Formation of New Mesoionic Pyrimidines

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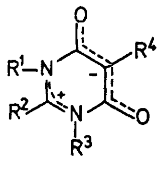
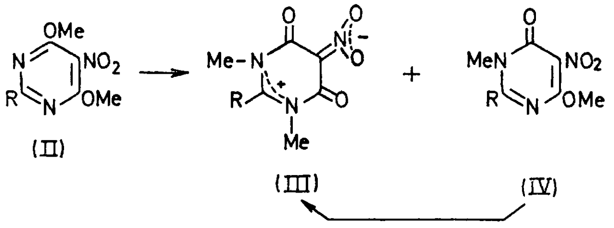
Summary Pyrolysis of 4,6-dimethyl-5-nitropyrimidines resulted in the formation of new mesoionic pyrimidines, anhydro-4-hydroxy-1,3-dimethyl-5-nitro-6-oxo-2-phenyl (or unsubstituted) pyrimidinium hydroxides.

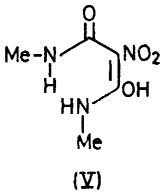


(I)

$R^1, R^3 = Me, Ph$
$R^2 = H, Me, Ph$
$R^4 = H, Me, Ph, CH_2Ph$



a; R = Ph, b; R = H



(V)

Much attention[1] has been directed towards the synthesis, characterization, and application of mesoionic heterocycles. Nevertheless, relatively few examples[2-4] of mesoionic systems with a diazine ring have been studied. Only simple mesoionic pyrimidines *e.g.*, (I), have been synthesised hitherto.[2,3]

We report a novel reaction which results in the formation of a new mesoionic pyrimidine (III), and which involves double 1,3-alkyl migrations from oxygen to nitrogen in the pyrimidine system.

When a 4,6-dimethoxy-5-nitro-2-phenyl (or unsubstituted) pyrimidine (IIa,b)[5] was heated without solvent at 200° for 15 min, anhydro-4-hydroxy-1,3-dimethyl-5-nitro-6-oxo-2-phenyl (or unsubstituted)pyrimidinium hydroxide (IIIa) (m.p. 278°); or (IIIb) (m.p. 315°)† was obtained in 80% and 70% yields, respectively. 1-Methyl-4-methoxy-5-nitro-2-phenyl(or unsubstituted)-6(1*H*)-pyrimidinones (IVa) (m.p. 200°); or (IVb) (m.p. 149°) were also isolated by silica gel chromatography from the reaction mixture.

Mass spectral and microanalytical data on (IIIa,b) established their molecular formulae as $C_{12}H_{11}O_4N_3$ and $C_6H_7O_4N_3$, positively excluding dimeric structures, and the i.r., u.v., and n.m.r. spectra of (IIIa,b) and (IVa,b) are in agreement with the structures assigned.

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† Although there are many alternative formulations for the mesoionic pyrimidines, we adopt here the formulation (IIIa,b) which seems to represent one of the more important contributions to the resonance hybrid.

Heating the by-product (IVa,b) at 200° resulted in its smooth conversion into (IIIa,b), suggesting the intermediacy of (IVa,b) in the formation of (IIIa,b). Upon treatment of (IIIa,b) with boiling aqueous potassium hydroxide, nitromalonic acid *NN'*-dimethylamide (V) was obtained quantitatively. Compound (V) was identical in every respect with a sample obtained by hydrolysis of nitrobarbituric acid.[6]

Prystas[3] has described the formation of mesoionic pyrimidines (*e.g.* I;$R^1 = R^3 = \mathrm{Me}$, $R^2 = \mathrm{H}$, $R^4 = \mathrm{Ph}$) from 5-substituted 4,6-dimethoxypyrimidines in poor yield by reaction with methyl iodide in a sealed tube. However, pyrolysis of 4,6-dimethoxy-2-phenylpyrimidine in a similar manner to that of (IIa,b) caused only an *O*→*N* alkyl group migration to give the corresponding *N*-alkyl derivatives.

The formation of (IIIa,b) from (IIa,b) apparently involves novel double 1,3-alkyl *O*→*N* migrations *via* a radical mechanism,[7] and a nitro-group of (IIa,b) seems to play a significant role in homolytic cleavage of O–Me bonds and stabilization of the mesoionic pyrimidines (IIIa,b) formed.

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