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Studies on Pyrazolones
II. Condensation Reactions between 1-Phenyl-3,4-dimethyl-5-pyrazolone and 1-Phenyl-3,4-dimethyl-4-halo-5-pyrazolones

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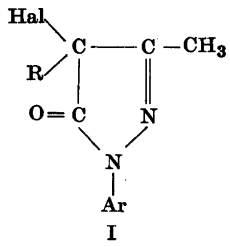
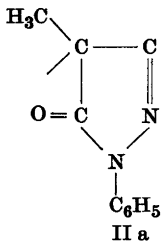
In 1-aryl-3-methyl-4-halo-5-pyrazolones (I a) and its 4-alkyl derivatives the halogen atom is activated by the adjacent C = O and C = N groups and can react with the active hydrogen atom in 1-aryl-3-methyl-4-halo (or alkyl)-5-pyrazolones at room temperature. Interaction between molecules of these kinds has already been described by Knorr [1], who observed the formation of pyrazole blue from 1-phenyl-3-methyl-4-bromo-5-pyrazolone. This reaction has been studied more recently by Smith [2], who discovered that cupric ions strongly catalyze the condensation.

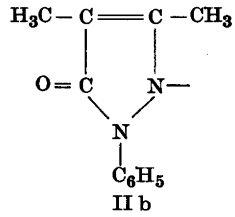


I

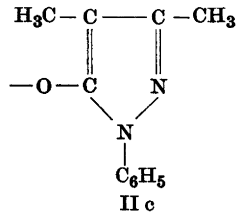
a) R = H
b) R = CH_3; Ar = C_6H_5



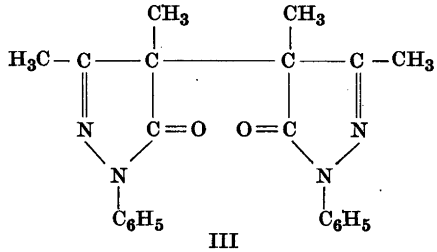
II a



II b



II c



III

The present work was undertaken to study the condensation between 1-phenyl-3,4-dimethyl-4-halo-5-pyrazolones[3] and 1-phenyl-3,4-dimethyl-5-pyrazolone.

In an alcohol solution buffered with sodium acetate, 1-phenyl-3,4-dimethyl-5-pyrazolone and 1-phenyl-3,4-dimethyl-4-halo-5-pyrazolones interact to give a bispyrazolone.

$$Py(CH_3)H\ ^* + Py(CH_3)Hal \rightarrow Py(CH_3) \cdot PyCH_3 + HHal$$

The iodopyrazolone reacts faster than the bromo-compound, the chloropyrazolone slower. When the iodo-compound is used, the yield of bispyrazolone is diminished because of the side-reaction

$$Py(CH_3)I + HI \rightleftharpoons Py(CH_3)H + I_2$$

$Py(CH_3) \cdot PyCH_3$ is only slightly soluble in alcohol at room temperature and precipitates as white crystals. It is a very stable product not readily attacked by either acids or bases.

The constitution of the bispyrazolone is not obvious from its way of preparation. Even if $Py(CH_3)Hal$ has only the one structure I b, there are three possibilities (*cf.* II a, b and c) for $Py(CH_3)H$, and thus $Py(CH_3) \cdot PyCH_3$ may have the structure III or alternative structures obtained by combination of II a with II b or c.

The light absorption curve of $Py(CH_3) \cdot PyCH_3$ (Westöö [3]) lies close to the corresponding curve of 1-phenyl-3,4,4-trimethyl-5-pyrazolone (Biquard and Grammaticakis [4]) and differs from the curves of antipyrine and 1-phenyl-3-methyl-5-methoxypyrazole (Valyashko and Bliznyukov [5]). This shows that the substance is 1,1′-diphenyl-3,3′,4,4′-tetramethyl-[4,4′-bi-2-pyrazoline]-5,5′-dione (III). The light absorption does not change when acid is added which also excludes coupling C to N. Even when $Py(CH_3)Na$ reacts with $Py(CH_3)Br$ in absolute alcohole, the same compound (III) is formed. It is identical with the $Py(CH_3) \cdot PyCH_3$-compound prepared by Knorr[1] by oxidation of $Py(CH_3)H$ with nitrous acid.

EXPERIMENTAL

1,1′-Diphenyl-3,3′,4,4′-tetramethyl-(4,4′-bi-2-pyrazoline]-5,5′-dione (III). A solution of 1-phenyl-3,4-dimethyl-5-pyrazolone (5.8 g) and 1-phenyl-3,4-dimethyl-4-bromo-5-pyrazolone [3] (8.0 g) in alcohol (150 ml) was mixed with 100 ml of acetate buffer (four parts of 1.8 *N* sodium acetate solution per part of 1.8 *N* acetic acid solution) and 5 ml of a 0.01 % solution of $CuSO_4 \cdot 5\ H_2O$. The next day white crystals had formed (by increasing the cupric ion concentration the reaction rate can be increased). They were filtered

* In this paper the radicals II a, b and c will be represented by $PyCH_3$.

by suction and washed successively with 60 % and 96 % alcohol. The combined filtrate and washings were precipitated with water, and the precipitate was recrystallized from alcohol. Yield 95 %. After recrystallization from acetic acid the product melted at 165° C alone or mixed with the $Py(CH_3) \cdot PyCH_3$ product of Knorr. (Found: C 70.4; H 5.9. $(C_{11}H_{11}ON_2)_2$ (374.4) requires C 70.6; H 5.9).

REFERENCES

1. Knorr, L. *Ann.* **238** (1887) 154.
2. Smith, L. *Kgl. Fysiograf. Sällskap Lund Förh.* **18** (1948) No 1, 3.
3. Westöö, G. *Acta Chem. Scand.* **6** (1952) 1499.
4. Biquard, D., and Grammaticakis, M. P. *Bull. soc. chim.* **8** (1941) 246.
5. Valyashko, N. A., and Bliznyukov, V. I. *J. Gen. Chem. U.S.S.R.* **10** (1940) 1343; **11** (1941) 23.

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