Diazoimine–Triazole Equilibrium in Fused 1,2,3-Triazolo[1,5-*a*]pyrimidines

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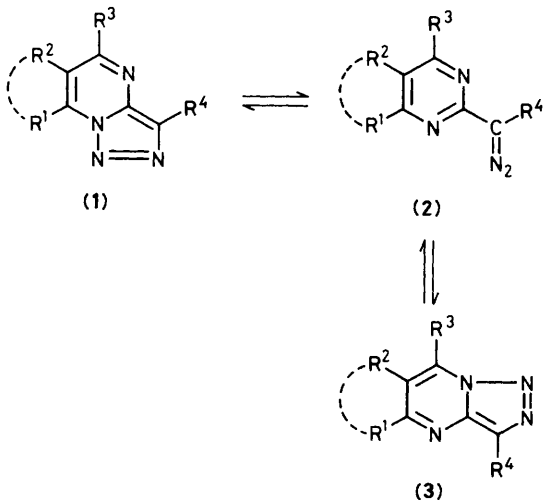
The elusive diazo isomers (**2**) of 1,2,3-triazolo[1,5-*a*]pyrimidines (**1**) can be stabilized by triazole fusion of the pyrimidine ring.

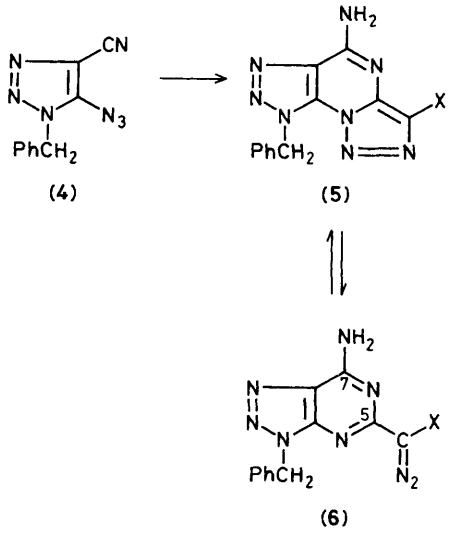
1,2,3-Triazolo[1,5-*a*]pyrimidines can thermally equilibrate between two isomeric structures (**1**) and (**3**) *via* the intermediacy of an open-chain diazo compound (**2**) (the so-called Dimroth rearrangement).[1] In all cases studied so far, the equilibria favour the bicyclic structures (**1**) and (**3**),[1,2] and the diazo form (**2**) has only been detected once and then at an elevated temperature.[1]

When the pyrimidine ring is fused at R^1 and R^2 to benzene[3] or to thiophene,[4] the equilibrium is shifted towards the angular structure (**1**). This is due to a destabilizing effect of the *ortho*-quinoid arrangement in the linear structure (**3**). We now report that the diazo form (**2**) can become the predominant isomer of the equilibrium when the ring fusion at R^1 and R^2 is performed with a π-deficient aromatic heterocycle, such as a *v*-triazole. Thus, (**5**) can undergo effectively ring opening to (**6**) and the equilibrium depends largely on the X-substituent.

The triazolopyrimidines (**5**) and/or (**6**) were prepared from 5-azido-l-benzyl-4-cyano-1,2,3-triazole (**4**) and active methylene compounds (phenylacetonitrile, malononitrile, ethyl



(1) (2) (3)



(4) (5) (6)

a; X = Ph
b; X = CN
c; X = CO_2Et
d; X = H

cyanoacetate, and cyanoacetic acid) in the presence of an alkoxide, following the procedure of Westerlund.[4]†

When X = Ph or CN (examples **a,b**), the compounds exist in the ring-closed tricyclic structure (**5**) both in the solid state and in $(CH_3)_2SO$ solution (i.r. and n.m.r. spectroscopic evidence). However, the i.r. spectrum (KBr) of (**5b**) discloses a weak diazo absorption at 2100 cm^{-1} which is indicative of (**6b**).

When X = CO_2Et (example **c**), the i.r. spectrum (KBr) has a strong absorption at 2120 cm^{-1} attributable to (**6c**). In the ^1H n.m.r. spectrum in $(CD_3)_2SO$ solution at room temperature, the absorptions of the ethyl protons (at δ 1.30 and 4.30) are broadened, and those of the benzyl methylene (at δ 5.66 and 5.76) and amine protons (at δ 8.25 and 10.45) are doubled. Coalescence of the benzyl methylene absorptions occurs at about 40 °C, and all absorptions are sharp at 90 °C, corresponding to a rapid interconversion of the two isomers on the n.m.r. time scale. The ratio of (**5c**) : (**6c**) at room temperature is estimated at 65 : 35%. In CD_3CN solution, the concentration of (**6c**) (80%) exceeds that of (**5c**), and this is further increased in $(CD_3)_2CO$ solution (*ca.* 93%). On cooling the acetone solution, the amount of (**6c**) decreases to about 50% at −50 °C. The diazo form (**6c**) is the only isomer present in $CDCl_3$ solution at room temperature, but at −40 °C a small amount (*ca.* 10%) of (**5c**) is present.

Finally, when X = H (example **d**), only the diazo isomer (**6d**) is observed in the i.r. (KBr) and n.m.r. [$(CD_3)_2SO$] spectra. For instance, the compound exhibits a diagnostic diazo proton resonance at δ 5.60 in the ^1H n.m.r. spectrum, and a diazo carbon resonance at δ 52.17 (d, $^1J_{CH}$ 200.9 Hz) in the ^{13}C n.m.r. spectrum. The ring carbon atoms at positions 5 and 7 of (**6d**) are found at δ 162.7 and 155.5 respectively, which have shifted downfield compared to those of (**5a**) (at δ 143.3 and 145.9 respectively).

In conclusion, the equilibrium concentration of the diazo form (**6**) increases in the following order of the X-substituent: Ph < CN < CO_2Et < H. The solvent also influences the equilibrium position, stabilizing the diazo form (**6**) in non-polar solvents; *i.e.* $(CD_3)_2SO$ < CD_3CN < $(CD_3)_2CO$ < $CDCl_3$. Upon cooling, the equilibrium shifts towards the ring-closed form (**5**).

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† The new compounds were fully characterized by i.r., ^1H n.m.r., ^{13}C n.m.r., and mass spectroscopy and high-resolution exact mass measurements.

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