The Photolysis of 1-[3-Alkyl(aryl)-2-thioureido]pyridinium Hydroxide Inner Salts

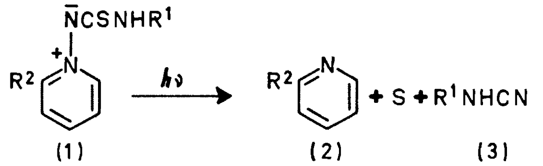
By K T POTTS* and R DUGAS

(*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York* 12181)

Summary Photolysis of the pyridinium hydroxide inner salts (**1**) results in high yields of the pyridine (**2**), sulphur, and the appropriate cyanamide (**3**)

RECENT studies on the photochemistry of various types of pyridinium *N*-betaines suggest that our results in this area would be of general interest Irradiation of an 1-ethoxycarbonyliminopyridinium hydroxide inner salt at 3500Å has been shown to yield 1-ethoxycarbonyl-1*H*-1,2-diazepine,[1a–c] and similar results have been obtained with 1-benzimido- and 1-acetimido-pyridinium hydroxide inner salts [1c] In the latter type, photochemical fragmentation also produced pyridine and methyl isocyanate, and a similar fragmentation to a pyridine and aniline was observed with 1-phenyliminopyridinium hydroxide inner salts [1d]

Our studies have shown that irradiation of 1-(3-methyl-2-thioureido)pyridinium hydroxide inner salt[2] (**1**, $R^1 = Me$, $R^2 = H$) at 3500Å in methanol over 24 hr gave in practically quantitative yield pyridine (**2**, $R^2 = H$) (characterized spectroscopically and as its picrate) and sulphur No third product which would account for the other components of (**1**) was obtained Photofragmentation was not quenched by oxygen, nor did change of solvents effect the results The undetected component in these reactions is most likely methyl cyanamide (**3**, $R^1 = Me$) whose decomposition is not unexpected under these reaction conditions †



(1) (2) (3)

Irradiation of 1-(3-phenyl-2-thioureido)-2-picolinium hydroxide inner salt (**1**, $R^1 = Ph$, $R^2 = Me$) over 96 hr in chloroform at 3500Å gave 2-picoline (**2**, $R^2 = Me$), sulphur, and phenyl cyanamide (**3**, $R^1 = Ph$) The phenyl cyanamide was identified by direct i r -spectral comparison with an authentic specimen (ν_{NHCN} 2230, 2260 cm^{-1}) and by conversion into phenylurea [3] Other picolinium hydroxide inner salts behaved in an analogous fashion to those described above

The mass-spectral fragmentation patterns‡ of these betaines were consistent with their photochemical fragmentation The molecular ion of 1-(3-methyl-2-thioureido)-pyridinium hydroxide inner salt (**1**, $R^1 = Me$, $R^2 = H$) *m/e* 167, lost sulphur giving an ion $C_7H_9N_3$, *m/e* 135, which readily lost methyl cyanamide to give the pyridinium ion *m/e* 79 Analogous fragmentations were observed for the other pyridinium betaines

These data indicate that the most likely pathway for the photochemical fragmentation involved an initial loss of sulphur The formation of any intermediate thiocarbonyl nitrene would be expected to yield either insertion products[1b] or an isothiocyanate[4] and no such compounds were detected in any of the reactions under investigation

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† The thermal decomposition of methyl cyanamide to trimethylmelamine has been observed [3]

‡ Determined at 70 ev on an Hitachi–Perkin Elmer RMU-6E Mass Spectrometer

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