# A Novel Rearrangement in the s-Triazolopyrazine Series

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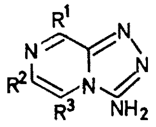
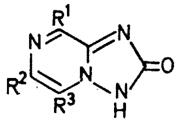
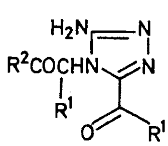
*Summary* The triazolo[4,3-*a*]pyrazines (I) rearrange in acid to the hitherto unreported 1*H*-imidazo[2,1-*c*]-*s*-triazoles (IV), and not to triazolo[2,3-*a*]pyrazines as believed previously.



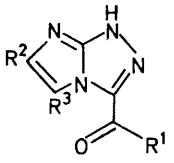
(I)



(II)



(III)



(IV)

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a; | H | Ph | Ph |
| b; | H | Me | Me |
| c; | $Pr^n$ | Me | H |

THE triazolo[4,3-*a*]pyrazines (Ia) and (Ib) have been stated[1] to rearrange in hot acid, with concomitant replacement of $NH_2$ by OH, to the [2,3-*a*] analogues (IIa) and (IIb), an isomerisation with precedents[2] in the related triazolopyrimidine series. We now report that the reaction in fact takes a wholly different course to give 1*H*-imidazo-[2,1-*c*]-*s*-triazoles (IV), members of a novel fused-ring system.

In 0·1 N-HCl at room temperature, (Ic)[3] is converted rapidly into a substance which remains stable under these conditions and whose u.v. spectrum (single peak at 291 nm, log $\epsilon$ 3·91) suggests a monocyclic heterocycle. On isolation this compound analysed for $C_9H_{14}N_4O_2$, and its n.m.r. spectrum† showed the coupled methyl ($\tau$ 7·72) and methine ($\tau$ 2·24) signals of the parent to have been replaced by those due to uncoupled methyl ($\tau$ 7·83) and methylene ($\tau$ 5·00) groups. These values suggest a $CH_3$–X–$CH_2$-Y part structure, where X and Y are both electronegative and contain no protons. In addition, $NH_2$ remains ($\tau$ 3·52, exchangable), the propyl group is intact, and there are carbonyl bands present (Nujol) at 1738 and 1672 cm$^{-1}$. These data can only be reconciled by structure (IIIc), according to which the pyrazine ring has cleaved at the 7,8-bond with loss of the 7-nitrogen function. On heating in the solid state, (IIIc) gives a substance $C_9H_{12}N_4O$ (with loss of $CH_2$, $NH_2$, and the 1738 cm$^{-1}$ carbonyl function), identical with the supposed 'isomerisation product' (IIc).[4] The latter must therefore have structure (IVc).

No similar intermediate has been obtained from (Ia) and (Ib), but examination of the final products suggests similar rearrangements to have taken place. In particular, each contains a singlet ($\tau$ *ca.* 0·3) now attributed to a formyl proton (this ring methine in the parent[1] is near $\tau$ 1·0), and the former has $\nu_{C=O}$ (Nujol) at 1682 cm$^{-1}$ [*cf.* 1665 cm$^{-1}$ in (IVc)]. It was noted previously[1] that '(IIb)' exists in the lactim form, an anomaly difficult to reconcile with either structure. This observation turns out to be an artefact. Its elemental analysis always shows the presence of some water; when dissolved in dimethyl sulphoxide, which acts as a dehydrating agent, the carbonyl function appears normally at 1675 cm$^{-1}$. The same result can be obtained in the solid state by drying the ground sample very thoroughly before making a Nujol mull. We presume therefore that the formyl group of (VIb) shows a strong tendency to hydrate to the diol (there is in fact a weak signal at $\tau$ 4·75 which may be due to a trace of this). Consistently, the hydrolysis of (Ib) in aqueous acid leads to a product showing u.v. end-absorption only, as expected for a simple aminotriazole.

The kinetics of hydrolysis of (Ic), which presents novel features consistent with the intermediacy of covalently hydrated species, will be reported elsewhere.

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† All data are recorded for $(CD_3)_2SO$ on a Varian HA 100 n.m.r. spectrometer.

[1] S. E. Mallett and F. L. Rose, *J. Chem. Soc.* (*C*), 1966, 2038.

[2] See, *e.g.*, G. W. Miller and F. L. Rose, *J. Chem. Soc.*, 1963, 5642.

[3] J. Maguire, D. Paton, and F. L. Rose, *J. Chem. Soc.* (*C*), 1969, 1593; J. Maguire and F. L. Rose, B.P. 1, 146, 770.

[4] F. L. Rose, unpublished data.