

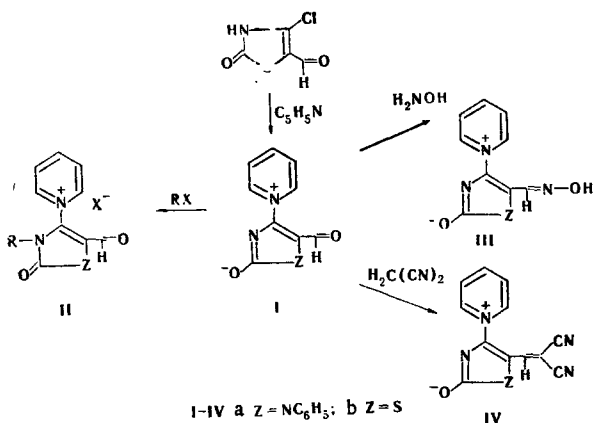
SYNTHESIS OF HETEROCYCLIC BETAINE ALDEHYDES

 R. O. Kochkanyan, A. N. Zaritovskii,
 G. I. Belova, and S. N. Baranov

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We have found that 4-chloro-5-formyl-substituted imidazolones and Δ^4 -thiazolin-2-ones react with pyridine in dimethylformamide (DMFA) to give heteroanalogs (I) of pyridinium cyclopentadienyliid. The latter, like aromatic aldehydes, react with malonotrile or hydroxylamine to give condensation products involving the aldehyde group (III, IV).

A considerable decrease in the frequencies of the vibrations of the carbonyl groups (1660 and 1550 cm^{-1}) as compared with the starting o-chloroaldehydes (1710 and 1680 cm^{-1}), which is due to the decrease in the double bond character of the carbonyl groups as a result of delocalization of the negative charge, is observed in the IR spectra of yield I. Betaines I and III are protonated and alkylated in the 3 position of the five-membered heteroring to give the corresponding salts of the II type.



EXPERIMENTAL

1-Phenyl-5-formyl-4-(1-pyridinium)imidazole 2-Oxide (Ia). This compound, with mp 272° (from DMFA), was obtained in 55% yield. Found: C 67.7; H 4.3; N 15.8%. C₁₅H₁₁N₃O₂. Calculated: C 67.9; H 4.2; N 15.8%. The methiodide (IIa), with mp 250° (from acetone), was obtained in 70% yield. Found: C 47.3; H 3.2; I 31.1; N 10.5%. C₁₆H₁₄IN₃O₂. Calculated: C 47.2; H 3.4; I 31.2; N 10.3%.

5-Formyl-4-(1-pyridinium)thiazole-2-Oxide (Ib). This compound, with mp 214-216° (dec., from DMFA), was obtained in 65% yield. UV spectrum: λ_{max} 257 (log ϵ 3.87), 317 nm (log ϵ 3.97). Found: C 52.6; H 3.1; N 13.5; S 15.5%. C₉H₆N₂O₂S. Calculated: C 52.5; H 2.9; N 13.6; S 15.5%. The methiodide (IIb), with mp 205-206° (dec., from DMFA), was obtained in 75% yield. Found: C 34.7; H 2.8; I 36.5; S 9.2%. C₁₀H₉IN₂O₂S. Calculated: C 34.5; H 2.6; I 36.5; S 9.2%. The oxime (IIIc), with mp 198° (dec.), was obtained in 70% yield. Found: C 49.1; H 3.3; S 14.5%. C₉H₇N₃O₂S. Calculated: C 48.9; H 3.2; S 14.5%.

1-Phenyl-5-(2,2-dicyano-1-ethenyl)-4-(1-pyridinium)imidazole 2-Oxide (IVa). This compound, with mp 205° (from DMFA), was obtained in 80% yield. Found: C 69.2; H 3.4; N 22.5%. C₁₈H₁₁N₅O. Calculated: C 69.0; H 3.5; N 22.4%.

5-(2,2-Dicyano-1-ethenyl)-4-(1-pyridinium)thiazolē 2-Oxide (IVb). This compound, with mp 289-290° (dec., from DMFA), was obtained in 90% yield. Found: C 57.0; H 2.5; S 13.1%. C₁₂H₈N₄OS. Calculated: C 56.7; H 2.4; S 12.6%.

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