Decomposition of 2-Pyridyldiazomethane 1-Oxides

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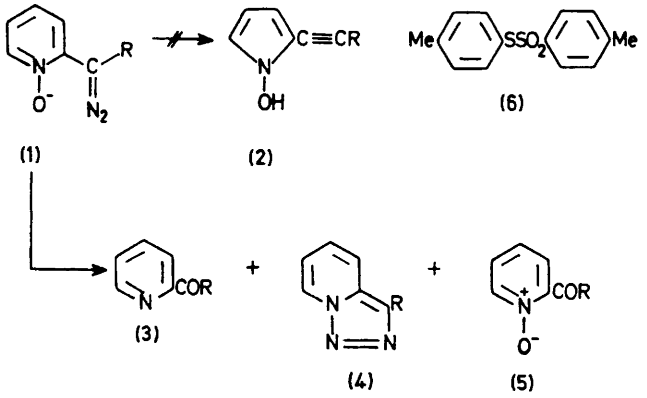
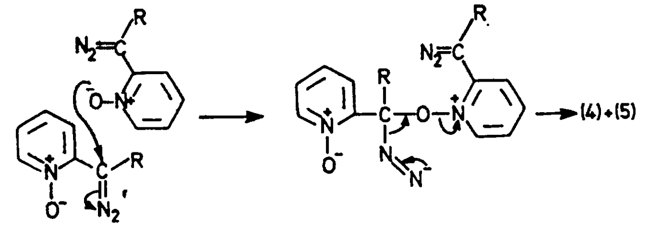
Summary On decomposition, 2-pyridyldiazomethane 1-oxides give 2-acylpyridines, usually in high yields, but no ring-contraction nor carbene-derived products; various mechanisms are considered.

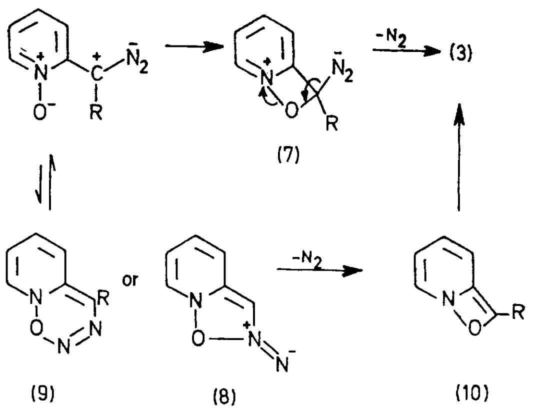
WE have recently shown that 2-azidopyridine 1-oxides[1] and related compounds[2] undergo ring contraction on thermolysis to give 2-cyano-1-hydroxypyrroles *via* a ring-opening and recyclisation process. Further, pyrolysis of 2-diazomethylfuran derivatives gives the corresponding ring-opened keto-acetylenes.[3] It was of interest, therefore, to see whether or not the corresponding 2-pyridyldiazomethane 1-oxides (**1**) would undergo similar ring-opening and recyclisation and thus lead to the corresponding acetylene derivatives (**2**).



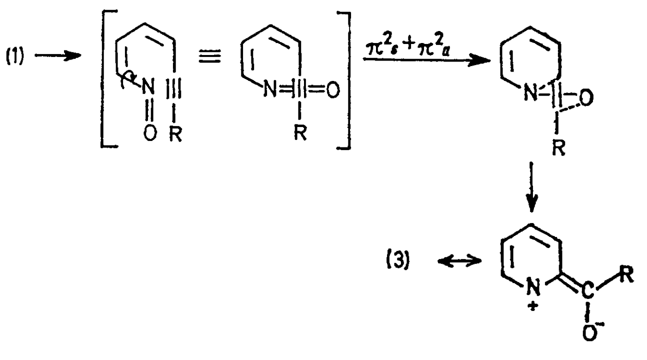
Unexpectedly, decomposition of the diazomethanes (**1**) under a wide variety of conditions gave mainly the 2-acylpyridine (**3**), often in near quantitative yield. Thus, thermolysis of (**1**; R = Ph) in benzene, MeOH, HCONMe$_2$, cyclohexane, or cyclohexene, photolysis in benzene or MeOH, and flash-vacuum pyrolysis gave (**3**) exclusively. Pyrolysis of (**1**; R = H) (from the tosylhydrazone salt) gave 11—28% yields of (**3**) together with (**6**) (6—8%). In some cases (R = Ph copper-catalysed decomposition, or R = Me uncatalysed and copper-catalysed decomposition) the pyridotriazole (**4**), and the 2-acylpyridine 1-oxide (**5**) were also isolated, but in no case was any acetylene (**2**) or its open-chain precursor obtained, nor could any be trapped with nucleophilic solvents (*cf.* ref. 1). In the hope of facilitating such trapping (**1**; R = *p*-NO$_2$C$_6$H$_4$) was also decomposed but it gave only (**3**) (100%).



SCHEME 1



No evidence for the formation of a free carbene intermediate was found. Indeed, the absence of any detectable hydrogen-migration products in the decomposition of (**1**; R = Me) or of trapping products (in cyclohexene) speak against the intervention of a free carbene in the thermal reactions. The formation of (**4**) and (**5**) in some cases and particularly the influence of copper powder suggests that these arise by a bimolecular process (Scheme 1). Formation of (**3**) in high yields and under such a variety of conditions by the corresponding four (or eight)-centre process appears highly unlikely and is eliminated by flash-vacuum pyrolysis experiments.†



SCHEME 2

There are a number of alternative mechanisms for the formation of (**3**). The first involves intramolecular nucleophilic attack by oxygen at the α-carbon to give the strained intermediate (**7**). Alternatively, cheletropic elimination of nitrogen from (**8**) would lead to (**10**).‡ A more likely

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† These also eliminate the possible formation of (**3**) by the intrusion of water into the system.

‡ The four-membered ring in (**10**) could have some resonance stabilization, being a 6π system.

process involves elimination of N_2 $[_\pi2_a + _\sigma2_s]$ from (**9**). A carbene may still be the reactive intermediate, particularly in the photochemical decompositions. It still remains to be answered why the corresponding azides[1,2] and furans undergo ring-opening while (**1**) does not. One hypothesis is that it does, but that the ring-opened product undergoes a novel $[_\pi2_s + _\pi2_a]$ addition to give (**3**) (Scheme 2). This would be analogous to the addition of ketens to ethylenes and to the cyclisation of *cis,cis*-octa-3,5-diene-1,7-diyne to benzocyclobutadiene,[4] and would account for the high yields of (**3**) and the smoothness of the reaction. To prevent such a cycloaddition the decomposition of (**1**; R = Bu^t) was examined in the hope that the bulky t-butyl group would sterically hinder the addition.§ Only (**3**; R = Bu^t) (75%) was obtained, however,[5] and no methyl migration was observed.

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[1] R. A. Abramovitch and B. W. Cue, Jr., *J. Org. Chem.*, 1973, **38**, 173; *Heterocycles*, 1974, **2**, 297.
[2] R. A. Abramovitch and B. W. Cue, Jr., *Heterocycles*, 1973, **1**, 227.
[3] R. V. Hoffman and H. Schechter, *J. Amer. Chem. Soc.*, 1971, **93**, 5940.
[4] G. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, 1969, **91**, 7520.
[5] A t-butyl group does not hinder the addition of t-butylcyanoketen to allene (H. A. Bampfield and P. R. Brook, *J.C.S. Chem. Comm.* 1974, 171) so that formation of (**3**) here does not necessarily preclude the intermediacy of an open-chain nitroso-acetylene.