

An Unusual Substitution Reaction in a Benzotetrazine Derivative

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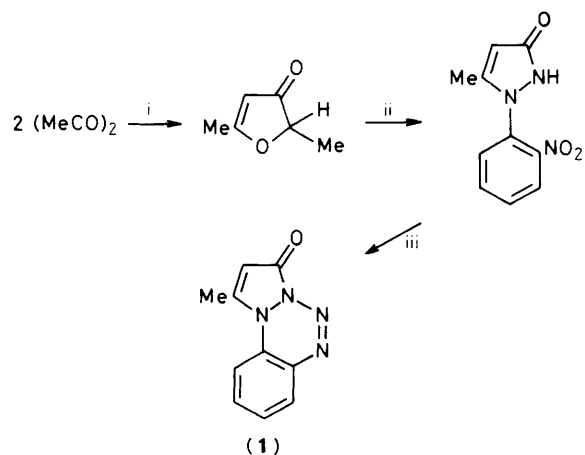
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1-Methyl-3*H*-pyrazolo[1,2-*a*]benzotetrazin-3-one decomposes in alcohols, with loss of nitrogen and intramolecular hydrogen transfer, to form 5-alkoxymethyl-1,2-dihydro-1-phenyl-3*H*-pyrazol-3-ones.

The literature¹ contains a number of examples of the 1,2,3,4-tetrazine ring system, but by far the majority contain saturated carbon atoms in the ring, and so lack cyclic π -conjugation. Benzotetrazine is unknown; although oxidation of 1-aminoindazole forms 1,2,3-benzotriazine,² 1-amino-benzotriazole instead generates benzyne.³ One 1,2-fused benzotetrazine has been reported,⁴ but with no details of its chemistry.

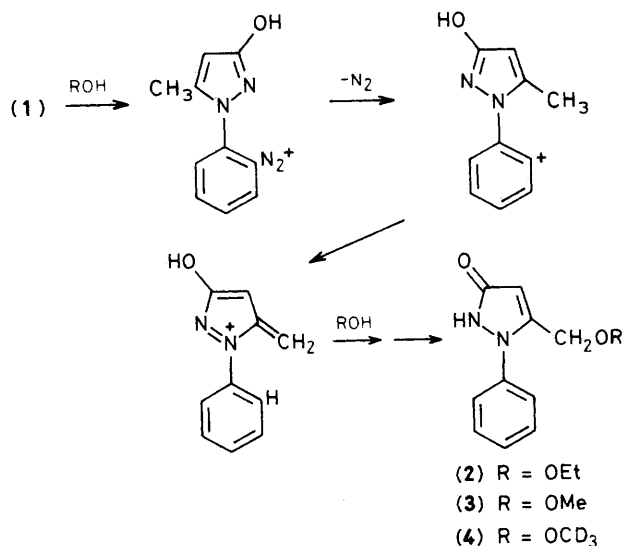
We have prepared 1-methyl-3*H*-pyrazolo[1,2-*a*]benzotetrazin-3-one (**1**), as outlined in Scheme 1,[†] and following literature precedent⁵ to the *o*-nitrophenylpyrazolinone. The fused tetrazine (**1**) formed fine red needles (from ethanol), m.p. 188–190 °C (decomp., turning yellow *ca.* 150 °C).

Prolonged (4 h) reflux of the fused tetrazine (**1**) in ethanol



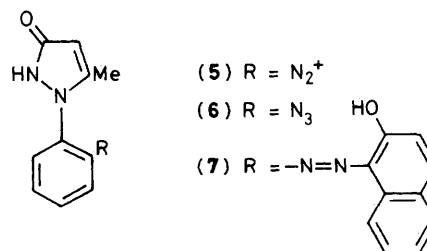
Scheme 1. Reagents: i: (a) KOH-H₂O, (b) HCl-H₂O; ii: (a) *o*-O₂NC₆H₄N₂⁺ Cl⁻, (b) HCl-H₂O; iii: (a) Pd/C-H₂, (b) HNO₂.

[†] All new compounds gave satisfactory microanalyses ($\pm 0.4\%$ in C, H, and N), and, except for compound (**1**), which exploded, mass spectra consistent with the molecular formulae assigned.



Scheme 2

led to loss of colour, and after chromatography (Al_2O_3 ; CH_2Cl_2 -EtOAc) the ethoxymethylpyrazolinone (2), m.p. 121 °C (55% yield), was isolated. Similar reflux in methanol formed the methoxymethyl compound (3) (50%), m.p. 112–114 °C after sublimation. In these reactions the origin of the hydrogen atom taking the place of the azo-function in the benzene ring is the methyl group, since, when (1) was decomposed in [$^2\text{H}_4$]methanol the trideuteriomethoxy product (4) had protium, not deuterium, in the phenyl group. In



acidic media the fused tetrazine (1) is evidently able to form the diazonium salt (5), as shown by its reactions with sodium azide to give the azide (6) and with 2-naphthol to form the deep-red azo-product (7). We therefore propose the route of Scheme 2 to explain the formation of the alkoxymethyl compounds (2)–(4).

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