N–N Bond Fission and Ring Opening in *s*-Triazolo[3,4-*a*]phthalazines

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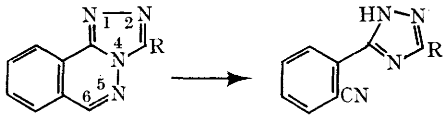
N–N and N–O bond fission with subsequent formation of cyano-compounds have been observed with various aliphatic systems containing such an arrangement of nitrogen and oxygen atoms, as well as in their heterocyclic analogues.[1] Base-catalyzed fission of the N–N bond, and also of the N–O bond, follows readily the initial removal of a β-proton in various aldehyde hydrazones and aldoximes, in isoxazoles, pyrazoles and pyrazolines,[2] as well as indazoles[3] and 1,2,3-triazoles.[4] Our experiences with a similar N–N bond fission in the tricyclic *s*-triazolo[3,4-*a*]phthalazine system are thus of particular interest.

Treatment of *s*-triazolo[3,4-*a*]phthalazine (I; R = H) and its 3-methyl derivatives (I; R = Me) in boiling ethanol with a catalytic amount of potassium hydroxide overnight gave 3-*o*-cyanophenyl-*s*-triazole (II; R = H) and its 5-methyl derivative (II; R = Me) in 75% and 60% yield, respectively. The structure of (II) follows readily from its spectral characteristics and analytical data.† Thus, for (II; R = H), m.p. 195°, infrared absorptions at 3240 and 2210 cm.$^{-1}$ show the presence of the imino- and cyano-groups and the u.v. absorption [λ_{max} (MeOH) 194, 230, 262 mμ; log ϵ 4·56, 4·15, 3·86] establishes the presence of the same chromophoric system which is present in 3-phenyl-*s*-triazole [λ_{max} (MeOH) 202, 242 mμ; log ϵ 5·30, 4·15]. Mass spectral fragmentation peaks [*m/e* (rel. abundance) 170 (M^+) (100), 143(10), 142(68), 129(68), 102(84), 88(68), 76(25)] are consistent with the above structural assignment. Additional support for structure (II; R = H) was obtained by alkaline hydrogen peroxide hydrolysis to the corresponding amide (ν_{NH} 3360, ν_{CO} 1690 cm.$^{-1}$). Similarly, for (II; R = Me), m.p. 216°, infrared absorptions (ν_{NH} 3275, ν_{CN} 2210 cm.$^{-1}$) and ultraviolet absorption [λ_{max} (MeOH) 213, 247, 290 mμ; log ϵ 4·82, 4·36, 3·84], together with the mass spectral fragmentation pattern [*m/e* (rel. abundance) 184(M^+) (100), 129(39), 102(38), 88(64), 76(15)], are consistent with the assigned structure.



(I) (II)

This ring opening is clearly analogous to those described above and is dependent on the presence of a hydrogen at position 6 of (I). This was shown by the stability of (I) to these reaction conditions when a phenyl substituent was introduced into the 6-position. There are two possible N–N bond fissions which can occur in this ring system. It is interesting to note that it is the N–N bond in the six-membered ring which undergoes fission and, apparently, the better leaving group characteristics of the *s*-triazole nucleus and product stability control the course of the reaction. A variety of aqueous alkaline conditions effect the isomerization of (I) to (II). However, we have not been able to bring about the reverse ring closure reaction.

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† Satisfactory analytical data were obtained for all products described.

[1] A useful compilation of references on this topic can be found in: Yu A. Naumov and I. I. Grandberb, *Russ. Chem. Rev.*, 1966, **35**, 9.

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