

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 DISSOLVING METAL REDUCTION OF TWO BROMONITROPICOLINES

F. L. Setliff^a; J. S. Greene^a

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

To cite this Article Setliff, F. L. and Greene, J. S.(1977) 'AN IMPROVED PROCEDURE FOR THE DISSOLVING METAL REDUCTION OF TWO BROMONITROPICOLINES', *Organic Preparations and Procedures International*, 9: 1, 13 – 14

To link to this Article: DOI: 10.1080/00304947709355654

URL: <http://dx.doi.org/10.1080/00304947709355654>

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.

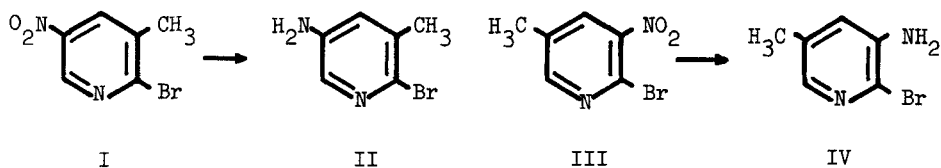
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any 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.

AN IMPROVED PROCEDURE FOR THE DISSOLVING
METAL REDUCTION OF TWO BROMONITROPICOLINES

F. L. Setliff* and J. S. Greene

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

We have previously reported the successful reduction of 2-bromo-3-methyl-5-nitropyridine (I) to 5-amino-2-bromo-3-methylpyridine (III)¹ and the reduction of 2-bromo-5-methyl-3-nitropyridine (III) to 3-amino-2-bromo-5-methylpyridine (IV)² in 35% and 57% yields respectively, employing an iron and acetic acid reducing medium. We now report that I and III may easily be reduced to II and IV with tin and conc. hydrochloric acid in



the respective improved yields of 60% and 70% without displacement of the bromide by chloride, although it is reported³ that 2,5-dibromo-3-nitropyridine undergoes displacement at the 2-position by chloride under these reductive conditions to produce 5-bromo-2-chloro-3-aminopyridine. We have also observed that 2-iodo-3-methyl-5-nitropyridine, previously reduced in our laboratories⁴ using a neutral reduction medium (aqueous iron powder), may be reduced to 5-amino-2-iodo-3-methylpyridine employing tin and conc. hydrochloric acid without displacement of iodide, although in slightly lower yield than that afforded by the former method.

EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were determined as KBr disks using a Perkin-Elmer 337 spectrophotometer.

5-Amino-2-bromo-3-methylpyridine (II). - Conc. hydrochloric acid (15 ml) was slowly added to a mixture of 2-bromo-3-methyl-5-nitropyridine I (6.00 g, 0.275 mole) and 7.4 g finely powdered tin (0.0625 g-at.), keeping the exothermic reaction under control by means of an ice bath. After the reaction mixture reached room temperature, it was heated at 80-85⁰ (steam bath) for 1 hr during which time all tin had dissolved. The reaction mixture was cooled to room temperature and poured into pre-cooled (10⁰) 25% sodium hydroxide (150 ml). The resulting slurry was extracted with four 40 ml portions of chloroform and the chloroform extracts were filtered, dried and evaporated affording the crude product. Recrystallization from methylcyclohexane yielded pure II, 3.1 g (60%) mp. 97-99⁰, lit.¹ mp 98-100⁰. The infrared spectrum was superimposable on that of an authentic sample, and a mixture melting point showed no depression.

3-Amino-2-bromo-5-methylpyridine (IV). - Using the identical procedure and quantities of reagents described for the reduction of I to II, 2-bromo-5-methyl-3-nitropyridine (III) was reduced to IV. Recrystallization from methylcyclohexane afforded 3.6 g (70%) of IV, mp. 106-107⁰, lit.² mp. 106-107⁰. The infrared spectrum was identical to that of an authentic sample and a mixture melting point showed no depression.

REFERENCES

1. F. L. Setliff and G. O. Rankin, *J. Chem. Eng. Data*, 17, 515 (1972).
2. F. L. Setliff, *Org. Prep. Proced. Int.*, 3, 217 (1971).
3. A. Berrie, G. Newbold, and F. Spring, *J. Chem. Soc.*, 2042 (1952).
4. F. L. Setliff and D. W. Price, *J. Chem. Eng. Data*, 18, 449 (1973).

(Received Jan. 11, 1977)