The Fragmentation of an *N*-Pyrryl Nitrene from the Oxidation of 6-Amino-1,4,5,7-tetramethylpyrrolo[3,4-*d*]pyridazine

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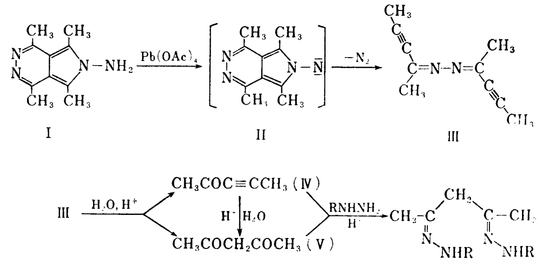
While pyrryl *N*-nitrenes do not undergo fragmentation,[1,2] those *N*-nitrenes derived from 1,2,4- and 1,2,3-triazoles,[2,3] tetrazoles,[3] imidazoles,[4] and 1- and 2-benzotriazoles[5] lose elemental nitrogen with formation of the corresponding triply bonded species. We now report evidence which suggests that fragmentation can be a reaction path for some pyrryl *N*-nitrenes.

When a solution of 6-amino-1,4,5,7-tetramethylpyrrolo[3,4-*d*]pyridazine (I)[6] was heated with lead tetraacetate under reflux for 3 hr, nitrogen was generated in about 36% yield. From the very dark brown reaction mixture, a crude semi-solid was obtained which exhibited a medium intensity band at 2035 cm^{-1} (shoulder at 2075 cm^{-1}) and a strong absorption at 1735 cm^{-1}. Treatment of this crude product with 2,4-dinitrophenylhydrazine under acidic conditions gave the bis-(2,4-dinitrophenyl)hydrazone of acetylacetone, mp 209—212°C, identical in all respects with an authentic sample. When the oxidation was carried out overnight at room temperature, the yield of nitrogen was about 22%. Addition of solid sodium carbonate to the dark reaction mixture, followed by removal of the solids and mild acidic hydrolysis of the filtrate, gave a 16% yield of acetylacetone. Its infrared spectrum was superimposable upon that of an authentic sample; its bis-(2,4-dinitrophenylhydrazone) was also identical in all respects to an authentic sample.



R=2,4-dinitrophenyl

The isolation of acetylacetone coupled with the evolution of nitrogen suggests that, in contrast to the *N*-nitrenes derived from pyrroles and carbazoles,[1,2] the *N*-nitrene (II) generated from I underwent fragmentation to the extent of ~36%. The primary fragment (III) might be expected to be somewhat unstable to the conditions of the reaction and to be hydrolyzed at least partially to 3-pentyne-2-one (IV) which would then presumably be hydrated to acetylacetone; alternatively, IV could give the bis-hydrazone by direct reaction with 2,4-dinitrophenylhydrazine.

The formation of large amounts of dark products suggests that the *N*-nitrene (II) undergoes further reactions *without* expulsion of nitrogen. The occurrence of the fragmentation path in this case may be the result of synergistic effect of two factors, namely the incorporation of the pyrrole ring in a quinoid structure[5] and secondly, the electron withdrawing effect of the two nitrogen atoms of the pyridazine ring which possibly weakens the "backbone" bond[8] sufficiently so that fragmentation can occur.

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1) a) D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Amer. Chem. Soc.*, **85**, 1944 (1963). b) L. A. Carpino, *J. Org. Chem.*, **30**, 736 (1965).

2) K. Sakai and J.-P. Anselme, *Tetrahedron Lett.*, **1970**, 3851.

3) K. Sakai and J.-P. Anselme, unpublished results.

4) K. Sakai and J.-P. Anselme, This Bulletin, **45**, 306 (1972).

5) C. D. Campbell and C. W. Rees, *J. Chem. Soc., C*, **1969**, 742.

6) W. L. Mosby, *J. Chem. Soc.*, **1957**, 3997; G. Adembri, F. DeSio, R. Nesi, and M. Scotton, *ibid., C*, **1970** 1536.

7) D. S. Noyce and K. E. DeBruin, *J. Amer. Chem. Soc.*, **90**, 372 (1968).

8) K. Sakai, A. Tanaka, G. Koga, and J.-P. Anselme, *Nippon Kagaku Zasshi*, **92**, 1065 (1971).