ACTA CHEMICA SCANDINAVICA 13 (1959) 679–682

Studies on Pyrazolones

XIII. The Reactions of 1-Phenyl-3-methyl-2-pyrazolin-5-one with Some Diketones

GUNNEL WESTÖÖ

Institute of Organic Chemistry, University of Lund, Lund, Sweden

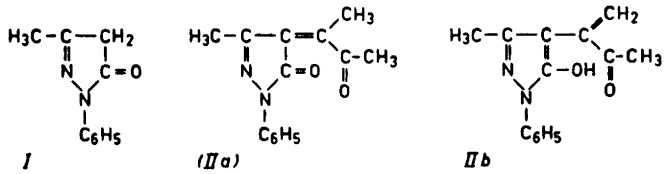
1-Phenyl-3-methyl-2-pyrazolin-5-one (I) reacts with 2,3-butanedione to form the acid 1-phenyl-3-methyl-4-(1-acetylvinyl)-5-hydroxypyrazole (II b). With 2,4-pentanedione I gives a neutral, tetracyclic product (III d) and with 2,5-hexanedione the bispyrazolone, V, which is stable in solid form but in solution is easily oxidized to VI even by the air at room temperature.

2,3-Butanedione and 1-phenyl-3-methyl-2-pyrazolin-5-one (I) react at room temperature with formation of a colourless acid, II b, a tautomer of the expected, coloured, neutral reaction product, II a. A CH_2=C-test on the acid according to Bricker and Roberts [1] was positive. The IR spectrum contains only one C=O stretching frequency (1 670 cm^{-1}) and a broad OH band around 2 500 cm^{-1} (solid state).

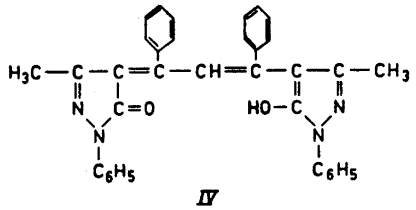
When I is heated with 2,4-pentanedione in methanol, a neutral, colourless compound separates. Piperidine catalyses the reaction. The analyses of the compound formed are in accordance with the structure III a, but since the lack of colour excludes this formula, the reaction sequence, Scheme I, leading to the structure III d, is proposed. The UV-curve of the product in methylene chloride solution (λ_{max} = 254 mμ, log ε = 4.26) is similar to the corresponding curve of 1-phenyl-3-methyl-5-methoxypyrazole in hexane [2]. The IR spectrum of the solid product also confirms the structure III d, having neither C=O, nor OH absorption bands. A very strong band at 1 090 cm^{-1} is probably associated with the ether linkages.

Only neutral solvents like ligroin, methylene chloride and chloroform dissolve the product in the cyclic form (III d). Alcoholic solutions are violet-red, indicating that III d is here in equilibrium with the open forms (ionized III b has a λ_{max} at 545 mμ). III d can be recovered from the red solutions.

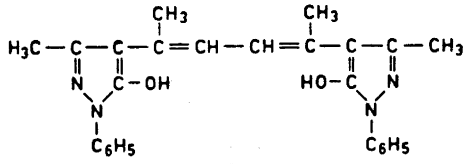
When dry hydrogen chloride is introduced into a chloroform or methylene chloride solution of III d, the ether linkages are split up, for the IR spectrum of the colourless compound which separates shows OH and NH bands. The



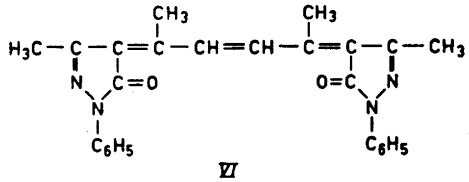
I (*IIa*) *IIb*



IV



V

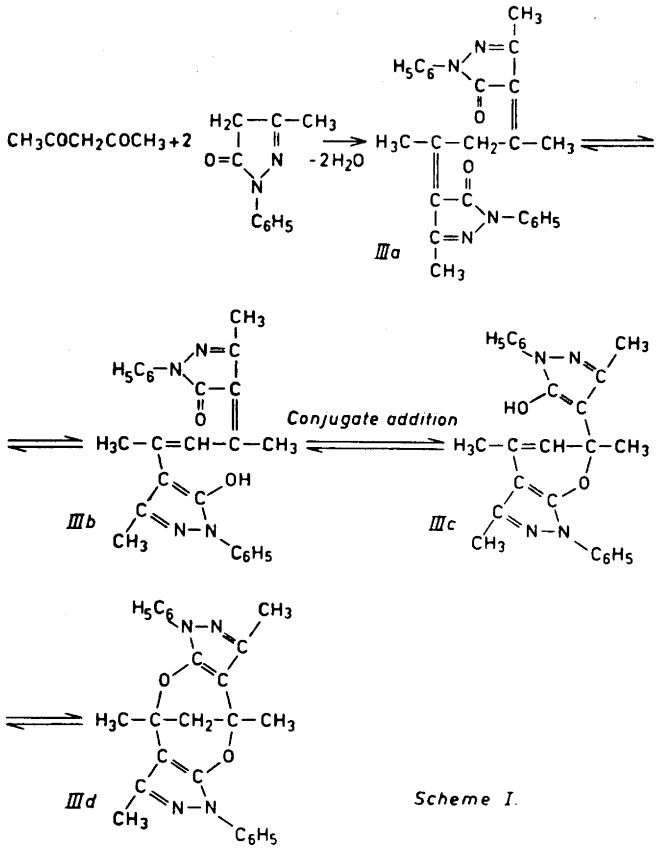


VI

structure of the reaction product is difficult to settle on account of its great instability. Both in solution and in the solid state the compound splits off hydrogen chloride with reformation of III d.

When the methyl groups in 2,4-pentanedione are exchanged for phenyl groups in the above reaction, the open form IV is strongly stabilized by resonance and no cyclization takes place. As is to be expected on account of the acidic hydroxyl group and the resonance possibilities of the corresponding ion, the colour of IV is pH-dependent, being blue in alkaline solution, red in the solid form and in acid solution.

Heating of I in 2,5-hexanedione gives rise to a colourless product, the properties of which are in accordance with the structure V. The IR curve of the compound in KBr has no carbonyl band but a broad hydroxyl band at about 2 600 cm^{-1}. V is stable in the solid state, but in solution it is rapidly oxidized by the air to form the deep red compound VI.



Scheme I.

EXPERIMENTAL

Preparation of 1-phenyl-3-methyl-4-(1-acetylvinyl)-5-hydroxypyrazole (II b). 1-Phenyl-3-methyl-2-pyrazolin-5-one (I) (10 g) was dissolved in 2,3-butanedione (30 ml), and the solution was kept at room temperature for 18 h. After cooling the crystals formed were collected by filtration and washed with cold ethanol. Yield: 11.7 g. After recrystallization from ethanol the product melted at 136° (decomp.). (Found: C 69.4; H 5.9; N 11.7; O 13.3; equiv. wt 242. Calc. for $C_{14}H_{14}N_2O_2$: C 69.4; H 5.8; N 11.6; O 13.2; equiv. wt 242.)

Preparation of III d. 2,4-Pentanedione (5.0 ml), I (5.0 g), methanol (20 ml) and one drop of piperidine were refluxed for 48 h. The piperidine was neutralized by addition of 2 drops of 5 N hydrochloric acid. The boiling was continued for 10 min. After cooling in ice for one hour, the colourless crystals, which had separated, were filtered and washed with methanol and water. Yield: 5.0 g, m. p. 171° (decomp.). The product can be recrystallized from benzene. (Found: C 72.7; H 5.9; N 13.6; O 7.7; mol. wt * 417. Calc. for $C_{25}H_{24}N_4O_2$: C 72.8; H 5.9; N 13.6; O 7.8; mol. wt 412.)

Preparation of IV. Dibenzoylmethane (2.2 g), I (3.5 g) and *n*-butanol (10 ml) were refluxed overnight. After addition of ethanol, the solution was poured into water and

* Cryoscopic determination in glacial acetic acid.

acidified with hydrochloric acid. The precipitate was filtered and washed with water. Yield of crude IV: 3.7 g. The product was recrystallized from ethanol repeatedly (0.8 g of deep red product remained). M. p. 211°. It was dried at 100° and 0.5 mm Hg. (Found: C 77.9; H 5.5; N 10.1. Calc. for $C_{35}H_{28}N_4O_2$: C 78.3; H 5.3; N 10.4.)

Preparation of V. 2,5-Hexanedione (5 ml), I (5.0 g) and ethanol (30 ml) were heated in a boiling water bath in N_2-atmosphere for 24 h. Colourless crystals of V separated. After cooling they were filtered, washed with ethanol and chloroform and dried in N_2-atmosphere. Yield: 4.45 g; m. p. about 220° (decomp.). (Found: C 73.0; H 6.2; N 13.2; O 7.6. Calc. for $C_{26}H_{26}N_4O_2$: C 73.2; H 6.15; N 13.1; O 7.5.)

V is only slightly soluble in most solvents. In solution it is easily oxidized by *e. g.*, perchloric acid or 1-phenyl-3-methyl-4,4-dibromo-2-pyrazolin-5-one and even by the air, the red compound VI being formed. In *e. g.*, methylenechloride in N_2-atmosphere, V is soluble without change of colour. When air is admitted the solution rapidly turns red. Besides by the colour change the formation of VI is proved by the IR spectrum, which, contrary to the spectrum of V, has a C=O band but no OH band. M. p. of VI: 217° (decomp.). (Found: C 73.5; H 5.9; N 13.2; O 7.7. Calc. for $C_{26}H_{24}N_4O_2$: C 73.6; H 5.7; N 13.2; O 7.5.)

The analyses were performed by Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mülheim, Germany. Dr. Andreas Rosenberg, University of Uppsala, carried out the IR measurements.

The author wishes to thank *Statens naturvetenskapliga forskningsråd* for financial support.

REFERENCES

1. Bricker, C. E. and Roberts, K. H. *Anal. Chem.* **21** (1949) 1331.
2. Valyashko, N. A. and Bliznjukov, V. I. *J. Gen. Chem.* (U.S.S.R.) **11** (1941) 23.

Received January 7, 1959.