Diazoalkylideneamine–1,2,3-Triazole Tautomerism in 1,2,3-Triazolo[1,5-*a*]-pyrimidines at Elevated Temperatures

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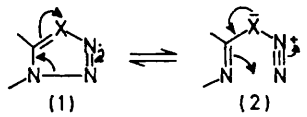
Summary Simple examples of diazoalkylideneamine–1,2,3-triazole equilibria have been demonstrated for the first time in a fused system by variable temperature ^{1}H n.m.r. studies of a series of 1,2,3-triazolo[1,5-*a*]pyrimidines.

DIAZOALKYLIDENEAMINE–1,2,3-triazole tautomerism [(**2a**) ⇌ (**1a**)] is now well known[1] in certain monocyclic 1,2,3-triazoles, but unlike azide–tetrazole tautomerism [(**2b**) ⇌ (**1b**)][2], clear-cut examples[3] have yet to be reported for fused 1,2,3-triazoles. Variable temperature ^{1}H n.m.r. studies have now demonstrated the occurrence of the ring–chain tautomerism [(**1a**) ⇌ (**2a**)] in a series of 1,2,3-triazolo[1,5-*a*]-pyrimidines† at elevated temperatures.

The triazolopyrimidines (**3a**—**d**) and the isomer mixtures [70% (**6a**): 30% (**8a**)], [75% (**6b**): 25% (**8b**)], [85% (**6c**): 15% (**8c**)], and [80% (**6d**): 20% (**8d**)] studied‡ were available by an established method,[3,4] and in all cases lacked i.r. diazo-absorption at *ca.* 2200 cm^{-1} demonstrating that at room



(1) (2)

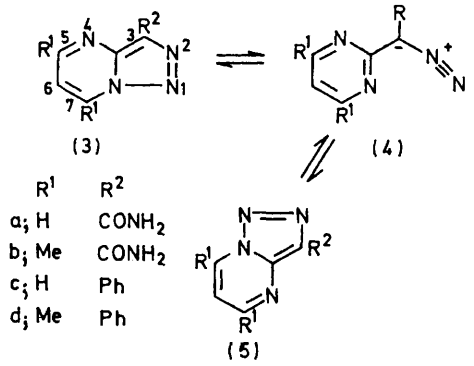
X
a; CR
b; N

temperature they exist entirely in the fused triazole form. At room temperature, the ^{1}H n.m.r. spectrum of the unsubstituted amide (**3a**) exhibited a trio of double doublets

† Satisfactory analyses and spectral data were obtained for all new compounds.

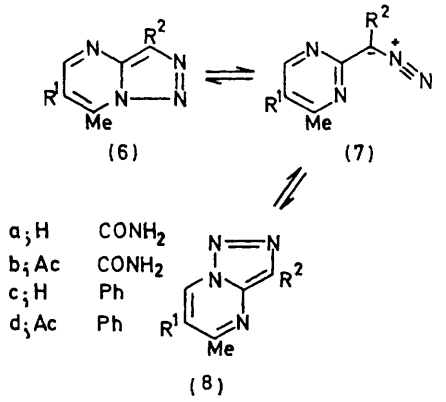
‡ Variable temperature ^{1}H n.m.r. studies were carried out in $(CD_3)_2SO$ at 100 MHz in the temperature range 15—175° using silicone oil as external standard.

centred at 0·37 [1H, q, $J_{6,7}$ 7 Hz, $J_{5,7}$ 1·75 Hz, H(7)], 1·02 [1H, q, $J_{5,6}$ 4 Hz, $J_{5,7}$ 1·75 Hz, H(5)], and 2·54 [1H, q, $J_{5,6}$ 4 Hz, $J_{6,7}$ 7 Hz, H(6)] p.p.m. However, the low-field doublets changed progressively on warming and ultimately



SCHEME 1

coalesced at 100°, before sharpening up to a doublet centred at 0·97 (2H, d, J 5 Hz) p.p.m. The high-field double doublet coalesced likewise and eventually emerged as a triplet centred at 2·74 (1H, t, J 5 Hz) p.p.m. The analogous coalescence of the methyl singlets at 7·10 and 7·32 p.p.m. in the ^{1}H n.m.r. spectrum of the triazolopyrimidine (**3b**) occurred at 88° and at higher temperatures gave rise to a six-proton singlet at 7·27 p.p.m. These changes, which reversed completely on cooling, involve a free energy of activation ($\Delta G^{\ddagger}$, calculated[5] from the observed coalescence temperatures, T_c = 100° and 88°) of *ca.* 76 kJ mol^{-1}, and may be attributed to the rapid interconversions [(**3a** and **b**) ⇌ (**4a** and **b**) ⇌ (**5a** and **b**)] at elevated temperatures [Scheme (1)]. The temperature dependence of the ^{1}H n.m.r. absorption of the isomer mixtures [(**6a**)/(**8a**)] (T_c = 91°) and [(**6b**)/(**8b**)] (T_c = 60°) is likewise attributable to the thermally induced equilibria [(**6a** and **b**) ⇌ (**7a** and **b**) ⇌ (**8a** and **b**)] [Scheme (2)]. The significantly lower coalescence temperature in the case of the isomer mixture [(**6b**)/(**8b**)] is consistent with enhanced stabilisation of the diazo-tautomer (**7b**) resulting from increased electron withdrawal (due to the presence of the acetyl group) by the pyrimidine ring. These contentions are supported by the appearance of i.r. diazo-absorption at 2100 cm^{-1} in a sample of the isomer mixture [(**6b**)/(**8b**)] kept at 80° for 20 h.



SCHEME 2

The ^{1}H n.m.r. spectra of the phenyl-substituted triazolopyrimidines (**3c** and **d**) and the isomer mixtures [(**6c** and **d**)/(**8c** and **d**)] also exhibited reversible coalescence at temperatures > 150°,§ corresponding to free activation energies for the anticipated equilibria [(**3c** and **d**) ⇌ (**4c** and **d**) ⇌ (**5c** and **d**)] and [(**6c** and **d**) ⇌ (**7c** and **d**) ⇌ (**8c** and **d**)] of at least 92·4 kJ mol^{-1}. The much lower coalescence temperatures (T_c = 60—100°) associated with the triazolopyrimidine carboxamides (see before) are thus a measure of the destabilisation of the triazole-tautomer (and conversely of the stabilisation of the diazo-tautomer) by the electron-withdrawing carboxamide group. These studies demonstrate conclusively the feasibility of diazoalkylideneamine–1,2,3-triazole tautomerism [(**2a**) ⇌ (**1a**)] in fused systems and therefore support the suggestion[6] that such ring–chain tautomerism precedes the thermolytic decomposition of 1,2,3-triazolo-heterocycles.

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§ Owing to the elevated temperatures involved, accurate coalescence temperatures have not as yet been determined for these equilibria.

[1] For leading references *cf.* ref. 3.
[2] R. N. Butler, *Chem. and Ind.*, 1973, 371.
[3] D. R. Sutherland, G. Tennant, and R. J. S. Vevers, *J.C.S. Perkin I*, 1973, 943.
[4] D. R. Sutherland and G. Tennant, *J. Chem. Soc.* (*C*), 1971, 2156.
[5] R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.*, 1963, 197; A. J. Boulton, A. R. Katritzky, M. J. Sewell, and B. Wallis, *J. Chem. Soc.* (*B*), 1967, 914.
[6] C. Wentrup, *Tetrahedron*, 1974, **30**, 1301.