

Studies on Pyrazolones

V. Reaction Products from Pyrazole Blue and Alcohol

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In a previous paper¹ it was shown that pyrazole blue reacts with the methylene group of 1-phenyl-3-methyl-5-pyrazolone with the formation of 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione. In the present investigation the great reactivity of the double bond system of pyrazole blue is further demonstrated by the easy preparation of addition compounds from pyrazole blue and alcohols. (That alcohols can be added to α,β -unsaturated carbonyl compounds is well known².)

Alkaline ethanol readily dissolves pyrazole blue (I) at room temperature with the formation of a colourless compound which is very soluble in ethanol, ether, ethyl acetate and benzene. The same compound is formed slowly without alkali at room temperature (*cf.* p. 452). When heated on a water-bath the reaction product decomposes into ethanol and pyrazole blue. It does not form pyrazole blue on treatment with nitrous acid (*cf.* p. 451).

Analyses show that the addition compound contains one mole of ethanol per mole of pyrazole blue. This fact in conjunction with the acidic qualities of the compound (equiv. wt. 390) indicates that the hydrogen atom from the hydroxyl group of the alcohol has been attached to the carbon atom 4 or a tautomeric position, probably the oxygen atom, of one of the pyrazolone nuclei and the ethoxyl group to the other. For the ethoxyl group a 4-position seems most reasonable. Consequently the compound is probably 1,1'-diphenyl-3,3'-dimethyl-4-ethoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione (II). The light absorption curve of the substance, which lies between the corresponding curves of 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione and 1-phenyl-3,4-dimethyl-4-hydroxy-5-pyrazolone³ in the range $2\ 300 > \lambda > 3\ 000\ \text{Å}$ (Fig. 1) favours this formulation.

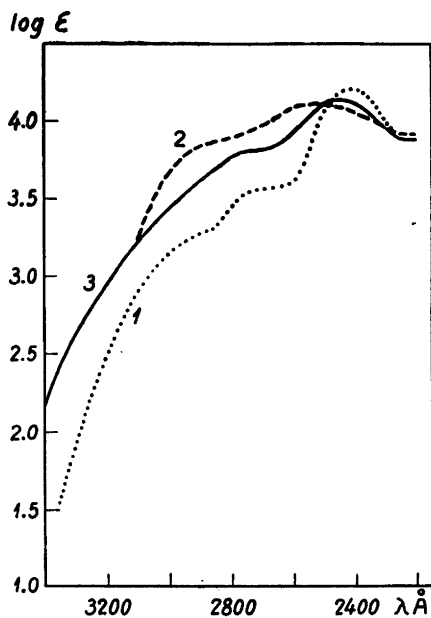
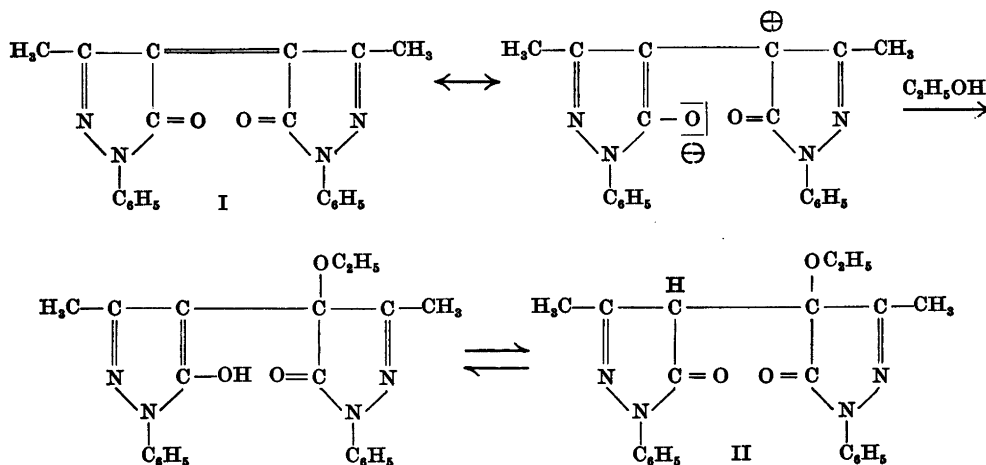
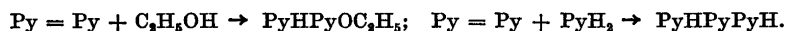
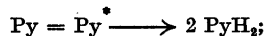


Fig. 1. 1) 1-Phenyl-3,4-dimethyl-4-hydroxy-5-pyrazolone in ethanol ($5.8 \cdot 10^{-3}$, $5.8 \cdot 10^{-4}$ and $5.8 \cdot 10^{-5}$ M solutions). 2) 1,1'-Diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione in ethanol ($4.0 \cdot 10^{-5}$ M solution). 3) 1,1'-Diphenyl-3,3'-dimethyl-4-ethoxy (or propoxy)-[4,4'-bi-2-pyrazoline]-5,5'-dione in ethanol ($3.8 \cdot 10^{-3}$, $3.8 \cdot 10^{-4}$ and $3.8 \cdot 10^{-5}$ M solutions). (The concentration, c , of the equation $\log \varepsilon = \log \log \frac{I_0}{I} - \log l \cdot c$ has been counted in pyrazolone units per liter solution.)



1,1'-Diphenyl-3,3'-dimethyl-4-methoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione and 1,1'-diphenyl-3,3'-dimethyl-4-*n*-propoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione have been prepared in the same way as the ethoxyl compound.

Knorr⁴, p. 173 suggests that 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione is formed when pyrazole blue is boiled with alcohol. This experiment has been repeated, but the bispyrazolone of Knorr was not obtained. Instead the main product of the reaction was 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione (64 % yield) identified by equivalent weight, decomposition temperature and the formation of pyrazole blue with nitrous acid. Traces of 1,1'-diphenyl-3,3'-dimethyl-4-ethoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione, together with unisolated decomposition products, were also formed. 1,1'-Diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione is so insoluble that it should separate if it were a reaction product. No precipitate was observed.

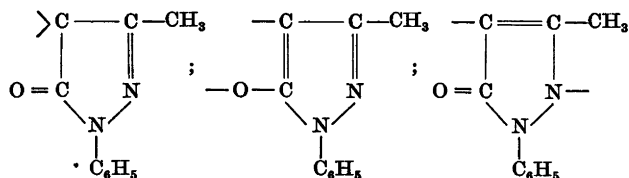


EXPERIMENTAL

1,1'-Diphenyl-3,3'-dimethyl-4-ethoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione. Pyrazole blue (0.765 g) was shaken with ethanol (10 ml) and dilute sodium hydroxide (2 ml of 2.5 *N* solution) until all $\text{Py} = \text{Py}$ had dissolved (3 min.). Addition of water (200 ml) and dilute sulphuric acid (2 ml of 5 *N* solution) to the yellow solution precipitated a colourless substance that was filtered by suction, washed with water and air-dried. Yield 0.80 g (92 %). (Found: C 67.7; H 5.5; N 14.28; equiv. wt. 390 on titration with 0.1 *N* barium hydroxide solution against phenolphthalein. Calc. for $\text{C}_{22}\text{H}_{22}\text{O}_3\text{N}_4$ (390.4): C 67.7; H 5.7; N 14.35; equiv. wt. 390.) The compound decomposed without melting but shrank considerably at 94° C. On decomposing the substance at about 100° C in a Reihlen-Weinbrenner oven and combusting the volatile parts, 49.6 per cent carbon and 13.1 per cent hydrogen were found. Calc. for $\text{C}_2\text{H}_5\text{OH}$: C 52.1; H 13.1. Pyrazole blue remained (87.8 %. Calc. for $\text{C}_{22}\text{H}_{22}\text{O}_3\text{N}_4$: 88.2 %.)

1,1'-Diphenyl-3,3'-dimethyl-4-methoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione. This compound was prepared by dissolving pyrazole blue (1.0 g) in methanol (50 ml) containing sodium hydroxide (5 ml of 2.5 *N* solution). Water (350 ml) and then dilute sulphuric acid (3 ml) were added to the yellow solution. The colourless precipitate that formed (1.05 g, 96 %) was filtered by suction, washed with water and dried at room temperature. It decomposed without melting to give pyrazole blue. (Found: C 67.2; H 5.3; N 14.86;

* Py represents the radicals



equiv.wt. 372. Calc. for $C_{21}H_{20}O_3N_4$ (376.4): C 67.0; H 5.4; N 14.89; equiv.wt. 376.) The compound is soluble in alcohol, slightly soluble in ether.

1,1'-Diphenyl-3,3'-dimethyl-4-n-propoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione. PyHPyOCH₂-CH₂CH₃ was prepared by dissolving pyrazole blue (2.0 g) in 1-propanol (50 ml) and dilute sodium hydroxide (3 ml). A dark yellow solution was obtained. Water (350 ml) and then dilute sulphuric acid (2 ml) were added. A grayish precipitate was formed. It was easily soluble in ethanol at room temperature, but it precipitated from the solution in a stabler crystal form in a few minutes. The precipitate was white, and from the mother liquor more white crystals could be obtained by dilution with water and seeding with the crystals already obtained. The product is only slightly soluble in ether. Heat causes the compound to decompose without melting. (Found: C 68.3; H 5.9; N 13.83; equiv. wt. 401. Calc. for $C_{23}H_{24}O_3N_4$ (404.5): C 68.3; H 6.0; N 13.85; equiv. wt. 404.5.)

Reaction between Pyrazole Blue and Ethanol at Room Temperature. Pyrazole blue (1.23 g) was shaken with ethanol (100 ml) and chloroform (100 ml) until decoloration occurred (10 days). The solvents were evaporated at room temperature. The crude, yellow product (1.45 g) was very soluble in alcohol. It gave pyrazole blue when heated at 100° C, but not when treated with nitrous acid. These facts show that 1,1'-diphenyl-3,3'-dimethyl-4-ethoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione had been formed, and also that neither 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione nor 1,1',1'-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione had been. (Found: equiv. wt. of the crude product 409. Calc. for $C_{22}H_{22}O_3N_4$ (390.4): equiv. wt. 390.)

Reaction between Pyrazole Blue and Alcohol at Boiling Temperature. Pyrazole blue (1.39 g) was boiled with 96 % ethanol (50 ml) during 9 hours. The yellow solution was precipitated with water and a few ml of 5 N sulphuric acid. The precipitate was filtered by suction and washed with water. The dry product (1.21 g) was extracted with ether. The ether-insoluble part (0.895 g, 64 %) was 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione¹, m.p. 200° C with decomposition after crystallization from alcohol. (Found: equiv. wt. 264. Calc. for $C_{30}H_{26}O_3N_6$: equiv. wt. 259.) The product was slightly contaminated with 1,1'-diphenyl-3,3'-dimethyl-4-ethoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione (strongly adsorbed by the surface-active terpyrazolone crystals) identified by the formation of small amounts of pyrazole blue on heating to 100° C. The ether solution also contained traces of 1,1'-diphenyl-3,3'-dimethyl-4-ethoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione.

SUMMARY

Pyrazole blue reacts with ethanol at room temperature to give 1,1'-diphenyl-3,3'-dimethyl-4-ethoxy-[4,4'-bi-2-pyrazoline]-5,5'-dione. The reaction is strongly catalyzed by alkali. Analogous products are obtained with methanol and 1-propanol. Pyrazole blue reacts with boiling ethanol to give 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione.

REFERENCES

1. Westöö, G. *Acta Chem. Scand.* **7** (1953) 355.
2. Purdie, T., and Marshall, N. *J. Chem. Soc.* **59** (1891) 464.
3. Veibel, S., and Westöö, G. *Acta Chem. Scand.* **7** (1953) 119.
4. Knorr, L. *Ann.* **238** (1887) 154.

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