Anomalous Products from 1,2,5-Triaza- and 1,5-Diaza-pentadiene Thermolyses: Formation of Amidines and Pyrroles, respectively

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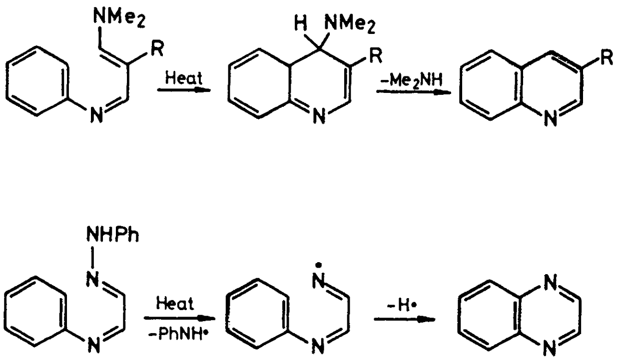
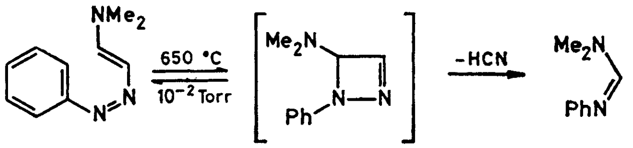
Summary Gas-phase thermolysis of the dimethylaminoazoalkene (**1**) gives the formamidine (**2**) by loss of HCN: in contrast, the related 1,5-diazapentadiene (**4**) under more forcing conditions gives aniline (30%) and *N*-methylpyrrole (43%).

THE thermal chemistry of azapentadienes is dominated by cyclisation reactions to give fused heterocycles. Jutz has shown that 3-substituted-1,5-diazapenta-1,3-dienes undergo a concerted cyclisation with elimination to give quinolines[1] while we have demonstrated that the superficially related formation of quinoxalines from 1,2,5-triazapentadienes proceeds in the gas phase *via* a conjugated iminyl radical[2,3] (Scheme 1). We now report the results of gas-phase thermolyses of related systems, in which the 1-aryl ring is not involved in the major reaction pathway.

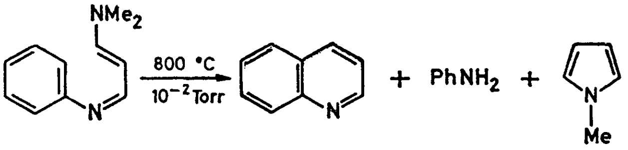


Scheme 1

Thus, when 5,5-dimethyl-1-phenyl-1,2,5-triazapentadiene[2] (1) is distilled through a silica tube at 650 °C (10^{-2} Torr), the major volatile product is not cinnoline, but *NN*-dimethyl-*N'*-phenylformamidine† (2) (41%). This is most likely to be formed by concerted ring closure to the diazetine (3) followed by loss of HCN from this species. Similar reactions have been noted for other '2-azadienes,' including nitrosoalkenes,[4] 2-azabutadienes,[5] and azoalkenes;[6] certain fused-ring diazetines are known to cleave to give nitriles on thermolysis.[7] The 2-aza-group may affect the position of the heterobutadiene–heterocyclobutene equilibrium [*e.g.* (**1**) $\rightleftharpoons$ (**3**)], but it seems more probable that the driving-force for the reaction is provided by the cleavage of the stable HCN molecule.

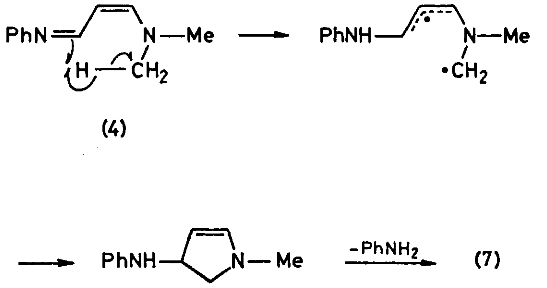


(1) (3) (2)



(4) (5) (6) (7)

As expected on this basis, thermolysis of compound (4)[8] required more vigorous conditions (800 °C at 10^{-2} Torr) and no amidines were detected in the pyrolysate. Surprisingly, quinoline (5) was present in only low yield (10%) (*cf.* Scheme 1, R = H) and the major volatile products were aniline (6) (30%) and *N*-methylpyrrole (7) (44%). This remarkable reaction, in which an *unactivated* N-methyl group becomes incorporated in the pyrrole ring as the C(2) unit, is to our knowledge unprecedented. The mechanism is unlikely to proceed *via* a concerted ($_{\sigma}2 + _{\pi}2$) hydrogen transfer in view of the *antarafacial* geometry required for the transition state. Intermolecular cleavage of a hydrogen atom from an N-methyl group is also improbable, since thermolysis of other NN-dimethyl compounds under conditions similar to ours results predominantly in loss of methyl groups instead.[9] We favour a third possible mechanism, in which an *intra*molecular hydrogen transfer to give a stabilised biradical is followed by ring closure, cleavage, and aromatisation (Scheme 2).



Scheme 2

This reaction is general to the extent that the pyrrole system is formed in the gas phase from thermolysis of a range of 1-phenyl-5,5-dialkyl- and 1,5-dialkyl-1,5-diazapentadienes. In many cases, mixtures of pyrroles are obtained; it is not clear at present whether this results from rearrangement or cleavage of groups during the course of the reaction, or from further transformations of the pyrroles themselves.[10]

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† Identified by comparison (n.m.r., m.p., mixed m.p.) of its picrate derivative with an authentic sample: H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, 1959, **92**, 837.

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