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Flash Vacuum Pyrolysis of *o*-Azidodiphenylmethanes. Nitrene Insertions with Temperature Variability

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The decomposition of *o*-azidodiphenylmethanes by flash vacuum pyrolysis (f.v.p.) (350—700 °C) gives acridan and acridine in contrast with the production of 10*H*-azepinoindole at lower temperatures in solution; similar f.v.p. treatment of 10*H*-azepinoindole gives some of the tautomeric 6*H*-azepinoindole.

We have reported[1—3] that pyrolysis of the *o*-azidodiphenylmethanes (**1**) gives predominantly the azepinoindoles (**2**) and we have suggested that these arise from singlet nitrenes by direct π-insertion. The acridans (**3**) can be formed, particularly from *o*-azidotriphenylmethanes,[3,4] and various pieces of evidence have been advanced to support the hypothesis that triplet nitrenes are intermediate in their formation. We have now subjected compound (**1**; R = H) to flash vacuum pyrolysis (f.v.p.) and find that the products are mixtures of acridan (**3**; R = H) and acridine (**4**) in proportions varying with temperature (Table 1). Since the accepted view[5] is that singlet nitrene products are favoured by higher temperature we cannot maintain the 'triplet nitrene → acridan' hypothesis. It seemed possible that the higher temperatures were causing isomerisation of the azepinoindole (**2**; R = H) to acridan (**3**; R = H). Passage of a sample of the azepinoindole through the f.v.p. apparatus at 500 °C gave a mixture containing starting material with its tautomer (**5**) in a ratio of 2:1 (unchanged by a further passage through the apparatus). The tautomer (**5**) was separated and fully characterised (the ^{1}H n.m.r. shifts, δ, for each hydrogen are given with the structural formula). We therefore suggest the mechanism in Scheme 1 for the nitrene insertion reaction. Singlet nitrene inserts into the adjacent benzene ring to give an azanorcaradiene. This can be cleaved to give the diradicals (**6**) or (**7**), of which the diradical (**6**) is the more easily formed, the two radical centres being stabilized both by the neighbouring nitrogen atom and by a double bond. An alternative ring opening of bond (a) could give the azomethine ylide (**8**). At lower temperatures (*ca.* 190 °C in solution) this route is preferred, giving the

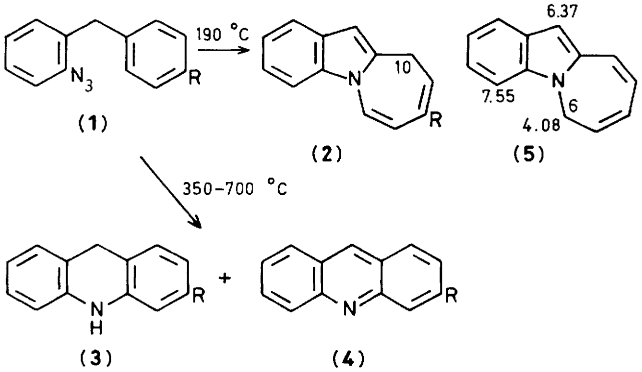
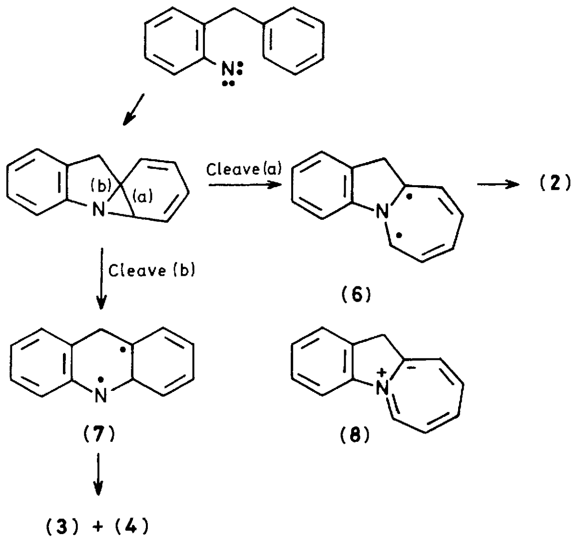


Table 1. F.v.p. products from *o*-azidodiphenylmethane.

Temp./°C	Crude yield (%)	(3) (%)	(4) (%)
350	>95	90	10
500	60[a]	66	33
700	>95	5	95

[a] Yield not optimized.



Scheme 1

azepinoindole. At higher temperatures the reaction proceeds *via* the less favourable diradical (**7**) producing the acridan (**3**) which has more resonance stabilisation than the azepinoindole (**2**).

We feel that the observed formation by f.v.p. of a less stable tautomer (**5**) from that normally obtained may be of general interest.

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