FLASH VACUUM PYROLYSIS OF PYRIDINE N-OXIDES

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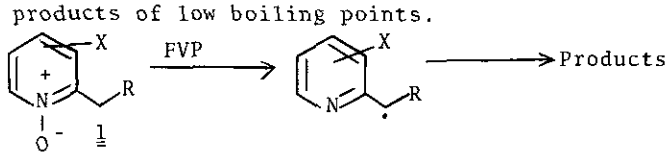
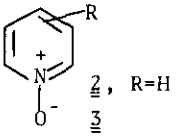
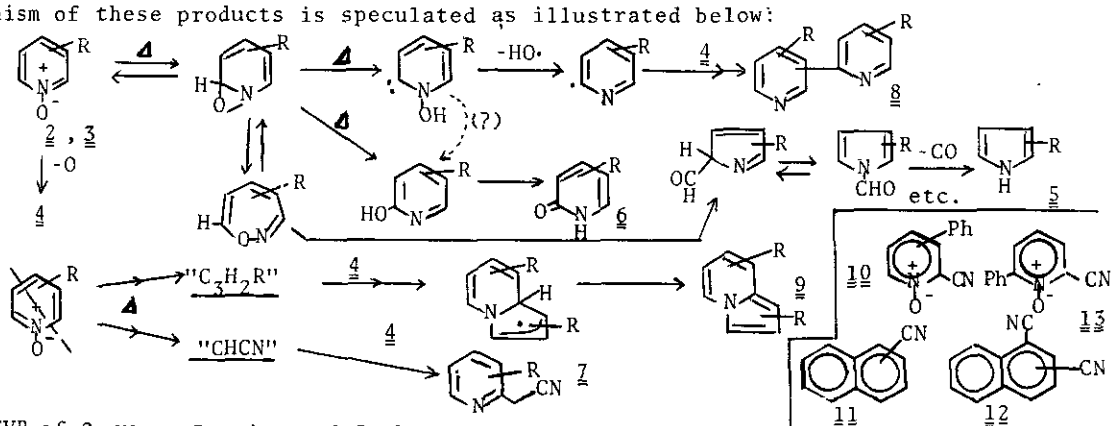
In connection with the study on flash vacuum pyrolysis (FVP) of N-oxides of 2-methylpyridine derivatives (1), whose FVP at 650°C gave products derived from intermediary 2-picolyl radicals, we have described that pyridine N-oxide (2) and 3- and 4-methylpyridine N-oxides strongly resisted FVP relative to 1, and that the FVP of those N-oxides at higher temperature (800°C) afforded complex mixtures of the products of low boiling points.



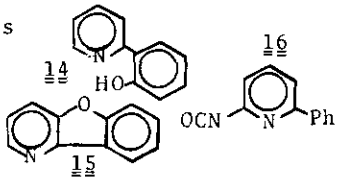


We wish to report the findings due to detailed examinations of the products of the above-mentioned FVP of 2 and of some substituted pyridine N-oxides.

The FVP of 2 and cyanopyridine N-oxides (3, R=CN) required a higher temperature than in the case of 1, and the FVP of 2 and 3 at 800°C under 0.1-0.001 mmHg (conact time: 0.01-0.001 sec) afforded pyridines (4), pyrroles (5), pyridones (6), 2-pyridylacetonitriles (7), and a mixtures of bipyridyls (8). Cyanoindolizines (9) are obtained in addition to 4-8 from the cyanopyridine N-oxides. The formation mechanism of these products is speculated as illustrated below:



FVP of 2-cyano-3-, 4-, and 5-phenylpyridine N-oxides (10) gave 1- and 2-cyanonaphthalenes (11) and dicyanonaphthalenes (12) in addition to 4-6, and the pyrolysis of 2-cyano-6-phenylpyridine N-oxide (13) gave the compounds 14 and 15 and products formed via the isocyanate 16.



Additionally, rearrangements of quinoline and isoquinoline were observed in the FVP of N-oxides of quinoline and isoquinoline.

Mechanisms for the described transformations will be discussed.