Simple Oxidations of Pyridines: Zinc Sulphates or Natural Sand as Remarkably Specific Catalysts

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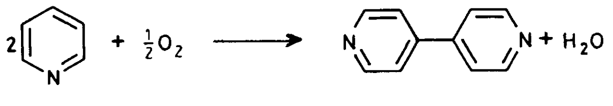
The clean oxidations in reasonable yields of pyridine to 4,4'-bipyridyl (catalysed by sand) and of pyridines to their 2-pyridones using zinc sulphate are described.

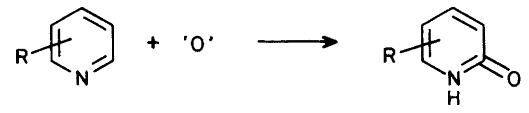
Pyridine is accessible and relatively cheap. Some of its derivatives are sought after, including 4,4'-bipyridyl (the precursor of such viologens as 1,1'-dimethyl-4,4'-bipyridylium salts: the chloride is the selective weed-killer paraquat[1]) and 2-pyridones. Approaches to 4,4'-bipyridyls have commonly been through reduction (for example, by sodium in an ICI synthesis) and oxidative coupling of the radicals thus produced (by air). A related formation[2] of 2,2'-bipyridyls on Raney nickel is well known. 2-Pyridones are often made by Decker's oxidation[3] [alkaline hexacyanoferrate(III) oxidation of quaternized pyridines as their pseudo-bases], though other synthetic methods are also available.

We now find that a mixture of laboratory sand and pyridine sealed in air or di-oxygen in a Carius tube and kept at 300 °C for 8 hours forms 4,4'-bipyridyl as in equation 1.

Under our conditions (no attempt has been made to optimize them), the yield is 12—15% of 4,4'-bipyridyl and well over 90% of the pyridine which reacts forms 4,4'-bipyridyl (*i.e.* the conversion is well over 90%).

After removing unreacted pyridine, the product could be extracted with benzene and crystallized in conversions up to 15% (no attempt has been made to optimize this). It was identified by analysis and by comparison of its properties (m.p., n.m.r., electronic spectrum) with authentic 4,4'-bipyridyl. We used BDH laboratory sand which is from a deposit at Loch Aline and remarkably pure (SiO_2 = 99.5%). Some





(2)

transition elements are present in traces: iron—whose low levels are unusual, titanium, and a little chromium.

In related work, the specific oxidation (2) occurs. Here, any of tri-aquopyridinezinc(II) sulphate, $[Zn(C_5H_5N)(OH_2)_3]SO_4$, zinc sulphate heptahydrate, or tricadmium sulphate octahydrate, $3CdSO_4 . 8H_2O$, when sealed with pyridine under air (or di-oxygen) and kept in a glass Carius tube at 300 °C for 8 hours yields 2-pyridone which, after removal of unreacted pyridine, can be extracted by benzene or chloroform and crystallized. Yields (again, we have not attempted to optimize them) are 10—15%. The solid product is identified as 2-pyridone from ^1H n.m.r., mass spectrometry, and electronic/fluorescence spectra as a function of pH. Zinc or cadmium sulphates will also react with 3-methylpyridine, giving a mixture of 2- and 6-pyridones and with 3,5-dimethylpyridine giving the 2-pyridone but not, so far, with 2- or 4-methylpyridines. In the absence of di-oxygen, no pyridone is formed.

Tomisik discovered[4] oxidation of pyridine to 2-pyridone by copper sulphate. We find that this does occur under di-nitrogen, so, as expected, copper(II) is the stoicheiometric oxidant in this case, copper metal often being a product. Copper is also a product of the thermolysis in air of tetrakispyridinecopper(II) peroxodisulphate, $[Cu(C_5H_5N)_4](S_2O_8)$, and covellite (CuS) is formed on thermolysis of $Cu(bipy)SO_4 . 2H_2O$ at 300 °C for 9 hours.

Other oxidations of pyridine(s) (to 2,2′-bipyridyls) by transition-metal species are well known: thermolysis of bis-(2-picolinato)copper(II) gives[5] 2,2′-bipyridyl, and pyridine heated with iron(III) chloride in an autoclave gives[6] bi- and ter-pyridyls chiefly linked at their 2-positions. However, in the present formation of pyrid-2-one, zinc and cadmium ions are not the oxidants, and there seems to be no reduced product from sulphate(VI). It is therefore probable, for both these remarkably specific catalytic oxidations of pyridine, that di-oxygen is the oxidant (in the pyridone case, mediated by sulphate: Tanabe has recently shown[7] that sulphate ions 'promote' the catalytic activity for isomerization of cyclopropane of several oxides, including Fe_2O_3, ZrO_2, TiO_2, Al_2O_3).

We were led to these oxidations by the analogy[8] between quaternization and pseudo-base formation on the one hand, and co-ordination in the presence of hydroxide (or sources of it) on the other. There are, of course, several related suggestions from studies of the irreversible adsorption of pyridine on heterogeneous catalysts (Al_2O_3,[9] Fe_2O_3,[10] Cr_2O_3[11]). These and the present work have in common the notion that the 2- (or 4-) position of pyridine becomes polarized by co-ordination to metal ions and can then be oxidized.

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