

Rappoport Z. Nucleophilic vinylic substitution. *Advan. Phys. Organ. Chem.* 7:1-114, 1969.

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This review paper dealt with the use of anionic or neutral nucleophiles to replace substituents in the vinylic position. It categorized the vinylic 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 SCI® 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 vinylic substitution. My first independent work afterwards was on the mechanism of the reaction of an exciting new compound, tetracyanoethylene, with *N,N*-dimethylaniline, which is both a nucleophilic vinylic and an electrophilic aromatic substitution.² This raised my interest in vinylic 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 S_N1 vinylic solvolysis would be interesting, he did not think that it would work, apparently due to the low stability of the intermediate vinylic 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 vinylic 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 vinylic substitutions by mechanistic subgroups; to discuss them critically; to give a detailed overview of them, 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 S_N1 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 vinylic 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 mechanistic work was done by several Soviet groups, including, for example, B.A. Shainyan's.⁴

Our mechanistic understanding of bimolecular vinylic substitution has been extended in recent years by the increasing evidence for carbanionic or zwitterionic 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 stereoconvergence are observed. More recently, we've tried to review the main mechanistic question of the bimolecular route⁵ and to show the versatility of nucleophilic vinylic 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 vinylic 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.

1. Patai S & Rappoport Z. Nucleophilic attacks on carbon-carbon double bonds. (Patai S, ed.) *The chemistry of alkenes*. London: Wiley-Interscience, 1964. p. 469-584. (Cited 110 times.)
2. Rappoport Z. Nucleophilic attacks on carbon-carbon double bonds. Part V. The reaction of dimethylaniline with tetracyanoethylene: π - and σ -complexes in electrophilic aromatic and nucleophilic vinylic substitutions. *J. Chem. Soc.* 1963:4498-512. (Cited 85 times.)
3. Stang P J, Rappoport Z, Hanack M & Subramanian L R. *Vinyl cations*. New York: Academic Press, 1979. 513 p. (Cited 185 times.)
4. Shainyan B A. Bimolecular nucleophilic substitution at a vinylic center. *Usp. Khim. SSSR* 55:942-73, 1986. (Cited 5 times.)
5. Rappoport Z. Nucleophilic vinylic substitution. A single or a multi-step process? *Account. Chem. Res.* 14:7-15, 1981. (Cited 70 times.)
6. ———. The rich mechanistic world of nucleophilic vinylic (S_NV) substitution. *Recl. Trav. Chim. Pays-Bas* 104:309-49, 1985. (Cited 15 times.)