

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>

### OXIDATIVE NITROMETHYLENATION (S<sub>N</sub>H SUBSTITUTION) IN PYRIDINIUM SALTS

Dick J. Buurman<sup>a</sup>; Henk C. van der Plas<sup>a</sup>

<sup>a</sup> Department of Organic Chemistry, Agricultural University, Wageningen, HB, THE NETHERLANDS

**To cite this Article** Buurman, Dick J. and van der Plas, Henk C.(1988) 'OXIDATIVE NITROMETHYLENATION (S<sub>N</sub>H SUBSTITUTION) IN PYRIDINIUM SALTS', *Organic Preparations and Procedures International*, 20: 6, 591 – 592

**To link to this Article:** DOI: 10.1080/00304948809356303

**URL:** <http://dx.doi.org/10.1080/00304948809356303>

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.

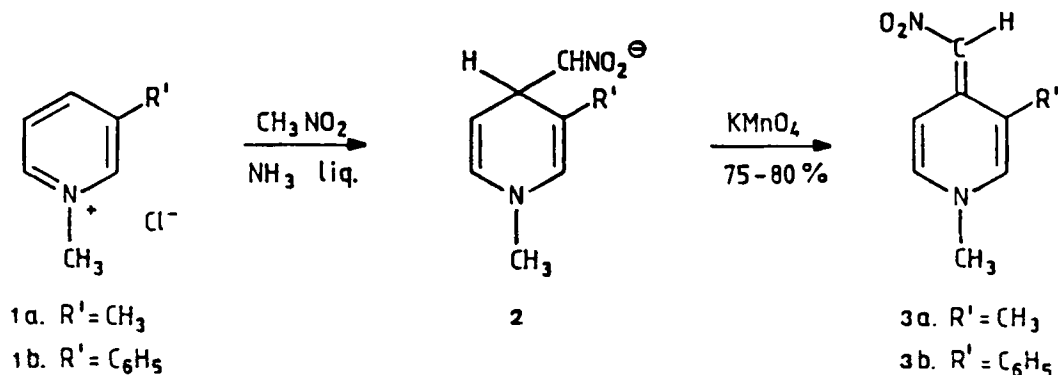
## OPPI BRIEFS

OXIDATIVE NITROMETHYLENATION ( $S_NH$  SUBSTITUTION) IN PYRIDINIUM SALTS

Submitted by Dick J. Buurman and Henk C. van der Plas\*  
(02/19/88)

Department of Organic Chemistry  
Agricultural University  
Dreijenplein 8, 6703 HB Wageningen  
THE NETHERLANDS

In an extension of our work on  $S_NH$  substitution reactions,<sup>1,2</sup> it was of interest to determine whether pyridinium salts are also able to undergo oxidative nitromethylenation (Eq. 1). Therefore, we studied the reaction of 1,3-dimethylpyridinium chloride (**1a**) with nitromethide in the presence of potassium permanganate. It has been reported<sup>3</sup> that nitromethide is readily formed from nitromethane and liquid ammonia at  $-10^\circ$  or lower temperatures. We now report that when **1a** or **1b** was dissolved in liquid ammonia ( $-40^\circ$ ) containing nitromethane, and the resulting suspension was treated with potassium permanganate, **3a**, or **3b** was isolated.



It has been established<sup>4</sup> that nitromethide in liquid ammonia adds easily at position 4 of pyridinium salts and thus it seems reasonable to assume that **2** is the intermediate of the nitromethylenation reaction of **1a** and **1b**.

## EXPERIMENTAL SECTION

Mps are uncorrected. Mass spectra were determined on an AEI MS 902 mass spectrometer equipped with a VG ZAB console. The  $^1\text{H}$  NMR spectra were recorded on a Varian EM-390 spectrometer. Compounds **1a** and **1b** were prepared from the corresponding iodides<sup>5,6</sup> by passage over a Dowex 1-X 2 column.

**General Procedure.**- To a suspension of 4 mmol of starting material and 8 mmol of nitromethane in 25-30 ml of liquid ammonia were added 4 mmol of potassium permanganate. After stirring this suspension at  $-40^{\circ}$  to  $-50^{\circ}$  for 4 hrs, ammonia was evaporated and the residue extracted with chloroform. The extract was evaporated *in vacuo* and the residue obtained was purified by column chromatography, using silica gel and chloroform-methanol (4:1). Crystallization from benzene gave pure products.

**1,4-Dihydro-1,3-dimethyl-4-nitromethylenepyridine (3a)**, mp. 229-230 $^{\circ}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 7.17 (d, 2 H), 8.65 (d, 5H), 7.32 (dd, 6H), 3.75 (s, N- $\text{CH}_3$ ), 2.04 (s,  $\text{CH}_3$ ), 6.87 (s, H-C $\text{NO}_2$ ),  $J_{5,6} = 7.3$  Hz,  $J_{2,6} = 1.6$  Hz. MS: Calcd. m/e 166.0742, found: m/e 166.0743.

**Anal.** Calcd. for  $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ : C, 57.82; H, 6.07; N, 16.86

Found: C, 57.64; H, 6.06; N, 17.03

**1,4-Dihydro-1-methyl-4-nitromethylene-3-phenylpyridine (3b)**, mp. 207-208 $^{\circ}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): d 7.16 (d, 2H), 8.73 (d, 5H), 7.36 (dd, 6H), 3.80(s, N $\text{CH}_3$ ), 6.76 (s, H-C $\text{NO}_2$ ), 7.25 and 7.40 (m,  $\text{C}_6\text{H}_5$ ),  $J_{5,6} = 7.3$  Hz,  $J_{2,6} = 1.8$  Hz. MS: Calcd. m/e 228.0899. Found, m/e 228.0899.

**Anal.** Calcd. for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 68.40; H, 5.29; N, 12.27

Found: C, 68.66; H, 5.28; N, 12.19

#### REFERENCES

1. D. J. Buurman and H. C. van der Plas, *J. Heterocyclic Chem.*, **23**, 1015 (1986).
2. For a recent review on  $\text{S}_{\text{N}}\text{H}$  substitution reactions, see O. Chupakhin, V. Charushin and H. C. van der Plas, *Tetrahedron*, **44**, 1 (1988).
3. J. A. Zoltewicz and J. K. O'Halloran, *J. Org. Chem.*, **39**, 89 (1974).
4. J. A. Zoltewicz, L. S. Helmick and J. K. O' Halloran, *ibid.*, **41**, 1308 (1976).
5. H. L. Bradlow and C. A. Vanderwerf, *ibid.*, **16**, 1143 (1951).
6. P. Krumholz, *J. Am. Chem. Soc.*, **73**, 3487 (1951).

\*\*\*\*\*