

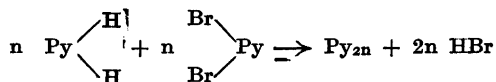
Studies on Pyrazolones

VII. Brominating Action of 1-Phenyl-3-methyl-4,4-dibromo-5-pyrazolone and 1-Phenyl-3,4-dimethyl-4-bromo-5-pyrazolone

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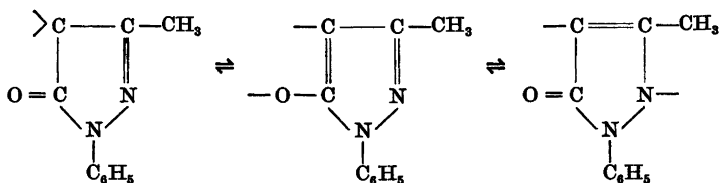
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During investigations of the couplings of 4-bromo-5-pyrazolones, some anomalous reactions were encountered. Thus furlone yellow¹ can be prepared from a buffered solution of 1-phenyl-3-methyl-5-pyrazolone and 1-phenyl-3-methyl-4,4-dibromo-5-pyrazolone. This reaction seems to contradict the formulation of furlone yellow as a Py_3^* -compound, for a condensation between the pyrazolone and the dibromopyrazolone ought to give rise to a Py_{2n} -product according to the equation:



Further, 1-*p*-bromophenyl-3-methyl-5-pyrazolone reacts with 1-phenyl-3-methyl-4,4-dibromo-5-pyrazolone to give a mixture containing 1,1'-diphenyl

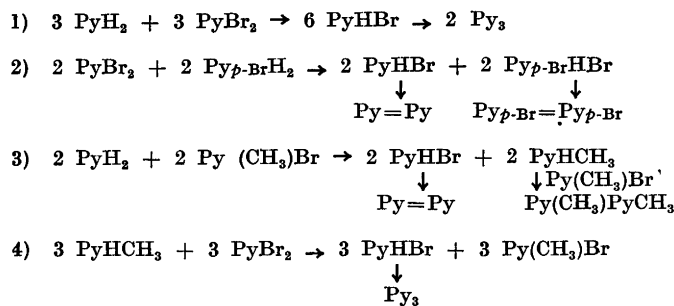
* Py is used to represent the radicals



3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione and 1,1'-di-*p*-bromophenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione.

Furthermore, attempts to prepare 1,1',1''-triphenyl-3,3',3'',4,4''-penta-methyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione from 1-phenyl-3-methyl-5-pyrazolone and 1-phenyl-3,4-dimethyl-4-bromo-5-pyrazolone² or from 1-phenyl-3,4-dimethyl-5-pyrazolone and 1-phenyl-3-methyl-4,4-dibromo-5-pyrazolone have not been successful. In the first case pyrazole blue or 1,1'-diphenyl-3,3',4,4'-tetramethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione has been obtained, in the second furlone yellow.

All these reactions can be explained by assuming that the bromo-compounds act as brominating agents:



It is known that replacement of a hydrogen of an acidic methylene group by bromine may give a product that can act as a brominating agent. Dibromobarbituric acid³, ethyl α -bromoacetoacetate⁴ and dibromomalodinitrile⁵ are examples of such products.

The formation of the suggested intermediates in reactions 1—3 is demonstrated by light absorption measurements on ethanol solutions of the reactants (Figs. 1 and 2; buffer and catalyst are excluded to eliminate the condensation reactions) and also by titration with sodium hydroxide solution, the right sides of the equations containing twice as many equivalents of acid as the left ones. The titrations accelerate the reactions by consuming the acids and consequently show rapid and complete brominations.

The above is in accordance with the electron-seeking character of the bromine atoms in 1-phenyl-3-methyl-4,4-dihalo-5-pyrazolones and 1-phenyl-3,4-dimethyl-4-halo-5-pyrazolones indicated in a previous paper².

Light Absorption Spectra. In the diagrams $\log \epsilon = \log \log \frac{I_0}{I} - \log l \cdot c$ is plotted against the wave length λ . When several light absorbing substances are present in the same solution, c is the total concentration of pyrazolone.

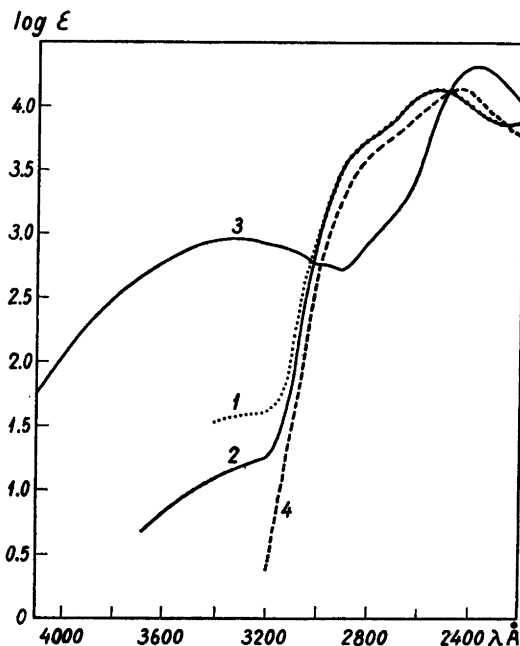


Fig. 1. 1) 1-Phenyl-3-methyl-5-pyrazolone and 1-phenyl-3-methyl-4,4-dibromo-5-pyrazolone in ethanol (both in $1.9 \cdot 10^{-3}$, $1.9 \cdot 10^{-4}$ and $1.9 \cdot 10^{-5}$ M solutions) measured $1\frac{1}{2}$ hours after the preparation of the solution. 2) 1-Phenyl-3-methyl-4-bromo-5-pyrazolone in ethanol ($4.0 \cdot 10^{-3}$, $4.0 \cdot 10^{-4}$ and $4.0 \cdot 10^{-5}$ M solutions). 3) 1-Phenyl-3-methyl-4,4-dibromo-5-pyrazolone in ethanol ($4.0 \cdot 10^{-3}$, $4.0 \cdot 10^{-4}$ and $4.0 \cdot 10^{-5}$ M solutions). 4) 1-Phenyl-3-methyl-5-pyrazolone in ethanol ($7.3 \cdot 10^{-3}$, $7.3 \cdot 10^{-4}$ and $7.3 \cdot 10^{-5}$ M solutions).

EXPERIMENTAL

Reactions between 1-Phenyl-3-methyl-5-pyrazolone and 1-Phenyl-3-methyl-4,4-dibromo-5-pyrazolone

1. *Formation of Furlone Yellow.* PyBr_2 (1.31 g) and PyH_2 (0.72 g) were dissolved in alcohol (65 ml). Sodium acetate (20 ml of 1.8 N solution), acetic acid (20 ml of 1.8 N solution) and catalyst (0.8 ml of a 0.01 % solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were added. The next day the yellow crystals which had deposited were filtered by suction and washed with 60 % alcohol. After one recrystallization from alcohol they melted at 157°C with decomposition; yield 0.80 g (59 %). (Found: C 69.6; H 4.7. Calc. for $(\text{C}_{10}\text{H}_8\text{ON}_2)_3$: C 69.7; H 4.7.) The light absorption spectra are identical for this product and furlone yellow, prepared from 1-phenyl-3-methyl-4-bromo-5-pyrazolone.

2. *Titration of an Ethanol Solution of the System $\text{PyH}_2 + \text{PyBr}_2 \rightarrow 2 \text{PyHBr}$.* An ethanol solution prepared from 1.00 millimole of PyH_2 and 1.00 millimole of PyBr_2 consumed 2.00 milliequivalents of sodium hydroxide on titration against thymolphthalein. No hydrogen bromide had been liberated. Thus PyHBr had been formed quantitatively.

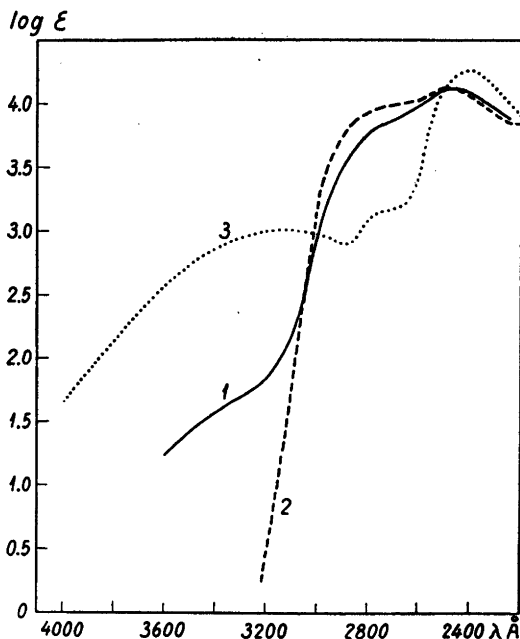


Fig. 2. 1) 1-Phenyl-3-methyl-5-pyrazolone ($2.4 \cdot 10^{-3}$, $2.4 \cdot 10^{-4}$ and $2.4 \cdot 10^{-5}$ M solutions) and 1-phenyl-3,4-dimethyl-4-bromo-5-pyrazolone ($2.3 \cdot 10^{-3}$, $2.3 \cdot 10^{-4}$ and $2.3 \cdot 10^{-5}$ M solutions) in 55 % ethanol measured 25 hours after the preparation of the solution. 2) 1-Phenyl-3,4-dimethyl-5-pyrazolone in ethanol ($2.1 \cdot 10^{-2}$, $4.5 \cdot 10^{-3}$, $4.5 \cdot 10^{-4}$ and $4.5 \cdot 10^{-5}$ M solutions). 3) 1-Phenyl-3,4-dimethyl-4-bromo-5-pyrazolone in ethanol ($4.0 \cdot 10^{-3}$, $4.0 \cdot 10^{-4}$ and $4.0 \cdot 10^{-5}$ M solutions).

3. *Light Absorption.* According to the light absorption measurements, 1-phenyl-3-methyl-4-bromo-5-pyrazolone had been formed in 95 % yield after 90 minutes when the initial concentrations of 1-phenyl-3-methyl-5-pyrazolone and 1-phenyl-3-methyl-4,4-dibromo-5-pyrazolone were $1.9 \cdot 10^{-3}$ moles per liter of ethanol (calculated on the assumption that Beer's law is valid from the values at 3 300 Å: $\log \frac{I_0}{I} = 0.147$, $\epsilon_{\text{PyHBr}} = 15.4$, $\epsilon_{\text{PyBr}_2} = 922$ and ϵ_{PyH_2} negligible).

Reactions between 1-Phenyl-3-methyl-5-pyrazolone and 1-Phenyl-3,4-dimethyl-4-bromo-5-pyrazolone

1. *Formation of Pyrazole Blue.* PyH_2 and excess $\text{Py}(\text{CH}_3)_2\text{Br}$ were dissolved in alcohol. When a few ml of a 3 % solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added, pyrazole blue precipitated.

2. *Formation of 1,1'-Diphenyl-3,3',4,4'-tetramethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione.* PyH_2 (0.8 g) and $\text{Py}(\text{CH}_3)_2\text{Br}$ (2.5 g) were dissolved in alcohol (100 ml), and sodium acetate (33 ml of 1.8 N solution), acetic acid (33 ml of 1.8 N solution) and catalyst (1.3 ml of a 0.01 % solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were added. White crystals (0.67 g) precipitated in the

course of three hours. After several crystallizations from acetic acid they melted at 165° C alone and mixed with 1,1'-diphenyl-3,3',4,4'-tetramethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione. The light absorption curves of the two products were identical.

3. *Titration of an Ethanol Solution of the System* $\text{PyH}_2 + \text{Py}(\text{CH}_3)\text{Br} \rightarrow \text{PyHBr} + \text{PyHCH}_3$. An alcohol solution of 1.00 millimole of both PyH_2 and $\text{Py}(\text{CH}_3)\text{Br}$ consumed 2.00 milliequivalents of sodium hydroxide on titration with thymolphthalein as indicator. No hydrogen bromide had been split off. Thus PyHBr and PyHCH_3 were formed quantitatively during the titration.

4. *Light Absorption Measurement.* The reaction $\text{PyH}_2 + \text{Py}(\text{CH}_3)\text{Br} \rightarrow \text{PyHBr} + \text{PyHCH}_3$ is slow in ethanol solution but can be accelerated by the addition of water. This is the reason why the light absorption has been measured in dilute alcohol (Fig. 2). In spite of the long reaction time no hydrogen bromide was split off. The first part of equation 3 was realized to 90 per cent after 25 hours in the 2.3–2.4 *M* solution of the reactants in 55 per cent alcohol (at $\lambda = 3300 \text{ \AA}$: $\log \frac{I_0}{I} = 0.235$, $\epsilon_{\text{PyBrCH}_3} = 875$, $\epsilon_{\text{PyHBr}} = 15.4$, ϵ_{PyH_2} and $\epsilon_{\text{PyHCH}_3}$ negligible).

Reaction between 1-Phenyl-3-methyl-4-alkyl-5-pyrazolone and 1-Phenyl-3-methyl-4,4-dibromo-5-pyrazolone

To a solution of PyHC_2H_5 or PyHCH_3 (1.2 g) and PyBr_2 (1.7 g) in alcohol (75 ml) were added 25 ml of 1.8 *N* acetic acid, 25 ml of 1.8 *N* sodium acetate solution and 2.5 ml of a 0.01 % $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution. The next day yellow crystals (0.4 g) were collected by filtration and recrystallized from alcohol; m.p. 157° C with decomposition. (Found: C 69.4; H 4.6. Calc. for $(\text{C}_{10}\text{H}_8\text{ON}_2)_3$ (516.6): C 69.7; H 4.7.) Light absorption curves are identical for this product and furlone yellow.

SUMMARY

1-Phenyl-3-methyl-4,4-dibromo-5-pyrazolone and 1-phenyl-3,4-dimethyl-4-bromo-5-pyrazolone act as brominating agents.

REFERENCES

1. WestöÖ, G. *Acta Chem. Scand.* **7** (1953) 360.
2. WestöÖ, G. *Acta Chem. Scand.* **6** (1952) 1499.
3. Gupta, B. M., and Thorpe, J. F. *J. Chem. Soc.* **121** (1922) 1896.
4. Kröhnke, F., and Timmler, H. *Ber.* **69** (1936) 614.
5. Ramberg, L., and Widequist, S. *Arkiv Kemi, Mineral. Geol.* **12 A** (1937) No 22.

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