SYNTHESIS AND HYDROLYSIS OF A NEW WATER SOLUBLE PYRYLIUM CATION

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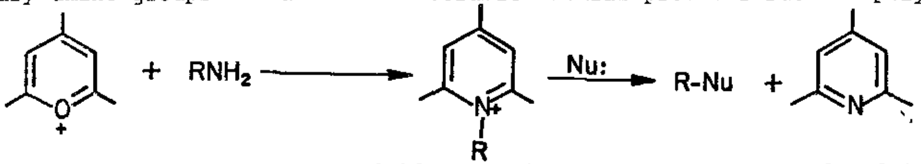
It is of great interest to carry out the following transformation on the primary amino groups found in water soluble natural products such as polypeptides:



To this end a prototype water soluble pyrylium cation was prepared and its hydrolysis in buffers of pH 4.5-9.5 studied. The pH-rate profiles for the conversion of cation to acyclic pseudobase (k_f) and for the reverse process (k_r) were obtained. Above pH 9 pseudobase was in equilibrium with its anion. At the same pH, the cation was converted to anion much faster than was pseudobase. Acidification of a solution containing anion gave pyrylium in a biphasic process. These results are indicative of the presence of the ketodienol tautomer of pseudobase (an enedione). Protonation of the anion could occur either on oxygen to give ketodienol or on carbon to give the enedione. Rate studies indicated that conversion of pseudobase to cation was the slow component of the biphasic process. The rate determining step in the conversion of pseudobase to cation is then ketonization of the ketodienol. The principle of microscopic reversibility indicates that the reverse process is rate determining for formation of pseudobase from pyrylium cation.