1-Pyridinio-4-pyridone Cations and 1-Pyridiniopyridinium Dications: Intermediates of Synthetic Potential[1]

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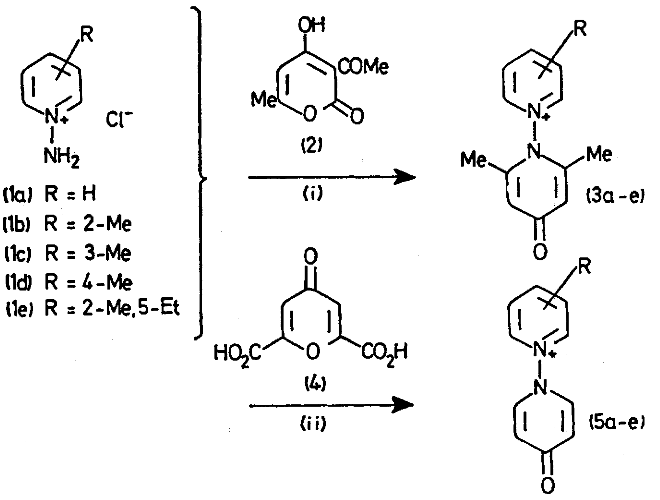
Summary 1-Aminopyridinium cations react with certain pyrones to give pyridiniopyridone cations which are converted by $POCl_3$ into chloropyridiniopyridinium dications; these cations are used to synthesise 1-arylpyridinium salts, 2-cyanopyridine, and also 2,4-bis-(benzenesulphonyl)pyridine.

A PREVIOUS paper[1] from one of our laboratories reported the preparation of 1-pyridinio-2-pyridones by the reaction of 1-aminopyridones with pyrylium salts. We have now discovered that 1-pyridinio-4-pyridones may be conveniently prepared from the readily available[2] 1-aminopyridinium cations and pyrone derivatives as illustrated by Scheme 1 which utilizes dehydroacetic acid (**2**) and cheli-

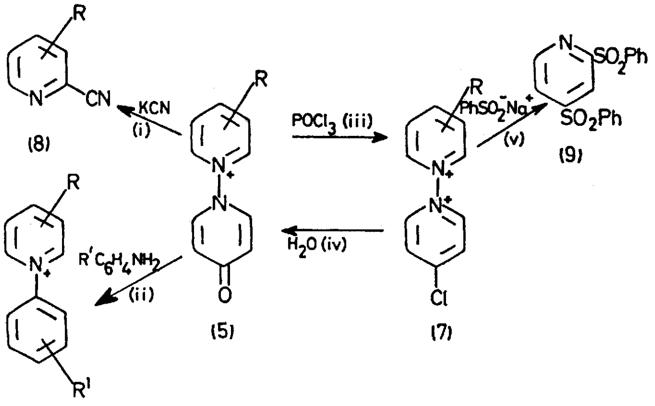


Scheme 1. Preparation of pyridinio-4-pyridone cations. Reaction conditions: (i) heat under reflux in conc. HCl for 3 h; (ii) heat under reflux in conc. HCl for 40 h.

donic acid (**4**). The products (**3**) and (**5**) were isolated as chlorides, and converted into borofluorides for further characterisation.† Yields were high (*ca.* 80%) except when a 2-methyl substituent was present in the pyridine ring, when yields were moderate to low.

The 1-pyridinio-4-pyridone (**5a**) is converted smoothly by $POCl_3$ into the 4-chloro-1-pyridiniopyridinium dication (**7**) in 80% yield, a process reversed by H_2O. Cations of types (**3**) and (**5**) and dications of type (**7**) are of considerable potential synthetic importance and we report illustrative applications (Scheme 2).

1-Arylpyridinium salts with additional substituents on the pyridine ring have been difficult to prepare;[3] we now find that the reaction of aniline and of *p*-toluidine with both (**5a**) and (**5c**) gives the 1-arylpyridinium salts (**6a**—**e**) in 30—50% yields. In contrast to an earlier report[4] of an analogous reaction in which 4-cyanopyridine was isolated in high yield, treatment of (**5a**) with aqueous KCN gives 2-cyanopyridine (**8**) (87%), contaminated with $< 5\%$ (n.m.r.) of the 4-isomer. Nucleophilic attack on the chlorine-containing ring of (**7**) by aqueous sodium benzenesulphinate yields the disulphone (**9**) (64%). The products (**6**), (**8**), and (**9**) may all be rationalised in terms of initial nucleophilic attack at the 2-position of a pyridine ring.



(6a) R = H, R' = H
(6b) R = 3-Me, R' = H
(6c) R = H, R' = 4-Me
(6d) R = 3-Me, R' = 4-Me

Scheme 2. Reactions of pyridinio-4-pyridone cations. Reaction conditions: (i) saturated aqueous KCN, room temp.; (ii) heat at 150° for 10 min; (iii) heat under reflux for 15 min; (iv) room temp. for 2 h; (v) saturated aqueous sulphinate, room temp.

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† All new products gave correct analyses and were characterised by n.m.r. and i.r. spectra. Compounds (**3a**), (**5a**), (**7**), and (**9**) were further characterised by mass spectrometry.

[1] *Cf.* the series '*N*-Oxides and Related Compounds.' For Part XLVII see A. R. Katritzky and J. W. Suwinski, *Tetrahedron Letters* in the press. See also A. R. Katritzky and J. W. Suwinski, *Tetrahedron*, in the press.

[2] R. Gösl and Meuwsen, *Org. Synth.*, 1963, **43**, 1. Products were isolated as chlorides.

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[4] T. Okamoto, M. Hirobe, C. Mizushima, and A. Osawa, *Chem. Pharm. Bull.* (*Japan*), 1963, **11**, 780 (*Chem. Abs.*, 1963, **59**, 9752e).