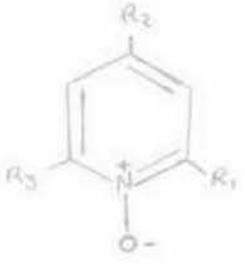
PREFACE

The thesis entitled, "Reaction of Aromatic N-Oxides", embodies the results of experiments carried out by the author during the period 21st January 1973 to 31st December 1976 in the Organic Chemical Laboratories of the University of North Bengal, North Bengal University. It incloses the results of the reactions of 2-Picoline, 2,6, Lutidine and 2,4,6 Collidine-1-Oxides (I) with methyl - Phenyl Propiolate (Ia).



I

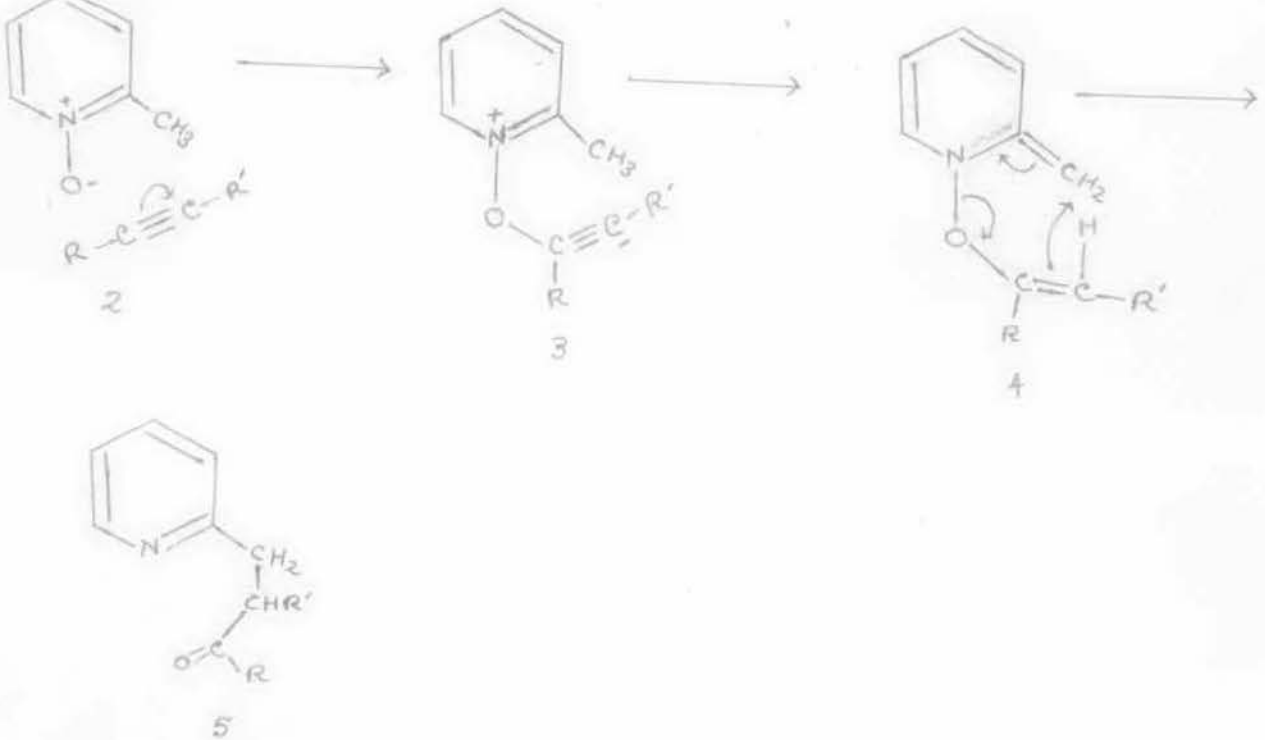
(1) Picoline $R_1 = CH_3$ $C_6H_5C\equiv C.COOCH_3$
$R_2 = R_3 = H$ Ia

(2) Lutidine $R_1 = R3 = CH_3$
$R_2 = H$

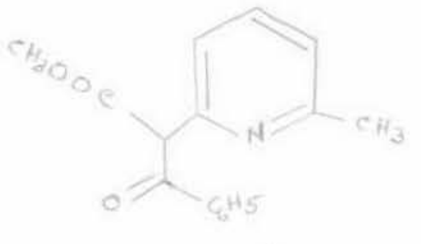
(3) Collidine $R_1 = R_2 = R_3 = CH_3$

In view of the contradictory reports about the nature of the products obtained by the reaction of different heterocyclic-N-Oxides with electrophillic acetylenes (discussed in detail in the main body of the thesis), it was planned to investigate the mechanism of the reaction. Taking into consideration the proposed N-vinyl oxide intermediate for such reactions, the possibility of an oxa-aza

Claisen re-arrangement as shown below with 2-methyl Pyridine-1-Oxide as an example~~s~~, was envisaged.



We hoped to isolate products of the type (5) along with products 6,7,8 and 9 described in literature. The theoretical basis for such assumption is discussed in detail in the thesis. Preliminar



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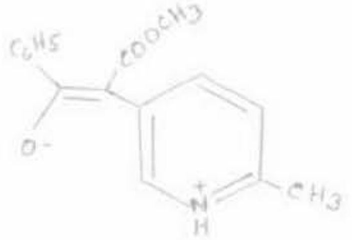

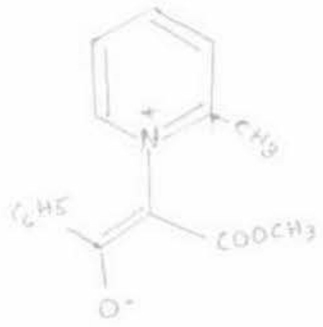

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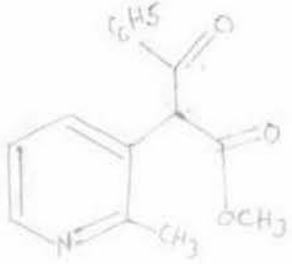
investigations were conducted on 2-Picoline-1-Oxide, 2,6 Lutidine-1-Oxide and 2,4,6, Collidine-1-Oxide. The results of these investigations have been discussed in the thesis. Picoline-1-Oxide was expected to give among other products (5). In actual practice a single product TLC) was obtained. On the basis of its I.R. and N.M.R. spectra the following structure has been proposed (10) for this compound.



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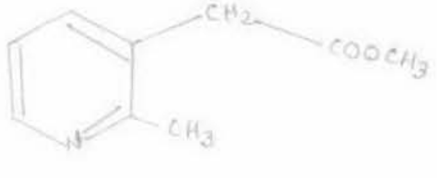

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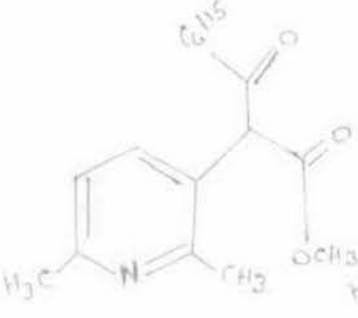
The compound has been found to be labile and it slowly hydrolysed on exposure to furnish (11) as the major product. A chromatographic hydrolysis method has been developed to enhance this transformation efficiently. The effect of Solvent change and change in the molar proportion on the rate and product yield has also been studied. With 2,6, Lutidine-1-Oxide and Collidine-1-Oxide and methyl phenyl Propiolate also no oxa-aza-claisen product was isolated. On the basis of their spectral properties these compounds have been assigned the following structures (12,13).



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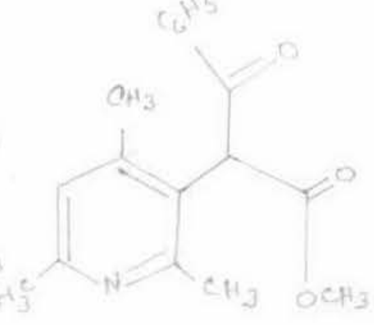

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Product from collidine-N-oxide was found to be remarkably stable to hydrolysis.

The reaction of these N-oxides with Methyl Phenyl propiolate was found to be dependent on the polarity of the solvents. Thus the yields of the (10), were found to vary from solvent to solvent and they were maximum in non polar solvents (eg. in Benzene and Toluene) and minimum in polar solvents. An alternative concerted mechanism has been proposed to account for the products. The theoretical basis for this mechanism has been discussed in detail in the main body of the thesis.

We also propose to study the biological activity of the products and with this in view we are trying to increase the over-all yield in this reaction.