ABSTRACTS OF POSTERS

ANODIC MONOFLUORINATION OF PYRIDINE

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Anodic fluorination involves electrochemical oxidation of an organic substrate to a cation which then reacts with fluoride anion in solution to form a carbon-fluorine bond (Rozhkov: Russ Chem Rev 1976; 45:615). The anode potentials used are lower than those at which fluoride would be oxidized to radical or elemental fluorine, and thus controlled fluorination can be performed. Benzene, naphthalene, and benz(a)anthracene can be anodically monofluorinated in acetonitrile solutions of tetraalkylammonium fluorides. We now report the extension of this method to pyridine.

Because pyridine is very resistant to oxidation, it has been used as a solvent for electrochemical reactions. 2-Fluoropyridine has been reported as a by-product of electrolysis in pyridine/anhydrous hydrogen fluoride mixtures in a specially constructed Teflon cell (Huba et al: Electrochim Acta 1979; 24:489).

Our electrolysis cell consists of a cooled 10-ml glass beaker into which are placed a 2.5 x 2.5 cm platinum sheet anode, a stainless steel cathode, and an Ag/Ag$^+$(0.1 M) reference electrode. The electrodes are connected to a Princeton Applied Research model 173 potentiostat. To minimize the entry of moisture into the cell, dried nitrogen is bubbled throughout electrolysis. The supporting electrolyte is tetramethylammonium dihydrogen trifluoride (TMAF.2HF, Ozark Mahoning) and the solvent is acetonitrile (HPLC grade, Caledon Labs) which has been dried by distillation from P_2O_5 and from CaH_2. Pyridine (10 µl, 124 µmol) is electrolyzed in 6 ml supporting electrolyte solution and the products are analyzed by HPLC.

Although pyridine oxidation begins at 1.8 V (vs Ag/Ag$^+$), the optimal conditions for production of 2-fluoropyridine in this cell are an applied potential of 2.5 V and 0.5 M TMAF.2HF; under these conditions the chemical yield is 22% in less than 90 minutes during which time 3 equivalents of electricity for a 2-electron process have passed. In 0.1 M TMAF.2HF, yields are about one-third lower; similarly, at lower applied potentials both yield and reaction rate are decreased. At higher potentials the supporting electrolyte/solvent system decomposes.

The choice and purity of supporting electrolyte is an important factor in determining the product distribution and yield. Tetra-n-butylammonium fluoride is very hygroscopic and cannot be efficiently dried; when it is used, 2-fluoropyridine is only a minor product. Anhydrous hydrogen fluoride is not an efficient fluoride donor in this system.

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