

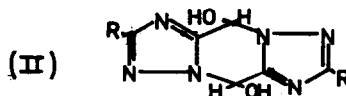
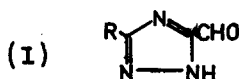
N-UNSUBSTITUTED-1,2,4-TRIAZOLE-3-ALDEHYDES

E.J. Browne

University of Tasmania, Hobart, Australia

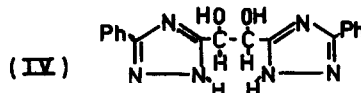
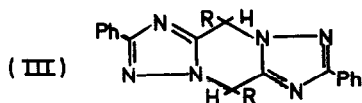
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No N-unsubstituted-1,2,4-triazole-3-aldehyde (I) has been described, although derivatives are known.¹ The NH group would be expected to modify the normal carbonyl properties shown by the N-substituted analogues,² as has been observed for the 1,2,4-triazolyl ketones.³



5-Aryl-1,2,4-triazole-3-aldehydes have been prepared by four routes, and the solid products have been found to exist essentially as semiaminals (II). Infrared spectra (nujol mulls) showed no carbonyl bands, and were consistent with the dimeric formulation. (II) were insoluble powders, melting with decomposition above 200°. Their properties resemble those of benzimidazole-2-aldehyde, for which a similar structure has been proposed.⁴ (IIa; R = Ph) was converted to the aminals (III; R = morpholino, piperidino) by reaction with the secondary bases.

Oxidation of 5-aryl-3-hydroxymethyl-1,2,4-triazoles^{5,6} with manganese dioxide⁷ in DMSO at 20° for 5 to 10 days produced the aldehydes (I) in solution, and DNP derivatives could be rapidly precipitated in yields of 20-80%. Infrared spectra on these concentrated DMSO solutions each showed a strong carbonyl band in the range 1678-1690 cm⁻¹, and a strong C=N band near 1600 cm⁻¹. These two bands appear to arise from complexed forms of (I). In the cases of (I; R = Ph, p-tolyl, p-chlorophenyl, p-nitrophenyl, 3- or 4-pyridyl) an additional weaker band was present near 1710 cm⁻¹, corresponding to the free aldehyde. Removal of the solvent precipitated (II) as powders difficult to free from Mn. (II) could be slowly converted to the normal DNP derivatives. In the case of (I; R = 2 pyridyl) the product m.p. >370° seemed a complex of (I) with Mn, and no (II) was detected. (IIa) was also formed, in low yield, by the oxidation of the alcohol⁵ with selenium dioxide in aqueous dioxan.



(IV) prepared in 15% yield from methyl benziminoate and tartaric acid dihydrazide, was smoothly oxidised to (IIa) with sodium metaperiodate in N sulphuric acid. This method gave

the best quality product. Hydrolysis of the dimethyl acetals of (I)¹ with N sulphuric acid, followed by neutralisation of the solution, gave (II; R = Ph, p-tolyl, p-chlorophenyl, 4-pyridyl).

The infrared spectra of (II) in hot DMSO solution, in contrast to those determined in nujol, each had a C=O band at 1710 to 1712 cm^{-1} , ascribable to the presence of (I). Removal of the solvent regenerated (II). The mass spectra of (IIa) at temperatures from 50 to 200° gave an apparent molecular ion of 173, corresponding to the aldehyde (I; R = Ph). Other assignments were consistent with this structure, and no peaks of mass number >174 were detected. The dimer (II) may thus be reconverted to the monomer (I) under suitable conditions; and (II) could be reformed from (I) on reversion to the solid state.

The conclusions regarding reversible dimerisation, which might involve structures derived from tautomers of (I), are supported by n.m.r. evidence. Further work is required to interpret the double signal at 2.69/2.82 derived from the CH protons on the central ring of (IIa); and which might be of physical, structural or configurational origin.

The ¹Hn.m.r. spectrum (CH protons; Ext. TMS; τ values) of (IIa) in DMSO-d₆ at 20° was -0.26 (~0.6H,s), 1.5-1.75(4H), 2.05-2.3(6H), 2.69 (~0.7H,s), 2.82 (~0.7H,s). At 100° this changed to the spectrum of the aldehyde (I; R = Ph) viz. -0.28 (1H,s), 1.45-1.7(2H), 2.0-2.25(3H). The analogous spectrum derived from (II; R = p-tolyl) at 100° had peaks at -0.36 (1H,s), 1.67(2H,d), 2.27(2H,d) and 7.2(3H,s); these values were substantially unchanged on cooling to 50°. The spectrum of (II; R = p-chlorophenyl) at 110° also showed only the aldehyde form, while peaks ascribable to both (I) and (II) were present at 20°. The n.m.r. spectrum of (II; R = 4-pyridyl) at 85° had peaks at -0.34 (~1.2H,s), 0.91(4H,d), 1.69(4H,d), 2.58 (~0.4H,s) and 2.72 (~0.4H,s). The proportion of aldehyde CH increased with temperature, but singlets arising from both species (I) and (II) were still present at 100°. On cooling and dilution with water (II) could be recovered apparently unchanged from these solutions.

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