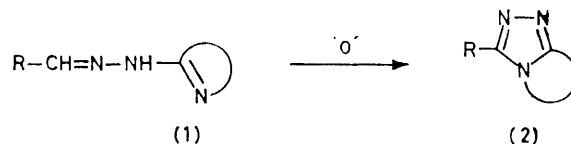


Detection of a Metallo-intermediate and Geometrical Isomerizations in an Oxidative Cyclisation of a Heterocyclic Hydrazone with Mercury(II) Acetate

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Summary Oxidative cyclisation of the *E*-isomer of 2-pyridylcarbaldehyde 2-pyridylhydrazone with mercury(II) acetate involved an amino-*N*-mercurio intermediate with a *Z*-structure and an *E* → *Z* → *E* series of isomerizations.

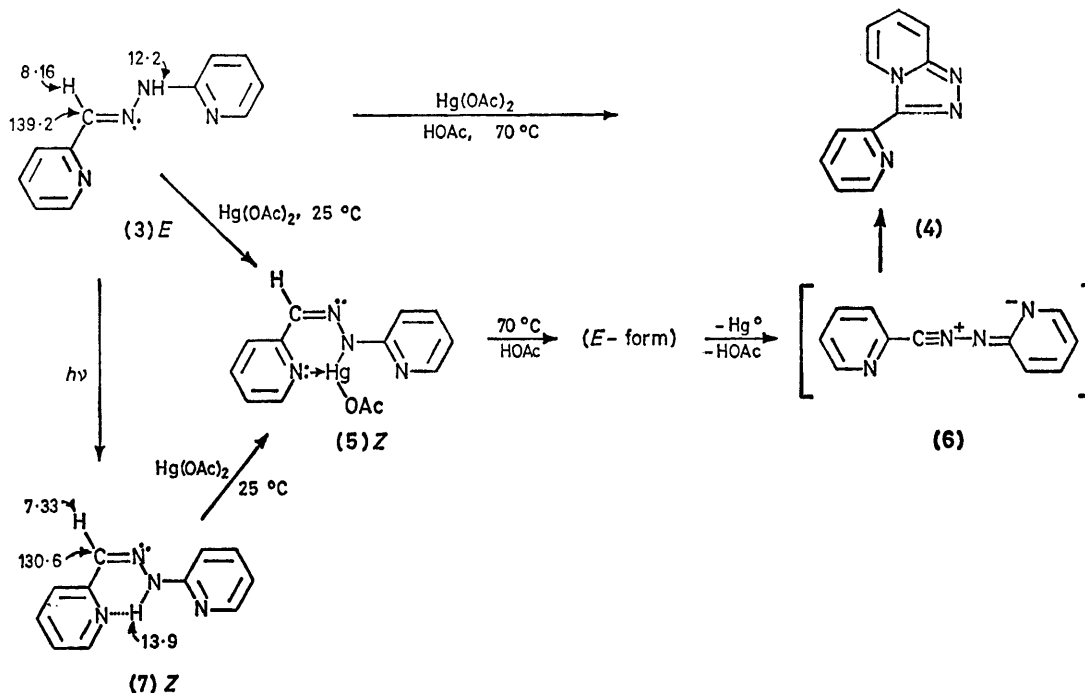
OXIDATIVE cyclisation of heterocyclic hydrazones (**1**) is a widely used route to fused 1,2,4-triazoles (**2**) and may be carried out with a variety of oxidising agents,¹⁻³ among the most widely used of which are metallic compounds. When the heterocyclic moiety is on the hydrazone methine carbon, cyclisation to 1,2,3-triazolium salts may also be observed⁴ and with a system such as (**3**) containing heterocyclic rings at both ends of the chain a cyclisation at either end is theoretically possible. No intermediate species have been detected in these cyclisations. Attempts to achieve dehydrogenative cyclisations of some π -excessive (5-membered) heterocyclic hydrazones and semicarbazones⁵ with mercury(II) acetate were unsuccessful, apparently owing to the low oxidation potential of Hg^{II}, and an oxidative cyclisation of a hydrazone with an Hg^{II} species has not been observed. We now report a ready cyclisation of the *E*-isomer of 2-pyridylcarbaldehyde 2-pyridylhydrazone (**3**)



with Hg(OAc)₂ at 70 °C in acetic acid (16 h) giving the *s*-triazolo-pyridine (**4**) in 37% yield along with decomposition resins and metallic mercury. In the same reaction at room temperature the intermediate mercury derivative (**5**), having the *Z*-structure, was isolated (97%).[†] The lability of this intermediate was reduced by electron donation to the mercury co-ordination shell by the pyridine nitrogen atoms. The *Z*-structure of (**5**) was suggested by ¹H and ¹³C n.m.r. spectra and was confirmed when the hydrazone *Z*-isomer (**7**)[‡] also gave compound (**5**) on treatment with mercury(II) acetate. The co-ordination in compound (**5**) required an *E*-*Z* isomerization of the substrate (**3**). This illustrates how the incomplete co-ordination shell of mercury(II) acetate may influence its behaviour in organic reactions, a feature not present in related oxidants, *e.g.* lead

[†] By addition of light petroleum (b.p. 60–80 °C); identified from microanalysis, i.r., ¹H, and ¹³C n.m.r. spectra which showed the absence of NH and all the expected proton and carbon signals; m.p. 146–147 °C.

[‡] The *Z*-isomer (**7**) (m.p. 81–83 °C) was obtained by u.v. irradiation of a benzene solution of the *E*-isomer (**3**) (m.p. 181 °C), followed by separation on a column of alumina (some ¹H and ¹³C shifts given). The intermolecular H-bond in (**3**) and the intramolecular H-bond of (**7**) were confirmed by dilution studies.



¹H and ¹³C n.m.r. δ values are given in p.p.m. for selected atoms.

tetra-acetate, where the metal co-ordination shell is complete.

When a solution of compound (5) in acetic acid was heated at 70 °C, it readily gave the triazolo-pyridine (4), along with metallic mercury and identical resins in the same proportions as observed for the direct cyclisation at 70 °C thereby confirming its intermediacy. Indeed the formation of the species (5) cannot be avoided since it is formed rapidly on mixing the reactants. Direct ¹H n.m.r. monitoring of the conversion of compound (5) into the cyclised product (4) at 70 °C in deuterioacetic acid showed a further isomerization back to the *E*-form. As the temperature was raised the methine CH=N of the *Z*-form (δ 7.26) rapidly decreased and was replaced by a signal due to the methine CH= of the *E*-form (δ 8.2) and at 70 °C the full spectrum was similar to that of the parent *E*-structure

(3). After about 1 h at 70 °C weak signals due to the product (4) and the resins began to appear and no further intermediates were detected. The overall reaction with the normal *E*-isomer (3) had involved *E* → *Z* → *E* isomerizations prior to the cyclisation. The final step in the formation of the fused triazolo-compounds is generally considered to involve nitrilimines (6). These, if present, apparently cyclise rapidly and they have not been detected or trapped by normal 1,3-dipolarophiles such as acrylonitrile.⁶ Their involvement is now supported by the presence of prior intermediates such as *E*-(5) from which they could be generated.

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