THE REACTION OF 1-SUBSTITUTED 3,5-DINITRO-4-PYRIDONES WITH PRIMARY AMINES

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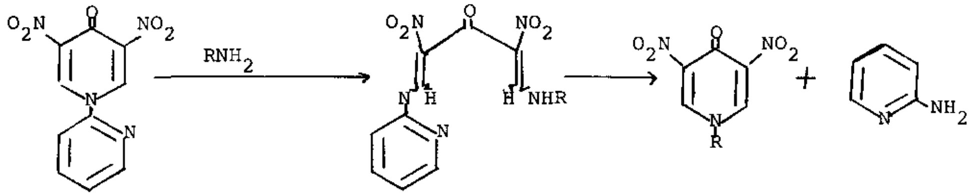
In the course of the investigation of the reaction of electron deficient pyridones with the nucleophilic reagents, a novel ring transformation reaction was found in a series of the reaction of 3,5-dinitro-1-(2-pyridyl)-4-pyridone with primary amines.

The reaction of 3,5-dinitro-1-(2-pyridyl)-4-pyridone (1a) with a primary amine (RNH_2) at room temperature or with gentle heating in DMF gave the corresponding 3,5-dinitro-1-R-4-pyridone and 2-aminopyridine in a good yield.

On treatment of 1a with ammonia, 1-amino-5-(2-pyridylamino)-2,4-dinitro-3-oxo-1,4-pentadiene was intermediately isolated, which was easily affected by dil. hydrochloric acid to give 3,5-dinitro-1H-4-pyridone. This fact suggests the reaction to proceed by a stepwise nucleophilic attack of an amine at the electron deficient 2 and 6-positions of the 4-pyridone.



The reaction of 3,5-dinitro-1-(p-nitrophenyl)-4-pyridone with a equimolar amount of hydroxylamine hydrochloride in pyridine yielded an adduct of 3,5-dinitro-1-hydroxy-4-pyridone and pyridine (2:1 in molar ratio) together with p-nitroaniline. On the other hand, with an excess of the reagent, another ring transformation product (2) was given in place of 3,5-dinitro-1-hydroxy-4-pyridone. The product 2 was also derived from 3,5-dinitro-1H-4-pyridone and hydroxylamine hydrochloride in pyridine, and was converted to an acetyl derivative by treating with acetyl chloride with liberation of pyridine hydrochloride. From the facts and the physical data, the product 2 was assumed to be a pyridinium salt of 3-hydroxy-4-nitroisoxazole. The same results were obtained from the reaction of 1a with hydroxylamine hydrochloride.