

## FLASH VACUUM PYROLYSIS OF SOME HETEROAROMATIC N-OXIDES.

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Flash vacuum pyrolysis (FVP) of pyridine and pyridazine N-oxides was carried out (temperature=500-800°C, pressure=0.1-0.01mmHg, contact time=0.1-0.001sec).

FVP of 2-picoline N-oxide (1b) gave pyridine, 2-picoline, 2-pyridylmethanol, 2-ethylpyridine, 2-vinylpyridine, di(2-pyridyl)methane, 1,2-di(2-pyridyl)ethane, and 1,2-di(2-pyridyl)ethylene, although the FVP of pyridine, 3-picoline, and 4-picoline N-oxides (1a, c, and d, respectively) gave complicated mixtures of products. From a detailed study of the reaction of 1b, 2-picolyl radical (2) was presumed to be a key intermediate and the precursor of all the products in this pyrolysis.

In the light of these observations, FVP of substituted 2-benzylpyridine N-oxides (3) was employed for synthesis of heteroaromatic compounds. The FVP of 3 gave the corresponding substituted pyrido(1,2-a)indoles (4) in moderate yields in most cases, and found to be superior to those previously reported preparations. FVP of 2-(o-methylbenzyl)- and 2-benzyl-3-methyl-pyridine N-oxides gave benzo(g)quinoline rather than 4.

Similar results were obtained in FVP of pyridazine N-oxides. Although the FVP of 3-substituted pyridazine-1-oxides (5) gave complicated mixtures of products, that of 3-methylpyridazine-2-oxide (6) gave the products such as pyridazine, 3-methylpyridazine, and naphthalene, and the radical 7 is supported to be the precursor.

It was assumed that interaction between the oxygen atom of N-oxide group and hydrogen atom of methyl group in  $\alpha$ -position favors the homolytic fission of N-O bond of the N-oxide to produce a heteroaromatic radical (2 and 7) and hydroxyl radical (Scheme I). The mechanisms of these reactions will be discussed.

