HETEROCYCLES, Vol. 23, No. 1, 1985

PERICYCLIC REACTIONS OF PYRIDINE N-OXIDES

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Pericyclic reactions of pyridine N-oxides were discussed in terms of the frontier orbital theory, based on kinetic and MO calculation data. Kinetic studies on the 1,3-dipolar cycloaddition of pyridine N-oxides with several dipolarophiles were carried out in order to provide additional information for the concerted nature of the reaction.

The reaction rates were not affected by the solvent polarity, indicating the reaction proceeds by a mechanism which involves very little charge separation between the ground state and the transition state.

On the basis of the MINDO/3 calculation data, the cycloadditivity and site selectivity were discussed in terms of the controlling factors such as charge-transfer complexation, dipole-dipole interaction and secondary orbital interaction. The perturbation calculation could not provide the satisfactory explanation for the low reactivity of acceptor substituted pyridine N-oxides. The aromaticity of the pyridine N-oxides may play an important role in reactivity determination, which was discussed in terms of the concept of cyclic conjugation.

In connection with the result mentioned above, the 1,5-sigmatropic rearrangement of the primary adducts to 2,3-dihydropyridines is discussed.