Mechanism of Cyclisation of Aryliminoiminyl Radicals

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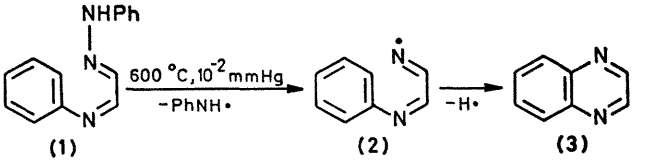
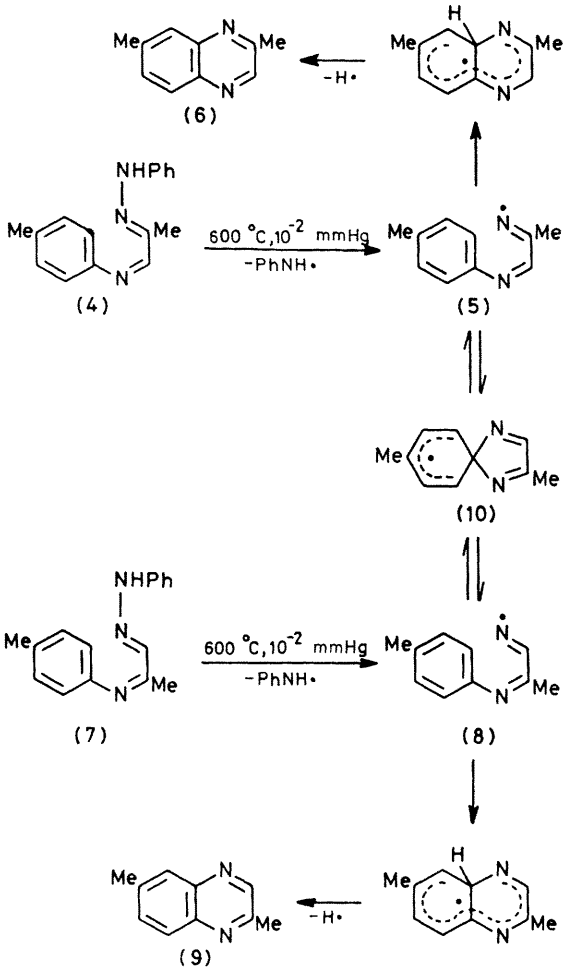
Summary The title radicals (**5**) and (**8**) cyclise to mixtures of quinoxalines (**6**) and (**9**), *via* competing pathways which involve *ipso* or *ortho* attack on the aryl ring.

WE have recently shown that pyrolysis in a flow system of 1,5-diaryl-1,2,5-triazapentadienes, *e.g.* (**1**), causes rupture of the N–N-bond to give the conjugated iminyl (**2**), which can either cyclise to quinoxaline (**3**) (35%) or decompose *via* stepwise loss of HCN to a variety of minor products.[1] This communication reports the results of further experiments which clarify the mechanism of the cyclisation step and which include the first examples of degenerate rearrangement of iminyls.



Thus, generation of the iminyl (**5**) by pyrolysis of the hydrazone (**4**)† was expected to lead exclusively to the quinoxaline (**6**) by direct cyclisation. In fact, *two* isomeric quinoxalines, (**6**) and (**9**), are formed in 73:27 ratio. Similarly, (**8**) leads to the same products in 35:65 ratio.

† All new compounds had satisfactory spectra and elemental analysis.



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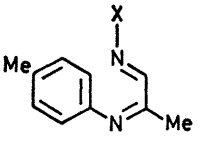
[1] H. McNab, *J. Chem. Soc., Perkin Trans.* 1, in the press.
[2] C. Jutz, *Top. Curr. Chem.*, 1978, **73**, 125.

These results suggest that the iminyls (**5**) and (**8**) can interconvert *via* the spirodienyl radical (**10**), but that this process competes with direct attack at the *ortho*-position (Scheme). If it is assumed that (**10**), once formed, has an equal probability of reverting to (**5**) or to (**8**), then the ratio of *ipso*:*ortho* attack from (**5**) is 3:5 and from (**8**) is 7:6.

The necessary control experiments have established that the reaction is strictly intramolecular and that neither the products nor the starting materials interconvert significantly under the conditions used. It has also been possible to show that the electrocyclic pathway which dominates the pyrolyses of 1-aryl-1,5-diazapentadienes[2] does not compete with the radical process under the present conditions. Thus variation of the radical leaving group X in (**11**) causes no change in the ratio of quinoxalines formed on pyrolysis at 600 °C (Table). An increased amount of (**9**) would have been anticipated from (**11**) (X = OH or NMe_2) if a concerted mechanism had been taking place.



(**11**)

TABLE. Ratio of quinoxalines (**6**):(**9**) formed by pyrolysis of (**11**) at 600 °C (10^{-2} mmHg).

X	(6):(9)
PhNH	35:65
Me_2N	33:67
HO	32:68
MeO	35:65

An authentic sample of (**6**) was kindly supplied by Dr. D. M. Smith, to whom I am also grateful for helpful discussion.

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