SUMMARY

CHAPTER I: a select review of reactions involving nucleophilic ring opening of cyclic anhydrides and imides for generation of heterocyclic structures. The heterocycles thus designed include indole, isoindole, quinoline, isoquinoline, benzoxazine, benzothiazines, among others. Several of these reactions turn out to be key steps in synthesis of several natural products. The chapter also presents a summary of the widely scattered synthetic applications of anilic acids and derivatives (such as imides and esters).

CHAPTER II: a summary of the available methods for formation of the nitromaleanilic acids, the starting materials for a novel quinoxaline synthesis accomplished by the present author. The earlier methods were generally not satisfactory. No direct method available for formation of nitrofumaranilic acids. The present work uncovered a new procedure: fusion of maleic anhydride (1 mol) with o-nitroanilines (1 mol) in presence of anhydrous AlCl₃ (0.25 mol) led to the formation of o-nitro maleanilic acids (1) (80-100°, 10 min, 90-95% yield) exclusively, however these reactants taken in the above molar ratios but heated at 160-200° for 20 min, furnished fumaranilic acids (2) in identical yields. Both 1 and 2 were converted to the corresponding methyl, ethyl and higher
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\text{Fe}^{2+} + c\rightarrow \left[ \begin{array}{c}
\text{Fe}^{2+} + \text{c}\ \\
\text{Fe}^{2+} + \text{c}
\end{array} \right] \\
\xrightarrow{\text{X}} \\
\text{Fe}^{2+} + \text{c} \quad \text{major} \\
\text{Fe}^{2+} + \text{c} \quad \text{minor} \\
\]
esters using the newly developed reagent, alky phosphate ester (APE) obtained from $P_4O_{10}$ and ROH. The E- and Z-esters were characterised by spectral and analytical methods. APE is also established as a general esterification reagent.

**CHAPTER IIIa**: A succinct tabulation of several methods available for formation of quinoxaline systems is made. Results of our investigations on reductive cyclisation of 2-nitromaleanilic and 2-nitrofumaric anilic esters to 1,2,3,4-tetrahydro-2-oxo-3-quinoxaline acetates (7). Use of Adams catalyst gave mixture of products. However, use of Raney nickel (W-2) furnished the desired product in good yields. The intermediate 2-amino esters were not isolated. All the products were adequately identified by spectral and elemental analyses.

**CHAPTER IIIb**: Report of the reactions of o-aminothiophenol (o-ATP) (as a bifunctional nucleophile) with two unsymmetrical cyclic anhydrides, phenylmaleic anhydride and methylnmaleic anhydride. Reactions of o-ATP with methylhydrogen maleate and methylhydrogen fumarate were also examined. All the compounds were fully characterised by spectral/elemental analyses. These reactions indicate that (1) o-ATP reacts with anhydride by aminolysis at the unhindered carbonyl (2) steric effects are more important than electrical effects in orienting the incoming nucleophile (3) the intermediate 2-mercaptoanilic acids/esters (12-13) were not isolated contrary to recent claims, (4) aminolysis at the ester carbonyl occurs more readily than at the carboxyl carbonyl.