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A NOVEL SYNTHETIC METHOD OF SOME HETEROAROMATIC N-OXIDES BY FLUORIDE-ION PROMOTED CYCLIZATION

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Linear substrates (generally $CH_3\text{-}\overset{NOH}{\overset{\|}{C}}\text{-}CH_2\text{-}X\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$ and $CH_3\text{-}\overset{NOH}{\overset{\|}{C}}\text{-}CH_2\text{-}NR'\text{-}\overset{O}{\overset{\|}{C}}\text{-}CHCl_2$ in particular) bearing both hydroxylimino and carbonyl group in α- and γ-positions with respect to each other could be successfully cyclized by the aid of tetraalkylammonium fluoride to the corresponding heteroaromatic N-oxides (viz., N-substituted 2-formylimidazole 3-oxides) in good yields. It was found that neither tetraalkyl ammonium chloride nor bromide was effective in this transformation. Supposed intermediate: the corresponding (2-dichloromethyl)imidazole 3-oxide could not be detected, which suggests that hydrolysis of 2-dichloromethyl in the imidazole 3-oxide to the corresponding formyl group was very rapid and presumably fluoride ion was involved in the hydrolysis.

The starting materials in the oxazole series were prepared from ω-bromoketones and appropriate carboxylic acids again by the aid of fluoride ion (Clark et al's procedure).

It was also found that fluoride ion was quite effective in the dimerization followed by aromatization of α-bromoketone oximes such as ω-bromoacetophenone leading to usually less accessible 2,4-disubstituted pyrazine 1-oxides.

The mechanism along with the scope and limitation of these fluoride-ion promoted transormation will be also discussed.