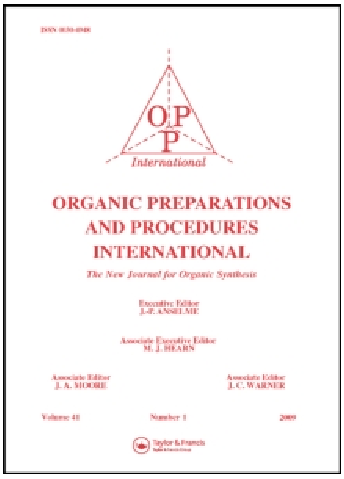

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AN IMPROVED PROCEDURE FOR THE DISSOLVING METAL REDUCTION OF TWO BROMONITROPICOLINES

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AN IMPROVED PROCEDURE FOR THE DISSOLVING METAL REDUCTION OF TWO BROMONITROPICOLINES

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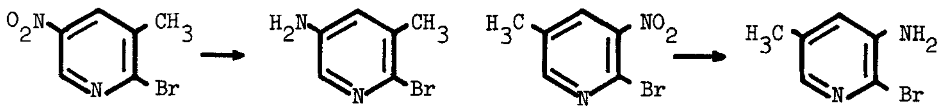
We have previously reported the successful reduction of 2-bromo-3-methyl-5-nitropyridine (I) to 5-amino-2-bromo-3-methylpyridine (III)[1] and the reduction of 2-bromo-5-methyl-3-nitropyridine (III) to 3-amino-2-bromo-5-methylpyridine (IV)[2] in 35% and 57% yields respectively, employing an iron and acetic 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 reported[3] 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 laboratories[4] using a neutral reduction medium (aqueous iron powder), may be reduced to 5-amino-2-iodo-3-methylpyridine empolying tin and conc. hydrochloric acid without displacement of iodide, although in slightly lower yield than that afforded by the former method.



I II III IV

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 80-85° (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 (10°) 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. 97-99°, lit.[1] mp 98-100°. 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. 106-107°, lit.[2] mp. 106-107°. The infrared spectrum was identical to that of an authentic sample and a mixture melting point showed no depression.

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