

Heterocyclic Systems with a Bridgehead Nitrogen III. The Synthesis of Tetrazolo[1,5-*a*]pyridines from Nitraminopyridines and Raney Nickel-hydrazine

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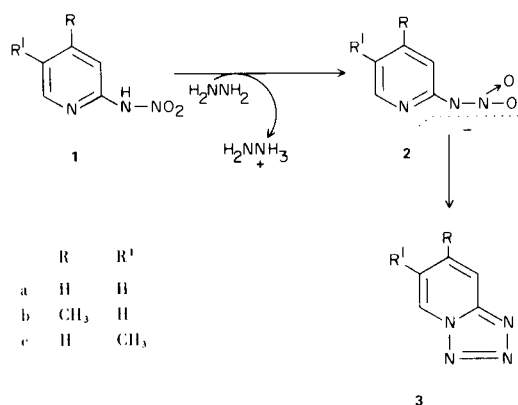
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Sir:

We wish to report a novel pyridotetrazole synthesis (1) which involves the interaction of 2-nitraminopyridines (1) (2), hydrazine and Raney nickel (3). Raney nickel (4) (ca. 5 g.) was added to a mixture of 2-nitraminopyridine (25 g.), 95+% hydrazine (25 ml.) and 80% ethanol (500 ml.) (5). This mixture was kept at 15° for ½ hour, then at room temperature for 16 hours. The nickel and ethanol were removed and the aqueous residue was acidified with concentrated hydrochloric acid. Tetrazolo[1,5-*a*]pyridine [3a, 50.3% yield, m.p. 154-156° - lit. (6) m.p. 159°] was obtained by chloroform extraction from the acidic mixture. [The aqueous phase was found to contain some 2-aminopyridine. This material could be the direct result of nickel-hydrazine reduction of 2-nitraminopyridyl anion 2a (7) and/or the result of the reduction of pyridotetrazole 3a (8)]. Using this procedure we also prepared 6-methyltetrazolo[1,5-*a*]pyridine [3b, 60.0% yield, m.p. 144-145° - lit. (9) m.p. 139-141°] and 7-methyltetrazolo[1,5-*a*]pyridine [3c, 2.3% yield, m.p. 97° - lit. (9) m.p. 95-97°].

That this procedure has limitations, which are apparently electronic in nature, became obvious when treatment of 5-chloro-2-nitraminopyridine, in the above manner, gave only 2-amino-5-chloropyridine. In a separate experiment, the reaction was quenched after ten minutes and only aminochloropyridine and unreacted starting material was obtained, which strongly suggests that no chloropyridotetrazole was formed.



Initially it was felt that this reaction proceeded *via* the interaction of a pyridonitrene (10) and either diimide or activated nitrogen (11). This idea could not be confirmed as we were unable to isolate an adduct from a reaction to which cyclohexene had been added to act as a nitrene trap.

As the nickel-hydrazine reagent is normally used to effect reduction, the possible intermediacy of the normal reduction products of 2-nitraminopyridyl anion 2a *viz.* 2-aminopyridine and 2-hydrazinopyridine (12) could not be ignored. In subsequent experiments, neither of these compounds was found to be altered by nickel-hydrazine treatment ruling out their involvement.

REFERENCES

- (1) For reviews on pyridotetrazoles see: (a) W. L. Mosby in "Heterocyclic Systems with Bridgehead Nitrogen Atoms" Part Two, "Heterocyclic Compounds," A. Weissberger, Consult. Ed., Interscience Publishers, Inc., New York, N. Y., 1961, pp. 861-865. (b) F. R. Benson in "Heterocyclic Compounds," 8, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, pp. 1-104.
- (2) For a review on nitraminopyridines see A. S. Tomcufcik and L. N. Starker in "Pyridine and Its Derivatives" Part Three, E. Klingsberg, Ed. from the series "Heterocyclic Compounds," A. Weissberger Consult. Ed. Interscience Publishers, Inc., New York, N. Y., 1962, pp. 50-55.
- (3) For a review on Hydrazine-Metal Catalyst Reactions see A. Furst, R. C. Berlo, and S. Hooten, *Chem. Rev.*, **65**, 51 (1965).
- (4) No. 28 Raney Active Nickel Catalyst in Water purchased from W. R. Grace and Co., Raney Catalyst Division, So. Pittsburg, Tennessee.
- (5) The nitraminopyridines used here were insoluble in 80% ethanol, but their hydrazinium salts, generated *in situ*, were readily soluble.
- (6) R. G. Fargher and R. Furness, *J. Chem. Soc.*, **107**, 688 (1915).
- (7) In our laboratory it was found that the Raney nickel catalyzed hydrogenation of 2-nitraminopyridyl anion (from 1a and potassium carbonate) gave 2-aminopyridine.
- (8) J. H. Boyer, M. S. Chang, and R. F. Reinisch, *J. Org. Chem.*, **25**, 286 (1960).
- (9) J. H. Boyer and R. F. Reinisch, *J. Am. Chem. Soc.*, **82**, 2218 (1960).
- (10) W. D. Crow and C. Wentrup, *Chem. Commun.*, 1082

(1968), reported that the thermal decomposition of pyridotetrazaoles gives 2-cyanopyrroles which are postulated to arise *via* nitrenes. An infrared spectrum of our crude reaction product showed no nitrile band.

(11) The involvement of diimide in hydrazine-metal catalyst reductions is not generally accepted, see ref. 3 as well as S. Hunig, *Angew. Chem. Intern. Edit. Engl.*, **4**, 276 (footnote 43) (1965). While diimide is detectable [T. Huang and J. T. Spencer, *J. Phys.*

Chem., **72**, 4198 (1965)], there has not yet been a report of its detection in hydrazine-metal catalyst reactions. Nitrogen is a normal product of the nickel catalyzed decomposition of hydrazine. While there is no evidence to show that this is activated nitrogen it was assumed that the nitrogen as it is first formed might possibly be in some high energy state.

(12) A. E. Chichibabin and B. A. Rasorenov, *J. Russ. Phys. Chem. Soc.*, **47**, 1286 (1915); *Chem. Abstr.*, **9**, 3057 (1916).