which were devoted to vinyl substitution. My first independent work afterward was on the mechanism of the reaction of an exciting new compound, tetracyanoethylene, with N,N-dimethylamino, which is both a nucleophilic vinyl and an electrophilic aromatic substitution.2 This raised my interest in vinyl substitution. Immediately after, I started my postdoctoral work with the late Saul Winstein, the carbonium ion expert. When once I suggested to him that the study of an S1 vinyl solvolysis would be interesting, he did not think that it would work, apparently due to the low stability of the intermediate vinyl cations. A young lecturer needs a research topic of his or her own; and when I returned to Jerusalem, I thought that both the bimolecular and the monomolecular routes of vinyl substitution would make such a topic. When I started to read about it, I received a flattering (to a young scientist) invitation to write a review on the topic. I spent a long time writing the review (and typing it with two fingers, since our department head regarded the departmental secretary as private property; he always gave her an old 1900 almanac to type whenever I gave her my review). The material at the time was scattered, and some of the most important work from G. Modena’s group at the University of Bologna was in Italian. What I tried to do in the review was to categorize the known vinyl substitutions by mechanistic subgroups; to discuss them critically; to give a detailed overview of the especially of the most important bimolecular route; and to be as comprehensive as possible.

The progress in the field in the intervening years has been uneven. The S1 route, which comprised less than 4 percent of the review, became an important, exciting, and competitive field in the 1970s. We participated in this activity. The field was reviewed several times within a few years; and a book dealing with vinyl cations, half of it devoted to vinyl solvolysis, was published in 1979.3 We know more about this route now than about any other substitution route, in spite of the probably greater importance of the bimolecular route. At the same time, the study of the latter route was not comprehensive, and progress was slow. Our group was one of the few groups working on it continuously. A large part of the mechanism work was done by several Soviet groups, including, for example, B.A. Shainyan’s.4

Our mechanistic understanding of bimolecular vinyl substitution has been extended in recent years by the increasing evidence for carbanionic or zwit- terionic intermediates in the substitution, resulting from kinetic and stereochemical studies of highly electrophilic systems. The stereochemistry of the bimolecular substitution is no longer regarded as exclusive retention. Both retention and stereocon- vergence are observed. More recently, we’ve tried to review the main mechanistic question of the bimolecular route5 and to show the versatility of nucleophilic vinyl substitution routes.6 I believe the paper is cited for a combination of reasons. First, at that time, the emphasis in physical organic chemistry was still on “mechanisms.” Nucleophilic aliphatic and aromatic substitutions had been extensively studied, and a review on vinyl substitution filled a gap. Second, it was a critical, timely (two-thirds of the references are from the 1960s) and comprehensive work, and it is always easy for workers in the field to rely on such reviews. Since a more comprehensive review has not been published in recent years, it is still quoted several times a year.