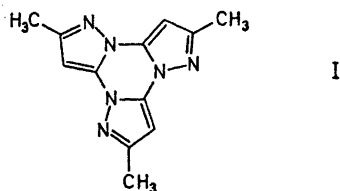


A Tetracyclic Condensation
Product from
3-Methyl-2-pyrazolin-5-one

BO BJÖRKQVIST, ERIK HELGSTRAND
and NILS E. STJERNSTRÖM

Research Laboratories, AB Astra, Södertälje,
Sweden

In an attempt to prepare 5-chloro-3-methylpyrazole, 3-methyl-2-pyrazolin-5-one was treated with phosphorus oxychloride. However, under certain experimental conditions the condensation product I was isolated as the main product.



A methyl derivative of I (together with linear products) is reported¹ to be formed by dehydrogenation of 3,4-dimethylpyrazole with bromine or similar reagents.

The structure of I was established by means of spectroscopy. The IR spectrum did not exhibit any absorption derived from N—H bonds. Compound I has an UV absorption at 239 μ with $\log \epsilon$ 4.6. These values are nearly identical with those reported for the methyl derivative.¹ The NMR spectrum consists of two singlets (area ratio 3:1) at δ 2.43 and 6.37 ppm (0.2 g substance/ml of deuteriochloroform; δ measured relative to TMS) corresponding to a methyl group and an aromatic proton, respectively. The most abundant ion in the

mass spectrum is the molecular ion with mass 240 and this seems to split off a methyl radical to give rise to a high peak at mass 225 (relative abundance 77 %). A relatively high peak at mass 39 (relative abundance 39 %) is probably due to the cyclopropenium cation.²

The condensation agent, phosphorus oxychloride, is probably also functioning as a Lewis acid, which enhances the reactivity of the carbonyl group of the pyrazolinone. An attempt to trap an eventual reactive intermediate with anthracene was not successful.

Preparation of I. A mixture of 3-methyl-2-pyrazolin-5-one (10.0 g, 0.102 mole) and phosphorus oxychloride (30.0 g, 0.196 mole) was refluxed for 12 h in xylene. After evaporation of the solvent *in vacuo* the residue was refluxed for 6 h with 7.5 g phosphorus oxychloride. The unreacted reagent was evaporated *in vacuo*. The residue was treated with 50 g of ice and solid sodium carbonate added until the pH was 8 and the precipitate formed was collected by filtration. Yield 5.5 g (67 %), m.p. 205–207°C (after recrystallization from ligroin, m.p. 205–207°C). (Found: C 60.14; H 5.03; N 34.79. Calc. for $(C_4H_4N_2)_n$: C 59.98; H 5.04; N 34.99).

In another experiment 3-methyl-2-pyrazolin-5-one was refluxed for 5 h with 1.5 equiv. of phosphorus oxychloride in xylene, the residue after evaporation not being treated with phosphorus oxychloride. The yield of I was 38 %.

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