

Chemical and X-Ray Crystallographic Study of Meso-ionic Derivatives of *s*-Triazolo[4,3-*a*]pyridine

By R. J. GROUT, T. J. KING, and M. W. PARTRIDGE*

(University of Nottingham, Nottingham NG7 2RD)

Summary The rearrangement product of the toluene-*p*-sulphonyl ester of *N*-hydroxy-*N'**N''*-diphenylguanidine reacts with pyridine or γ -picoline to give anhydro-1-phenyl-3-phenylimino-*s*-triazolo[4,3-*a*]pyridinium hydroxide or its 7-methyl derivative; the structure of the 7-methyl derivative has been unambiguously assigned by X-ray analysis and chemical considerations.

WE report a novel reaction of pyridine and γ -picoline leading to meso-ionic derivatives of *s*-triazolo[4,3-*a*]pyridine. Thus, *N*-hydroxy-*N'**N''*-diphenylguanidine (1), on reaction with toluene-*p*-sulphonyl chloride and γ -picoline in benzene at 0° overnight and then at room temperature for 24 h, furnished the colourless toluene-*p*-sulphonate (3), m.p.

252—254°. This salt with alkali gave a red anhydro-*s*-triazolo[4,3-*a*]pyridinium hydroxide (4), m.p. 222—223°.

The mass spectrum and elemental analysis of the anhydro-hydroxide (4) were consistent with the molecular formula, C₁₉H₁₆N₄. Its i.r. spectrum showed strong absorptions at 1640, 1580, 1450, and 1150 cm⁻¹, in agreement with main bands in 1-methyl-*s*-triazolo[4,3-*a*]pyridinium iodide¹ and, as with its n.m.r. spectrum, the absence of NH absorption; its u.v. spectrum showed bands at 256 (log ϵ 4.26), 291 (4.24), 340 (3.70), and 432 (3.01) n.m.

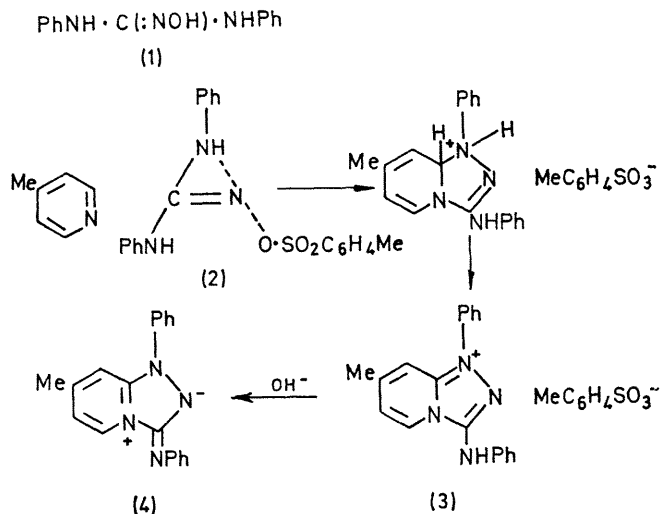
The anhydro-compound was monoclinic, space group *P*2₁/*c* with $a = 7.35(3)$, $b = 10.88(3)$, $c = 19.53(4)$ Å, $\beta = 104^{\circ}30' \pm 8'$, $U = 1512$ Å³, $D_m = 1.319$, $Z = 4$, $D_c = 1.328$.

The intensities of 4505 reflections were measured on a Hilger-Watts linear diffractometer using Mo- K_{α} radiation for the layers $0kl-8kl$, E values were calculated for the reflections, and the phases of 327 of the reflections with the largest E values were estimated by symbolic addition, using the program developed by Dr. F. Ahmed and his colleagues of the N.R.C., Ottawa. The E -map plotted using these phases revealed the skeleton of the molecule. Block-diagonal least-squares refinement was carried out using the 1877 reflections deemed to be 'observed'. After 4 cycles, the R value was 13% and the bond lengths and bond angles were all close to the usual values. The phenyl rings are rotated out of the plane of the rest of the molecule by about 15° . The X -ray measurements do not at this stage enable distinction to be made between carbon and nitrogen, but chemical and mechanistic considerations lead unambiguously to the assignment shown in (4). Refinement is continuing.

Only a rearrangement of the tosyl ester of the hydroxyguanidine (2) could lead to the transformation, $\text{PhN}\cdot\text{C}(=\text{N})\text{NPh} \longrightarrow \text{PhN}\cdot\text{N}=\text{C}\cdot\text{NPh}$, required for the assigned structure (4); an analogous rearrangement has been observed² in sulphate esters of hydroxyguanidine and its alkyl derivatives. Dimroth rearrangements have been described¹ in *s*-triazolo[4,3-*a*]pyridines; such a rearrangement of any mechanistically feasible product of interaction of the tosyl ester of the hydroxyguanidine (2) and γ -picoline could not yield the anhydro-hydroxide (4).

When pyridine was substituted for γ -picoline, the red

anhydro-hydroxide ($\text{C}_{18}\text{H}_{14}\text{N}_4$), m.p. $204-205^{\circ}$, (colourless toluene-*p*-sulphonate, m.p. $228-229^{\circ}$), of similar u.v., i.r.,



n.m.r., and mass spectroscopic properties, was obtained. Notable in the mass spectrum of each anhydro-compound was the appearance of a first fragmentation peak at $M - 117$ ($\text{PhN}-\text{C}-\text{N}$).

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¹ K. T. Potts, H. R. Burton, and S. K. Roy, *J. Org. Chem.*, 1966, **31**, 265.

² A. Heising, G. Imsieke, G. Maleck, R. Peppmüller, and H. Schulze, *Chem. Ber.*, 1970, **103**, 529.