

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

### 3-NITROPYRIDINE

G. B. Barlin<sup>a</sup>

<sup>a</sup> Department of Medical Chemistry, Australian National University, Canberra, ACT, Australia

**To cite this Article** Barlin, G. B.(1972) '3-NITROPYRIDINE', *Organic Preparations and Procedures International*, 4: 2, 63 — 66

**To link to this Article:** DOI: 10.1080/00304947209458263

**URL:** <http://dx.doi.org/10.1080/00304947209458263>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

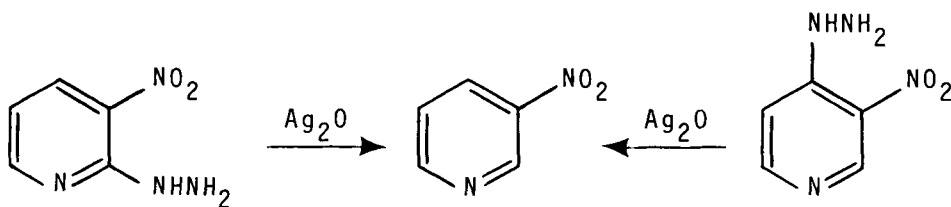
This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## 3-NITROPYRIDINE

G. B. Barlin

Department of Medical Chemistry  
 Australian National University, Canberra, A.C.T. Australia



3-Nitropyridine has been prepared previously by nitration of pyridine<sup>1-4</sup> at ca 300°; and from 3-aminopyridine either by oxidation with hydrogen peroxide in fuming sulphuric acid,<sup>5,6</sup> or through the diazonium salt with cuprous cupric sulphite in concentrated nitrite solution<sup>6</sup> or with copper powder and nitrate solution.<sup>7</sup> 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.<sup>8</sup>

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

G. B. BARLIN

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<sup>9</sup> (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.<sup>10</sup> 164°).

Anal. Calcd. for C<sub>5</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>: 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<sup>11,12</sup> and hydrazine hydrate in ethanol on warming similarly gave 96% yield of 4-hydrazino-3-nitropyridine.<sup>13</sup>

2-Hydrazino-5-nitropyridine.— This compound was prepared in 85% yield from 2-chloro-5-nitropyridine and hydrazine hydrate as described.<sup>14</sup>

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<sup>0</sup>) to give 3-nitropyridine (2.19 g.; 54.4%), m.p. 38-40<sup>0</sup> (lit.<sup>1</sup> 41<sup>0</sup>).

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.

#### ACKNOWLEDGEMENTS

I thank Professor A. Albert and Dr D.J. Brown for helpful discussion and Miss V.J. Richardson for technical assistance.

#### REFERENCES

1. F. Friedl, Ber., 45, 428 (1912).
2. F. Friedl, Monatsh. Chem., 34, 759 (1913).
3. A. Kirpal and E. Reiter, Ber., 58, 699 (1925).
4. H. J. den Hertog and J. Overhoff, Rec. Trav. Chim. Pays-Bas, 49, 552 (1930).
5. A. Kirpal and W. Böhm, Ber., 65, 680 (1932).
6. O. v. Schickh, A. Binz, and A. Schulz, Ber., 69, 2593 (1936).
7. G. B. Barlin and A. C. Young, J. Chem. Soc. B, 1675 (1971).

G. B. BARLIN

8. A. Binz and C. R ath,  
Justus Liebigs, Ann. Chem., 486, 95 (1931).
9. Y. Ahmad and D. H. Hey, J. Chem. Soc., 4516 (1954).
10. T. Talik and Z. Talik, Roczn. Chem., 41, 483 (1967).
11. A. Albert and G. B. Barlin, J. Chem. Soc., 5156 (1963).
12. S. Kruger and F. G. Mann, J. Chem. Soc., 2755 (1955).
13. E. Koenigs and K. Freter, Ber., 57, 1187 (1924).
14. A. Mangini and B. Frenguelli,  
Gazz. Chim. Ital., 69, 97 (1939).

(Received February 22, 1972; in revised form April 6, 1972)