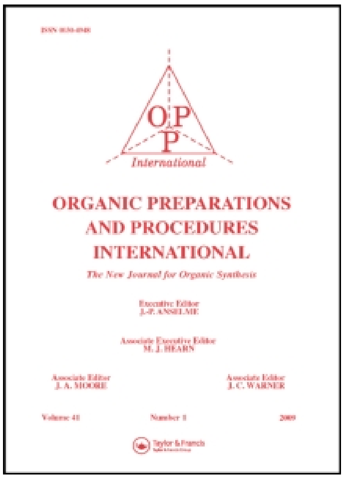

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3-NITROPYRIDINE

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3-NITROPYRIDINE

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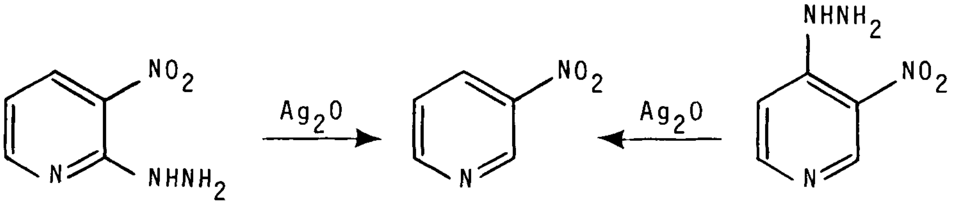

3-Nitropyridine has been prepared previously by nitration of pyridine[1-4] at ca 300°; and from 3-aminopyridine either by oxidation with hydrogen peroxide in fuming sulphuric acid,[5,6] or through the diazonium salt with cuprous cupric sulphite in concentrated nitrite solution[6] or with copper powder and nitrate solution.[7] However the product was obtained in all these cases in poor yield, and often of low purity. 3-Nitropyridine has apparently been obtained also by oxidation of 2-hydrazino-5-nitropyridine with copper sulphate, but no experimental details are given.[8]

In this communication convenient preparations of 3-nitropyridine are described from hydrazino-3-nitropyridines by the action of silver oxide in aqueous solution. 2-Hydrazino-3-nitropyridine gave a 54.4% yield of pure 3-nitropyridine and 4-hydrazino-3-nitropyridine gave 47.3%, but 2-hydrazino-5-nitropyridine gave 12.7% only of the required product. In each case the 3-nitropyridine was readily purified.

The hydrazino compounds required were readily prepared from the corresponding chloronitropyridines.

EXPERIMENTAL

Hydrazino-3-nitropyridines

2-*Hydrazino*-3-*nitropyridine*.— 2-Chloro-3-nitropyridine[9] (10.0 g) and hydrazine hydrate (10 ml; 98%) in ethanol (200 ml) were refluxed for 30 min. After chilling, the precipitate was collected and recrystallised from ethanol to give a nearly quantitative yield of 2-hydrazino-3-nitropyridine, m.p. 168-172° (lit.[10] 164°).

Anal. Calcd. for $C_5H_6N_4O_2$: C, 39.0; H, 3.95; N, 36.35. Found: C, 38.9; H, 4.25; N, 36.5.

4-*Hydrazino*-3-*nitropyridine*.— 4-Chloro-3-nitropyridine[11,12] and hydrazine hydrate in ethanol on warming similarly gave 96% yield of 4-hydrazino-3-nitropyridine.[13]

2-*Hydrazino*-5-*nitropyridine*.— This compound was prepared in 85% yield from 2-chloro-5-nitropyridine and hydrazine hydrate as described.[14]

3-*Nitropyridine*.— A solution of 2-hydrazino-3-nitropyridine (5.0 g) in water (1000 ml) at *ca* 80° was stirred as silver oxide (20.0 g) was added in portions and stirring continued for 1 hr. Nitrogen was evolved and the solution became colorless. The mixture was filtered, the filtrate was extracted with chloroform, and the product (3.1 g) was chromatographed in benzene over alumina and recrystallised from light petroleum (b.p. 60-80°) to give 3-nitropyridine (2.19 g.; 54.4%), m.p. 38-40° (lit.[1] 41°).

4-Hydrazino-3-nitropyridine when similarly treated gave 47.3% of 3-nitropyridine, and 2-hydrazino-5-nitropyridine gave 12.7% 3-nitropyridine when the mixture was refluxed for 2 hr.

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