## OXIDATION OF 4-PHENYL-1,2-DIAMINOIMIDAZOLE WITH MANGANESE DIOXIDE

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Ring transpositions of heterocycles have been a topic of current interest <sup>1</sup> As a continuation of our investigations of the fragmentation of heteroaryl N-nitrenes, <sup>2</sup> we have oxidized 4-phenyl-1,2-diaminoimidazole(I)<sup>3</sup> and now report our results briefly

Oxidation of I in benzene at reflux for 7 hrs with freshly prepared manganese dioxide gave in addition to tarry products, 5-phenyl-3-amino-1,2,4-triazine(II) and 4-phenyl-1,2,3-triazole(III) in 22% and 20% yields respectively, in dioxane at room temperature for 24 hrs, the yields of II and III were 15% and 34%. Compounds II and III were identified by comparison with authentic samples. No product traceable to the fragmentation of a putative N-nitrene could be isolated.

While it is possible to ascribe the formation of II to diazene-hydrazone type rearrangement, we prefer to postulate the formation of a C-nitrene (or nitrenoid) as suggested by Takimoto and Denault <sup>5</sup> The ring opening of C-nitrene IV to the cyanomine hydrazine V followed by recyclization to 5-phenyl-3-amino-1,2,4-triazine(II) also finds precedent in the previously cited work <sup>5</sup> Further oxidation of V to the diazoalkane VI followed by cyclization could yield 5-phenyl-1-cyano-1,2,3-triazole

Hermes and Marsh<sup>6</sup> had shown that many  $\alpha$ -diazo-N-cyanoimines exist in tautomeric equilibrium with corresponding N-cyanotriazoles. The cyanation of 4-(5-)-phenyl-1,2,3-triazole anion with cyanogen bromide<sup>6</sup> yielded what appears to be mainly an N-cyanotriazole tautomer,<sup>7</sup> which was found to be surprisingly stable under the conditions of our reaction. These findings suggest that V cyclizes directly to 4-(5-)phenyl-1,2,3-triazole with little or no involvement of the  $\alpha$ -

Ph 
$$NH_2$$
  $Ph$   $NH_2$   $NH_2$ 

diazo-N-cyanoimine VI. The scope of this reaction is currently under investigation.

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- 7. The IR spectrum exhibited a strong absorption at  $\sim 2257$  cm<sup>-1</sup> (CN) while the band at  $\sim 2222$  cm<sup>-1</sup> (>C= $\frac{1}{N}$ ) was much weaker. Cyanation is presumed to have taken place at the 1-position to give mainly 4-phenyl-1-eyano-1,2,3-triazole.