Ring Contraction in Heterocyclic Nitrenes

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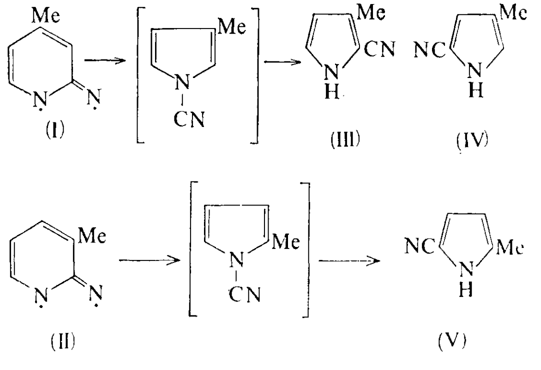
PHENYL azides[1,2] and triazoloarenes[3] eliminate molecular nitrogen on gas-phase pyrolysis to give aryl nitrenes and 1,3-biradicals respectively, which subsequently undergo ring contraction to give cyclopentadienecarbonitriles. Extension of these reactions into the heterocyclic field has established the generality of the reaction, and shed further light on the mechanism operating in the case of the triazoles.

Triazolo[4,5-*b*]pyridine and triazolo[4,5-*c*]pyridine are pyrolysed quantitatively at 500° to give pyrrole-2- and -3-carbonitrile respectively. As with the carbocyclic analogues, these products interconvert at elevated temperatures. The third isomer in this series, tetrazolo[1,5-*a*]pyridine gives pyrrole-2-carbonitrile *via* the unstable pyrrole-1-carbonitrile. Thus, the 7- and 8-methyl derivatives, which give rise to the intermediate 1,3-biradicals (I) and (II) break down, as shown, to give the products (III)—(V) which are stable under the reaction conditions. Other products formed are 2-aminopyridine (yield decreased by higher temperature) and glutacononitrile (yield increased by higher temperature), the former arises from H-capture and the latter from ring cleavage. The nitrene formed from 4-azidopyridine behaves exactly as phenyl azide,[1,2] to give 4,4′-azopyridine or a mixture of pyrrole-2- and -3-carbonitrile, pyridine, and pyridine-4-carbonitrile.



In the pyrimidine series similar reactions are encountered. Tetrazolo[1,5-*a*]pyrimidines give pyrazole-1-carbonitriles and 2-aminopyrimidines *via* the azido-form (the stable form of the tetrazolo[1,5-*a*]pyrimidines at higher temperature†). Tetrazolo[1,5-*c*]pyrimidines give a quantitative yield of imidazole-1-carbonitriles, and it is presumed that this is a concerted reaction, since some of the

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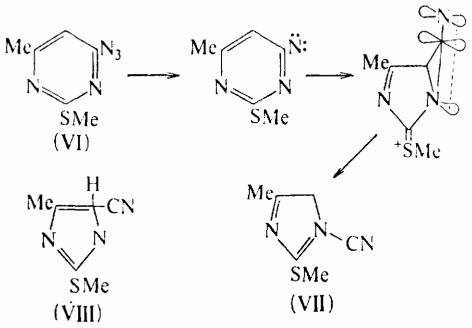
† The azide band in the i.r. spectrum shows a marked increase in intensity even with small (10°) increases in temperature.

4-azidopyrimidines are stable, and give lower yields, *via* the nitrene. The presence of methoxy-groups does not prevent reaction and 4-azido-2,6-dimethoxypyrimidine gives a 12% yield of 2,4-dimethoxyimidazole-1-carbonitrile. With 4-azido-6-methyl-2-methylthiopyrimidine (VI) the reaction is easier and 88% of 4-methyl-2-methylthioimidazole-1-carbonitrile (VII) is obtained; a 75% yield is obtained merely on injection onto a gas chromatography block at 200°.

That all the nitrenes and biradicals in this series give rise to *N*-cyano-compounds is consistent with ring contraction of the singlet nitrene through the bicyclic intermediate postulated previously.[2,3] Such a transition state arising from (VI) would be greatly stabilised by the sulphur atom, and orbital overlap with the bridgehead nitrogen would require collapse to (VII) rather than (VIII). Similarly, with the benzotriazoles, the cyano-group always appears on the carbon atom which carried the other radical site (*i.e.* the 3a-position), and it seems logical to assume that this is for similar reasons. The extension of this concept to the formation of pyrrole-1-carbonitriles from (I) follows.



Product analysis was by g.l.c. and identification was by spectroscopic comparison with samples prepared by alternative routes. The pyrolysis technique has been described previously.[1,4]

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[1] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, **1967**, 4379.
[2] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, **1968** to be published.
[3] W. D. Crow and C. Wentrup, *Chem. Comm.*, **1968**, 1026.
[4] W. D. Crow and R. K. Solly, *Austral. J. Chem.*, **1966**, 2119.