

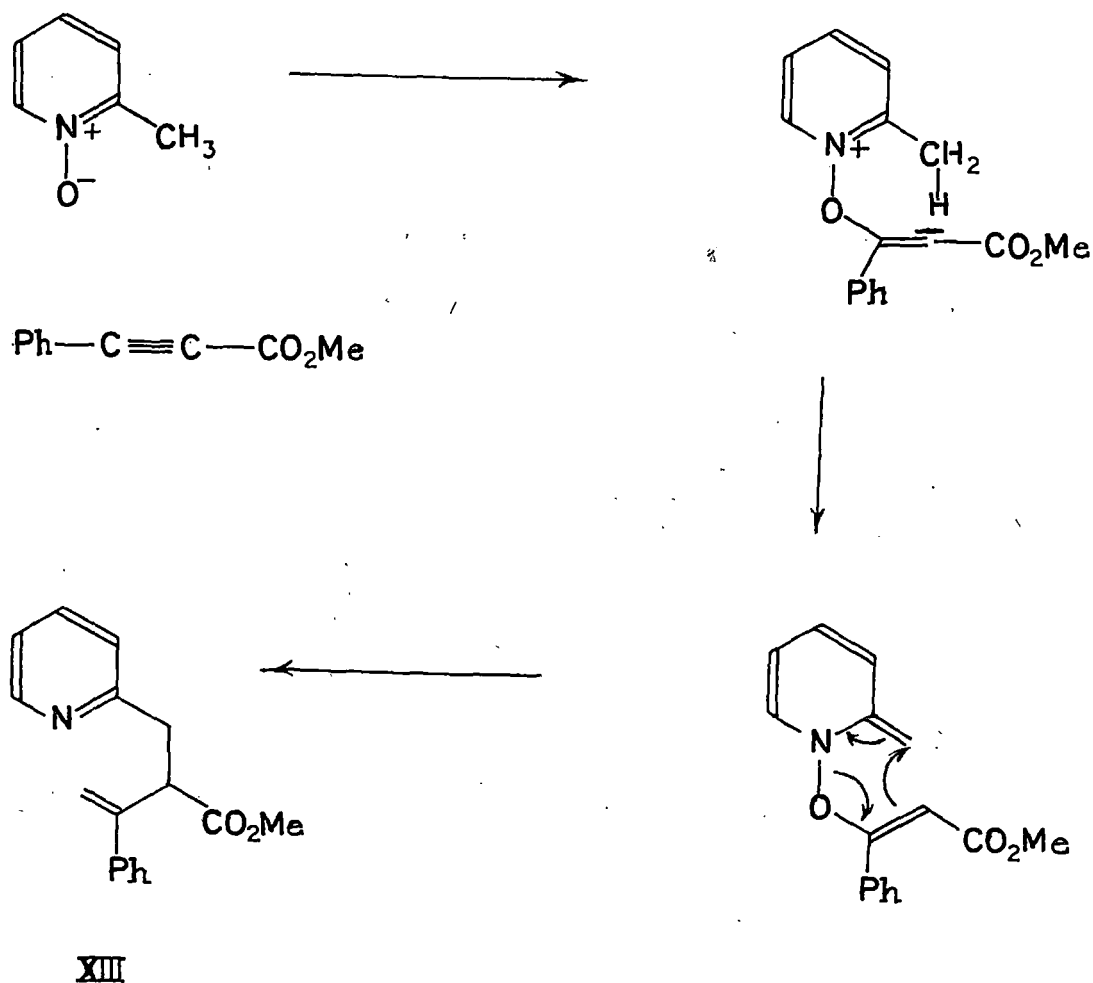
CHAPTER - IV

Results and Discussions

The primary objective of the kinetic experiments was to find out whether a cycloaddition or a three-body mechanism was operative in the reaction of aromatic N-oxides with electrophilic acetylenes. The most important observation was that the reaction of pyridine or picoline N-oxide with phenyl acetyl propiolate satisfied a second-order rate equation. The rate of the reaction (as deduced from the amount of the acetylene compound consumed) gradually increased on increasing the amount of either of the components from the initial ratio of 1:1. The effect of the solvent was also quite marked. Keeping the ratio of the reactants constant there was observed a marked decrease in rate, as the amount of solvent was increased. Steric effect was also observed in going from pyridine N-oxide to picoline N-oxide. Under exactly identical conditions, while the yield of the product with the former N-oxide was 29.53%, the yield with the latter N-oxide was only 19.6%. The decrease in yield was presumably due to the methyl group present in picoline N-oxide. If a three-body mechanism were operative, a further drastic

fall in yield of the product would have been observed in this case.

The most important question was whether the cycloaddition reaction had been a concerted or a two-step one. If a two step cycloaddition were operative, the reaction would have preferred an alternative pathway as shown below.



However, no trace of the product (XIII) was observed. It appears, therefore, from the above experiments that a concerted cycloaddition is the initial step in the reaction of aromatic N-oxides with electrophilic acetylenes.

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