

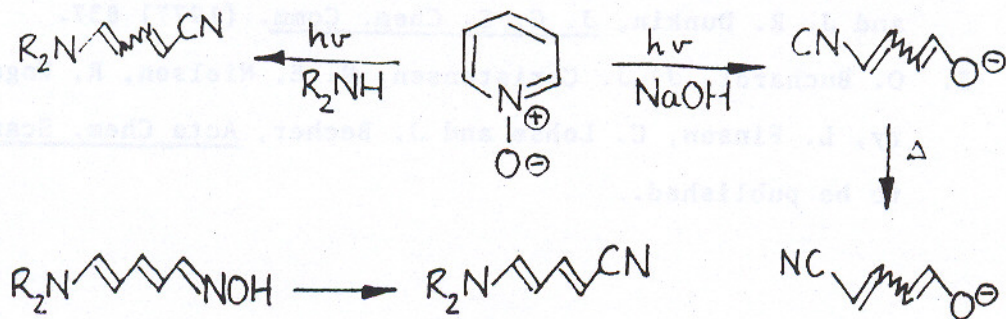
PHOTOCHEMICAL RING-OPENING OF PYRIDINE-N-OXIDE

Jan Becher

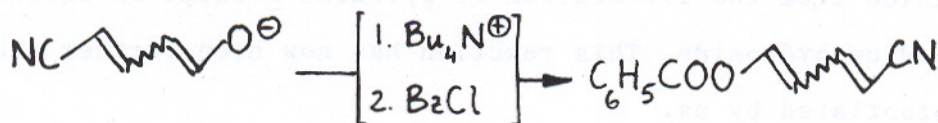
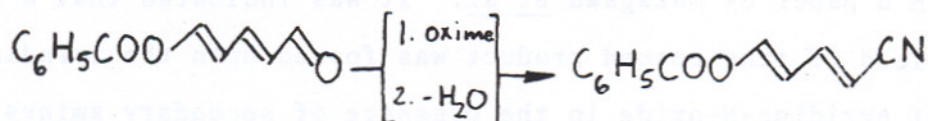
Department of Chemistry, Odense University, DK-5230 Odense, Denmark.

In a paper by Nakagawa et al.¹ it was indicated that a low yield of ring opened product was formed upon the irradiation of pyridine-N-oxide in the presence of secondary amines. Later Buchardt et al.² demonstrated the formation of a stable anion from the irradiation of pyridine-N-oxide in aqueous sodium hydroxide. This reaction has now been further substantiated by us.³

Irradiation of dilute solutions of pyridine-N-oxide in aqueous sodium hydroxide at 254 nm results in the formation of the anion of 4-isocyano-1,3-butadien-1-ol, whereas if the irradiation is performed in the presence of secondary amines, derivatives of 5-amino-2,4-pentadienoic nitrile are generated, both reactions gives high yields:



Upon derivatization the primary isocyanide as a rule rearranged to the corresponding cyanide, which was identified by independent synthesis. This reaction was general and takes place for a number of Pyridine-N-oxides with a free 2-position.



References.

1. M. Nakagawa, T. Kaneko and H. Yamaguchi, J. C. S. Chem. Comm. (1972) 603.
2. O. Buchardt, J. J. Christensen, C. Lohse, J. J. Turner and J. R. Dunkin, J. C. S. Chem. Comm. (1977) 837.
3. O. Buchardt, J. J. Christensen, P. E. Nielsen, R. Kogant, L. Finsen, C. Lohse and J. Becher, Acta Chem. Scand. to be published.