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THE STABILITY OF 4-AMINO-1,2,3-TRIAZOLE

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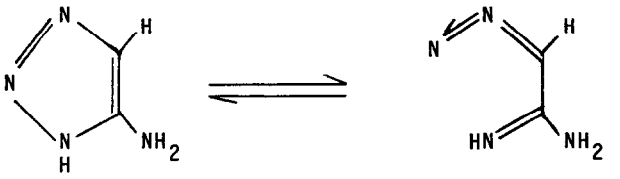
Although 4-amino-1,2,3-triazole is well known[1] as the hydrochloride, its free base has never been examined, apparently because it was thought to be, like some 5-substituted 4-diethylamino-1,2,3-triazoles,[2] subject to ring-chain tautomerism (1 $\rightleftharpoons$ 2).



1 2

In the present work, the free base (1) was obtained by the following modification of Hoover and Day's method[1a] for preparing the hydrochloride. After addition of a slight excess of sodium to 4-amino-3-benzyl-1,2,3-triazole, stirred in liquid ammonia, the mixture was allowed to evaporate at room temperature and then dried *in vacuo*. The residue, in water, was clarified by filtration. The filtrate, after neutralisation with 1N-hydrochloric acid, was taken to dryness *in vacuo* and the residue extracted with hot ethyl acetate. After evaporation of the solvent, recrystallization from ethyl acetate gave 4-amino-1,2,3-triazole, m.p. 74-75° (Found: C, 28.8; H, 4.6; N, 66.6. $C_2H_4N_4$ requires C, 28.6; H, 4.8; N, 66.6%).

Neither free base nor hydrochloride of 4-amino-1,2,3-triazole absorbed in the 2100 cm^{-1} region typical of a diazo-group[2a,3] (examined in water and in a Nujol mull). This result indicated that there was no significant proportion of diazoacetamidine (2) in equilibrium with 4-amino-1,2,3-triazole (1). The n.m.r. spectrum in various solvents supported this conclusion. Thus, in D_6DMSO, D_2O, D_5Pyridine, or 1N-NaOD, a sharp singlet peak in the range τ2.62-3.02 was observed; but there was no peak around τ4, the value expected for a proton attached to the carbon bearing a diazo-group.[3] The n.m.r. spectra of the hydrochloride in D_2O or D_6DMSO (or of the free base in DCl or CF_3CO_2H) showed a sharp singlet in the range τ1.79-2.31, namely a downfield shift of a magnitude characteristic of protonation on a 1,2,3-triazole ring-nitrogen atom.[4] 4-Amino-1,2,3-triazole was found not to be affected by boiling with 1N-hydrochloric acid or 1N-sodium hydroxide.

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