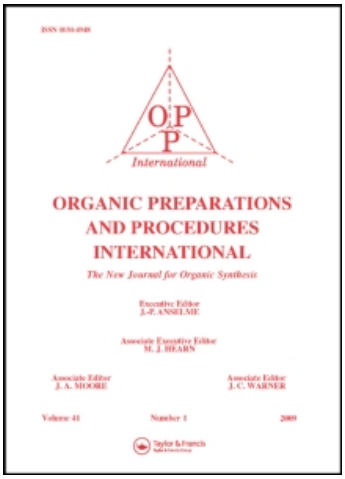

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A CONVENIENT SYNTHESIS OP 4-HTDROXY-3-NITROPYBIDINE

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OPPI BRIEFS

A CONVENIENT SYNTHESIS OF 4-HYDROXY-3-NITROPYRIDINE

Submitted by Danuta Rasala* and Ryszard Gawinecki
(12/12/84)

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4-Hydroxy-3-nitropyridine (1H-3-nitropyridine-4-one) is the ideal starting material for the preparation of some 4-substituted-3-nitropyridines (where the 4-substituent is halogen, CO_2R, $CONH_2$, CN, OR, SR, SCN and NHR).[1] Of the several methods for the nitration of 4-hydroxypyridine, some require long periods of heating,[2-4] while others use 65% oleum[5] or a large excess of the nitric acid.[6] The yield of some of these reactions does not exceed 40%[4] and at 140°, the yield of 3,5-dinitro derivative increases.[3,5,7] Sometimes it is necessary to extract the product from a large volume of reaction mixture.[7] We now describe an improved method for the preparation of the title compound.

EXPERIMENTAL SECTION

4-Hydroxy-3-nitropyridine.- 4-Hydroxypyridine nitrate (25 g, 0.16 mole) was treated dropwise at room temperature with a mixture of nitric acid (d 1.5, 33 ml) and 20% oleum (26.5 ml). A vigorous reaction (safe in a flask equipped with a reflux condenser) ensued; the mixture was then heated for 1 hr on a steam bath and then poured into ice-water (125 ml). The precipitated crystals were recrystallized from water to yield 14.6 g (70%) of pale cream-colored solid, mp. 276-277 (dec.); the lit. mps [2-5,7-9] ranged from 275-277° to 280-281°. IR (KBr): 3200-2500, 1650 cm^{-1}; MS: m/e 140 (100%), 93 (70%).

Anal. Calcd. for $C_5H_4N_2O_3$: C, 42.86; H, 2.88; N, 20.00

Found: C, 42.80; H, 2.94; N, 20.35

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A CLEAN AND REPRODUCIBLE SYNTHESIS OF 1-BROMO-2-ETHOXYETHANE

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The first synthesis of 1-bromo-2-ethoxyethene (1) was accomplished by treatment of bromoacetaldehyde diethyl acetal with zinc dust in refluxing ethanol.[1] The discovery that alkyl vinyl ethers could be prepared from alcohols using an alkaline catalyst,[2] made ethyl vinyl ether commercially available at low cost in the mid-1940's. Compound 1 is now most commonly