Tetrahedron Letters,Vol.23,No.1,pp 121-124,1982
Printed in Great Britain

0040-4039/82/010121-04$03.00/0

CONVERSION OF 3-AZIDO-5-PHENYL-1,2,4-OXADIAZOLE INTO BENZOYL CYANIDE; A NEW THERMAL FRAGMENTATION

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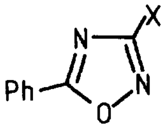
SUMMARY: Flash vacuum pyrolysis of 3-azido-5-phenyl-1,2,4-oxadiazole (1a) gives benzoyl cyanide for which a mechanism involving the formation and fragmentation of N-benzoylpentaazafulvene (3) is proposed.

Interest in the chemistry of azidoazoles has focussed primarily on their participation in azidoazomethine-tetrazole tautomerism[1] and on their thermal ring cleavage reactions[2]. On pyrolysis, β-azido five-membered heterocyclic rings generally suffer fragmentation into two units containing two and three of the original ring atoms, a process which could proceed directly from the azide or from derived nitrene[3]. We now report the synthesis of a new heterocyclic azide whose pyrolytic fragmentation proceeds from the tetrazole tautomer and results in an alternative distribution (4 + 1) of the ring atoms between the two fragments.

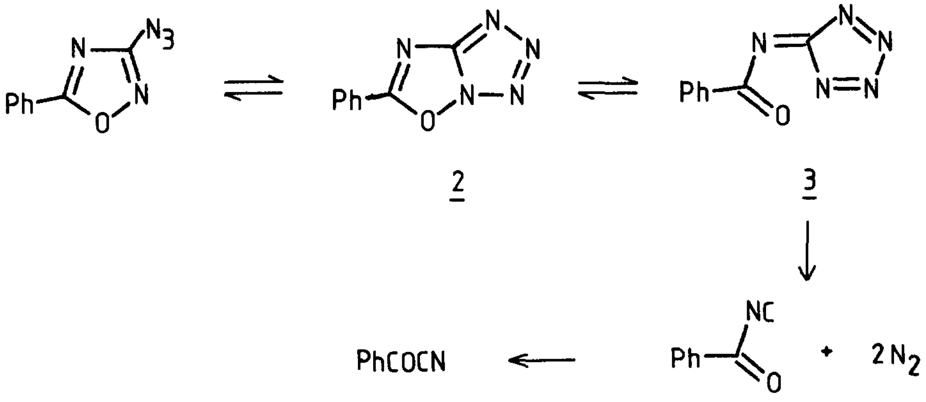
Attempts to effect displacement of bromide from 3-bromo-5-phenyl-1,2,4-oxadiazole (1b)[4] using NaN_3 (aqueous dimethylformamide, 100°, 1 h, or with sodium iodide, 50°, 72 h), LiN_3[5] (boiling methanol, 48 h), or $Bu^n_4\overset{+}{N}N_3^-$[6] (boiling acetonitrile, 24 h) all led to a quantitative recovery of the bromide (1b). However, the azide (1a) could be obtained (50%) by heating the bromide (1b) with KN_3 and 18-crown-6, or with LiN_3, in anhydrous dimethylformamide (90°, 72 h and 45 h respectively), as colourless needles, m.p. 66-68° ($EtOH-H_2O$)[7]. In the solid state (KBr) and in solution ($CHCl_3$), the product (1a) showed a strong ir band at 2140 cm^{-1}, indicative of the azide tautomer; ^{13}C nmr spectroscopy ($CDCl_3$) showed that the compound existed predominantly as one tautomer.

Flash vacuum pyrolysis (FVP) of the azide (1a) at $550^\circ/7.5 \times 10^{-2}$ torr gave benzoyl cyanide (70%) identified by comparison of its m.p. and spectroscopic properties with those of a specimen prepared by reaction of benzoyl chloride with sodium cyanide under phase transfer conditions[8].



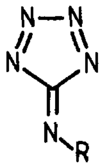
1 a X = N_3
b X = Br

This transformation can be explained (Scheme) by conversion of the azide into its tetrazole tautomer (2) and thence to the pentaazafulvene (3) by N-O bond cleavage. Loss of nitrogen from (3) by a [2 + 2 + 2] cycloreversion gives benzoyl isocyanide which rearranges to the product. Isocyanides have been shown to isomerise to cyanides readily under FVP conditions[9].



Scheme

Support for the suggested mechanism is provided by the spontaneous fragmentation in solution of the pentaazafulvenes (4)[10] and (5)[11] to give simple isocyanides and *N*-isocyanoimines, respectively. Compounds (4) and (5) were generated by oxidation of the appropriate 5-amino and 5-hydrazono-tetrazoles. Although none of these pentaazafulvenes have been isolated, this pattern of their formation and rapid fragmentation seems very reasonable. Another analogy for the above formation of benzoyl cyanide is provided by the proposed thermal decomposition of tetraazafulvenes (6) to acetylenes, R-C≡C-R [12].



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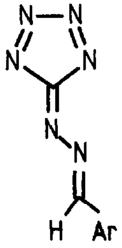

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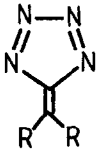

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We thank Smith Kline and French, Welwyn Garden City, for generous support.

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(Received in UK 26 October 1981)