An *N*-Aminopyridone–Pyridazine Rearrangement; a New Decarbonylation Reaction

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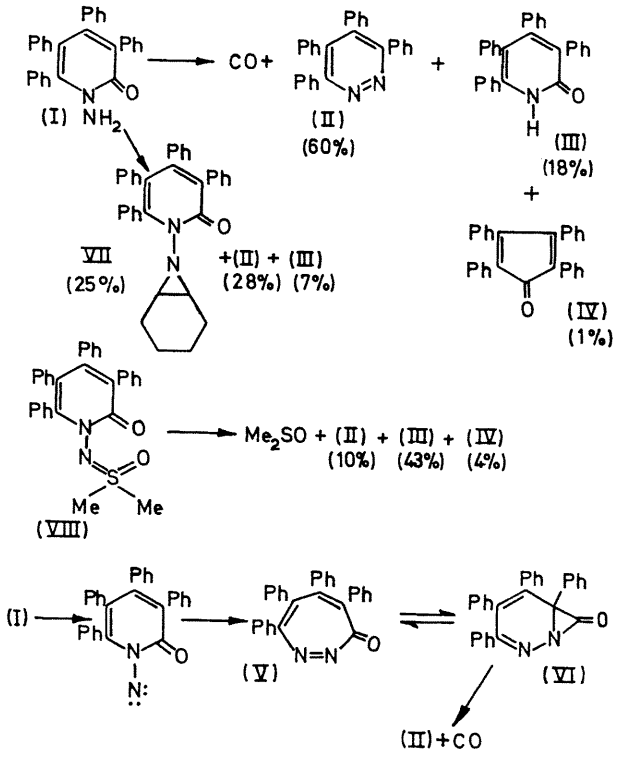
Summary Oxidation of 1-amino-3,4,5,6-tetraphenylpyrid-2(1*H*)-one (I) results in loss of carbon monoxide, rather than nitrogen, to give tetraphenylpyridazine (II); this new rearrangement is thought to involve ring expansion of the amino-nitrene, valence isomerization, and extrusion of carbon monoxide.

WHEN 1-amino-3,4,5,6-tetraphenylpyrid-2-one (I), m.p. 188° (benzylidene derivative, m.p. 205°) was oxidised with lead tetra-acetate in methylene chloride at room temperature the gas evolved was carbon monoxide rather than nitrogen. The other major product (60%) was 3,4,5,6-tetraphenylpyridazine (II); tetraphenylpyridone (III) and a trace of the tetracyclone (IV) were also formed.

Very few intramolecular rearrangements of amino-nitrenes in which the nitrogen is retained have been described; the two known to us involve rearrangement of 5- to 6-membered rings.[1] We suggest that (I) is oxidised to the nitrene which rearranges to the 7-membered diazepinone (V). Valence isomerization of this unstable α-carbonylazo-compound gives (VI) from which carbon monoxide is readily extruded to give the stable, aromatic pyridazine (II). It seems likely that concerted elimination of carbon monoxide from (VI) is thermally allowed[2] whilst that of nitrogen from (V) with formation of a new σ-bond to give (IV), is not; the latter represents only a minor pathway (*ca.* 1%).

Evidence for discrete intermediacy of the nitrene was provided by repeating the oxidation in the presence of cyclohexene; the expected nitrene adduct (VII), m.p. 220°, was formed in competition with rearrangement to (II) and (III). Furthermore, oxidation of (I) in dimethyl sulphoxide gave the sulphoximine (VIII) (*cf.* ref. 3), m.p. 248°, which on brief heating (10 min.) at 270° gave dimethyl sulphoxide and the same three products as room temperature oxidation of (I). The distribution of products was different, however, since pyridone formation was now favoured, possibly by intramolecular hydrogen transfer from the *S*-methyl groups.

The above mechanism, involving ring-expansion and valence isomerization, was supported by oxidation of 5-aminophenanthrid-6-one, m.p. 175°. This mechanism would now require disruption of the aromaticity of the fused benzene rings, and the analogous reaction product,



benzo[*c*]cinnoline, could not be detected. Benzocoumarin and phenanthridone were formed in high combined yield.

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[1] H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977; D. M. Lemal and T. W. Rave, *ibid.*, 1965, **87**, 393.

[2] R. B. Woodward, lecture on "The Conservation of Orbital Symmetry", Chemical Society Symposium, Cambridge, January, 1969.

[3] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Comm.*, 1969, 146.