

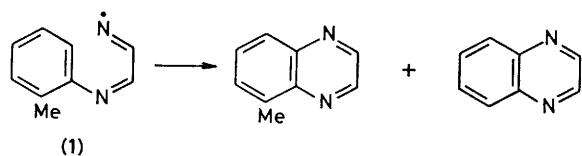
Effect of Blocked *ortho*-Positions on the Cyclisation of Aryl-1,4-diazabuta-1,3-dienyl Radicals

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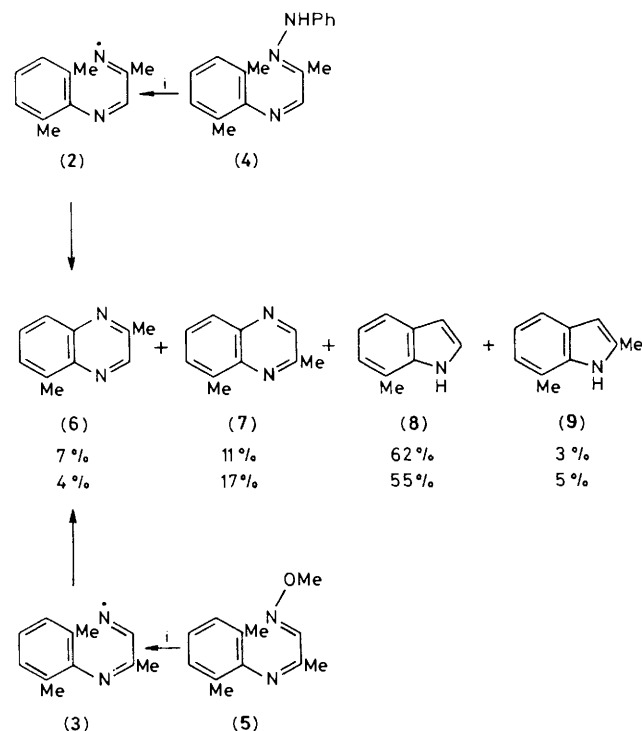
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Indoles are the main products from the cyclisation of (2,6-dimethylphenyl)-1,4-diazabuta-1,3-dienyl radicals, together with small amounts of quinoxalines; both ring systems arise predominantly *via* an intermediate spirodienyl radical.

We have shown that aryl-1,4-diazabuta-1,3-dienyl radicals cyclise to give quinoxalines.^{1,2} Since two quinoxalines are formed from the *o*-tolyl compound (1) (Scheme 1), owing to



Scheme 1

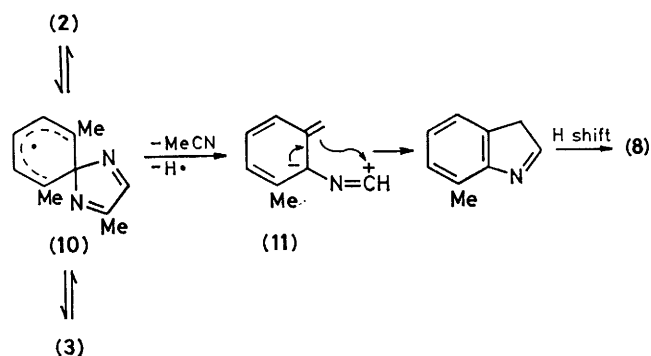


Scheme 2. i, 650 °C, 10⁻² Torr. Yields below structures (6)–(9) are from (4) (top) and (5) (bottom).

competitive ejection of the hydrogen atom and the methyl group,³ we expected that the presence of two *ortho*-substituents should lead to an efficient synthesis of 5-substituted quinoxalines.

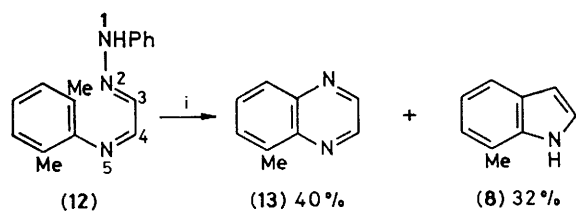
Generation of the isomeric iminyls (2) and (3) by gas-phase pyrolysis of the hydrazone† (4) and the oxime ether (5) respectively, leads to only small quantities of quinoxalines, and the major product is instead 7-methylindole (8) (Scheme 2). This requires formal loss of MeCN and a hydrogen atom from the iminyls, a reaction which can only occur from (3) following a rearrangement reaction. A similar rearrangement is required to explain the small amount of 2,7-dimethylindole (9) obtained from (2). Indeed the overall similarity in product distribution from both precursors is best explained by the involvement of the common symmetrical intermediate (10); we have previously invoked similar spirodienyl radicals to account for partial rearrangements in iminyls.³

The spirodienyl (10) can give the quinoxalines (6) and (7), as before,^{1,2} by C–N migration and loss of a methyl group. The indole (8) can arise *via* the nitrile ylide (11) formed by preferential loss of MeCN from the spirodienyl (10) (Scheme 3), while the trace of 2,7-dimethylindole (9) can arise by a



Scheme 3

† All new compounds gave satisfactory spectra and elemental analyses.

Scheme 4. i, 650 °C, 10⁻² Torr.

similar mechanism after loss of HCN. It is possible that this unprecedented selectivity of at least 10:1 in the cleavage of the nitrile function may be due to steric factors.

As expected on this basis, quinoxaline formation is relatively favoured from (12), where formation of the indole requires the loss of HCN from the iminyl (Scheme 4). We have also established the extent of involvement of the spirodienyl

in this reaction, by the use of the precursor (12) specifically labelled with ¹⁵N at N(2). The ¹⁵N n.m.r. spectrum of the crude pyrolysate shows peaks at -51 and -54 p.p.m. (relative to external nitromethane) of relative intensity 10:8.5. These were assigned as N(1) and N(4) respectively of the quinoxaline (13) by comparison with the spectrum of authentic [1-¹⁵N]-5-methylquinoxaline. The results are consistent with a mechanism involving the spirodienyl to the extent of at least 92%.

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