

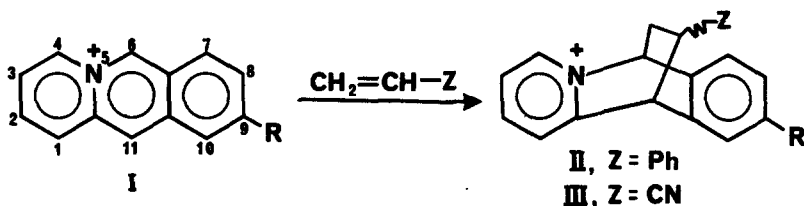
THE ELECTROPHILIC NATURE OF POLAR CYCLOADDITION

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The new type of stereoselectivity observed^{1, 2} in certain polar³ cycloadditions is explicable only in terms of coulombic repulsions in the transition state leading to the second step. It also requires that the first step in the cycloaddition must be the electrophilic attack of the cation on the nucleophile.

In the extension of the polar cycloaddition⁴ of the acridizinium ion (I) to unsymmetrical addends, Fields, et al⁵ observed that the reaction was regiospecific. With one exception, the product was that expected if the more negatively polarized end of the alkene was always the one that reacted with the electron-deficient center at position 6 of the acridizinium ion. Since the adduct (III) from the acrylonitrile was not that expected from the ground state polarization of



acrylonitrile, Fields, et al⁵ took refuge in the view that "... the polarity of the reactant molecules is not thought to be the decisive factor in structural directivity in the diene synthesis."

It has been shown⁶ that the cycloaddition of styrene with 9-substituted acridizinium cations (I→II) was accelerated by electron-withdrawing substituents, and that the rates afforded a significant Hammett plot. It was explained that the 9-substituents affected the cycloaddition

rate by altering the availability of the positive charge at position 6 of I.

Since acrylonitrile was the only apparent exception to the polarization rule of Fields et al.⁵ it seemed desirable to ascertain whether acrylonitrile, like styrene, acted as a nucleophile or whether polar effects were indeed unimportant. By use of the general method previously described,⁶ the cycloaddition rates of the acridizinium and four 9-substituted cations (as the fluoroborates) were measured at 130⁰ in sulfolane, using a 36:1 ratio of acrylonitrile to cation to ensure pseudo first order kinetics. A Hammett plot of the data was made (Fig. 1) using primary⁷ para substituent constants where available, and fitting the curve by the least

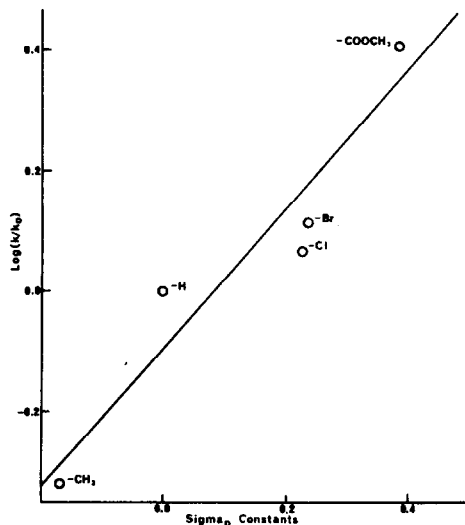


Figure 1. - Hammett plot of reaction rate data

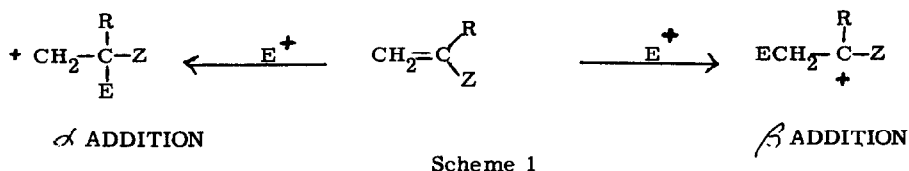
squares method. The calculated ρ was 1.13 (with a standard deviation of ± 0.21) while the correlation constant (0.95), although minimal, showed the plot to be significant.⁸

The possibility that the substituent (R) at the 9-position on the acridizinium ion might exert influence on the formation of the bond to position 11 was explored by repeating the plot using meta substituent values. The resulting plot gave poor correlation (0.73) and was not significant. The new data suggest that although acrylonitrile is somewhat less responsive to polar influences than styrene ($\rho = 1.74$), it reacts by the same mechanism, one involving an electrophilic attack upon the alkene by the positively charged 6-position of the acridizinium nucleus.

Another electrophilic system used extensively in the study of polar cycloaddition is the

N-methylenium amide cation which, with a single exception,⁹ has always reacted with alkenes regiospecifically⁹⁻¹¹ and in the direction predicted by ground state polarization. The exception, methyl methacrylate, was regarded by Schmidt⁹ as evidence for the synchronous course of the cycloaddition.

It seems more likely that the regiospecificity or regioselectivity observed in polar cycloaddition always has a polar origin and is not only understandable in terms of ground state polarization and polarizability but also provides a new tool for the study of orientation in the electrophilic addition of large cations. The "anomalies" of Fields et al⁵ and of Schmidt⁹ both arise in the addition of a large cation to an ethene which has a moderately strong electron-withdrawing group at one end and no substituent at the other. An analysis of electrophilic addition to such an alkene is given in Scheme 1.



Solely on the basis of ground state polarization α -addition of the electrophile would be expected, creating a relatively unstable primary carbonium ion. Alternatively, β -addition would afford a secondary (or tertiary) carbonium ion destabilized by an α electron-withdrawing group. While the difference in energy between the two carbonium ions is smaller than it would be in an alkene of the same type, but bearing a β alkyl or aryl substituent, the advantage certainly rests with the α adduct when the electrophile is a proton.^{12, 13} There is also experimental data extant which suggests that for nearly every alkene of the type represented in Scheme 1, there is some minimum size of electrophile which will favor β -addition. Unfortunately, the situation is obscured by almost universal acceptance of β -addition in such systems as evidence of a free radical mechanism.^{14, 15} Evidence of the importance of electrophile size is provided by the reaction of some polar reagents with methacrylate esters or acrylonitrile. Hypochlorous acid,¹⁶ nitrosyl chloride¹⁷ and nitryl chloride¹⁸ show α -addition with methacrylate esters, but of the same three reagents,^{15, 18-20} only nitryl chloride^{15, 18} gives β -addition with acrylonitrile.

While the data offered in support of our argument concerning the importance of the size

of the cation do not as yet amount to a demonstration, they suggest the -addition to alkenes of the class shown in Scheme 1 is not per se evidence of a radical mechanism.

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