

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>

AN IMPROVED PROCEDURE FOR THE OXIDATION OF 2,5- AND 5,6-DIHALO-3-METHYLPYRIDINES

F. L. Setliff^a; W. R. Huie^a; R. L. Adams^a

^a Department of Chemistry, University of Arkansas at Little Rock, Little Rock, Arkansas

To cite this Article Setliff, F. L. , Huie, W. R. and Adams, R. L.(1983) 'AN IMPROVED PROCEDURE FOR THE OXIDATION OF 2,5- AND 5,6-DIHALO-3-METHYLPYRIDINES', *Organic Preparations and Procedures International*, 15: 1, 67 – 68

To link to this Article: DOI: 10.1080/00304948309355433

URL: <http://dx.doi.org/10.1080/00304948309355433>

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.

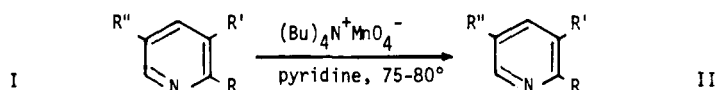
9. a) U. Krueerke, E. Wittouck, Chem. Ber., 95, 174 (1962).
 b) P. Ch. Wälchli, C. H. Eugster, Helv. Chim. Acta, 61, 885 (1978).
 10. N. Campbell, A. H. Sommers, Org. Synth. Coll. Vol., 3, 446 (1955).
 11. F. Degering, L. G. Boatright, J. Am. Chem. Soc., 72, 5137 (1950).
 12. O. L. Chapman, K. C. Mattes, R. S. Cheridan, J. A. Klun, *ibid.*, 100, 4878 (1978).
 13. F. L. M. Pattison, J. B. Stothers, R. G. Woolford, *ibid.*, 78, 2255 (1956).

AN IMPROVED PROCEDURE FOR THE OXIDATION
 OF 2,5- AND 5,6-DIHALO-3-METHYLPYRIDINES

Submitted by F. L. Setliff*, W. R. Huie and R. L. Adams
 (7/26/82)

Department of Chemistry
 University of Arkansas at Little Rock
 Little Rock, Arkansas 72204

Oxidations of 2,5- and 5,6- dihalo-3-methylpyridines to the respective 2,5- and 5,6- dihalonicotinic acids with aqueous potassium permanganate proceed in low yields (10-50%)¹⁻⁵. The use of tetrabutylammonium permanganate (TBAP) in pyridine⁶ significantly improves the yields of the aforementioned oxidations (Table 1).



- | | |
|--|--------------------------------|
| a) R = Cl; R' = Br; R'' = CH ₃ | a) R = Cl; R' = Br; R'' = COOH |
| b) R = Br; R' = Br; R'' = CH ₃ | b) R = Br; R' = Br; R'' = COOH |
| c) R = Br; R' = CH ₃ ; R'' = I | c) R = Br; R' = COOH; R'' = I |
| d) R = Cl; R' = CH ₃ ; R'' = Br | d) R = Cl; R' = COOH; R'' = Br |
| e) R = Br; R' = CH ₃ ; R'' = Br | e) R = Br; R' = COOH; R'' = Br |
| f) R = F; R' = CH ₃ ; R'' = Br | f) R = F; R' = COOH; R'' = Br |
| g) R = Cl; R' = CH ₃ ; R'' = I | g) R = Cl; R' = COOH; R'' = I |
| h) R = Br; R' = CH ₃ ; R'' = Cl | h) R = Br; R' = COOH; R'' = Cl |

Table 1. Comparative Yields (%) of Nicotinic Acids (II) from Oxidations

Method	IIa	IIb	IIc	IIId	IIe	IIf	IIg	IIh
KMnO ₄	50 ¹	45 ¹	16 ⁵	25 ¹	30 ¹	28 ¹	30 ⁴	43 ⁵
TBAP	62	72	66	61	64	73	72	60

EXPERIMENTAL

5,6-Dibromonicotinic acid (Iib). Typical Procedure.-A solution of 8.63g (24 mmol) of freshly prepared⁶ TBAP (dried in vacuo) in dry pyridine (110 ml) was added dropwise over a period of 1.5 hr. under nitrogen to a magnetically stirred solution of 5,6-dibromo-3-methylpyridine (Ib, 2.0g, 8 mmol) in dry pyridine (30 ml) maintained at 75-80° (oil bath). The resulting mixture was stirred under nitrogen for an additional hour at 75-80°. After cooling to 15°, sodium bisulfite (13g) was added and this was followed by the slow addition of 6 M HCl (400 ml) with stirring. The resulting clear solution was refrigerated overnight whereupon the crude product Iib crystallized⁷ as small needles, which were collected by filtration. Extraction of the filtrate with ether (400 ml) followed by evaporation of the solvent afforded an additional amount of product. Recrystallization of the combined crude material from aqueous ethanol yielded 1.62g (72%) of pure 5,6-dibromonicotinic acid, mp. 171-172°, lit.¹ mp. 173-174°. The IR spectrum was identical to that of an authentic sample. (IR verification of identity was done with all products.)

Acknowledgement.-Support of this work by a University of Arkansas at Little Rock Faculty Research Grant is gratefully acknowledged.

REFERENCES

1. F. L. Setliff, *J. Chem. Eng. Data*, **15**, 590 (1970).
2. F. L. Setliff and G. O. Rankin, *ibid.*, **17**, 515 (1972).
3. F. L. Setliff and D. W. Price, *ibid.*, **18**, 449 (1973).
4. F. L. Setliff and J. E. Lane, *ibid.*, **21**, 246 (1976).
5. F. L. Setliff and J. S. Greene, *ibid.*, **23**, 96 (1978).
6. T. Sala and M. V. Sargent, *Chem. Comm.*, **253** (1978).
7. In some cases there was no crystallization on overnight refrigeration; therefore, the product was isolated by ether extraction as described.