

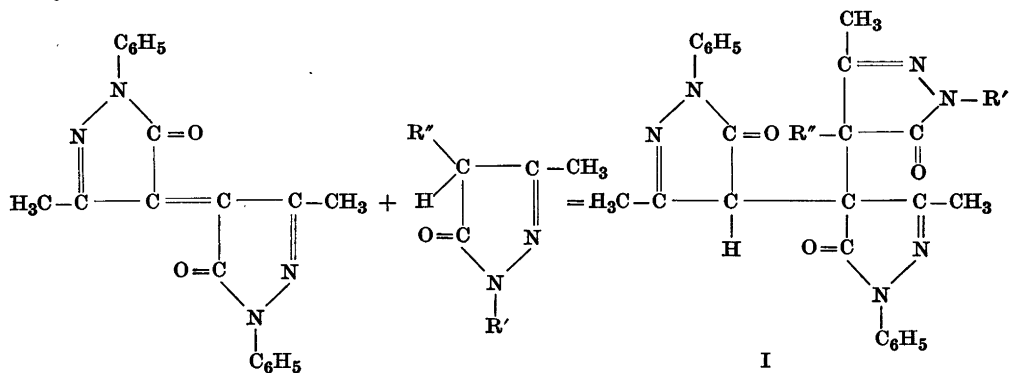
## Studies on Pyrazolones

### III. Michael Condensations between Pyrazole Blue and the Addenda 1-Phenyl-3-methyl-5-pyrazolone, 1-*p*-Bromophenyl-3-methyl-5-pyrazolone and 1-Phenyl-3-methyl-4-bromo-5-pyrazolone

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A chloroform solution of pyrazole blue is easily decolorized by 1-aryl-3-methyl-5-pyrazolones, Michael condensations taking place. Reactions of this kind usually require catalyzing by amines or sodium alkoxides (*cf.* Ingold and Powell <sup>1</sup>, Kloetzel <sup>2</sup>, Kohler and Dewey <sup>3</sup>), but the double bond system of pyrazole blue is so reactive that the additions proceed smoothly without catalyst even at room temperature.



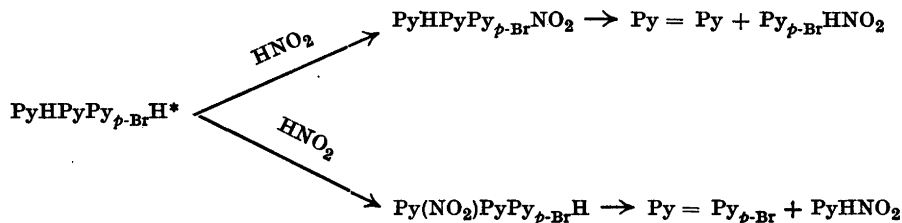
Pyrazole blue

- |   |         |
|---|---------|
| a) R' = C <sub>6</sub> H <sub>5</sub> ;             | R' = H  |
| b) R' = <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> ; | R' = H  |
| c) R' = C <sub>6</sub> H <sub>5</sub> ;             | R' = Br |

From pyrazole blue and 1-phenyl-3-methyl-5-pyrazolone the white 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione (I a) is formed. It is insoluble in ether but markedly more soluble in ethanol than is the corresponding bis-compound, 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione. Like 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione the terpyrazolone gives pyrazole blue with nitrous acid.

Of especial interest is the reaction with nitrous acid of 1,1'-diphenyl-1''-*p*-bromophenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione (I b). Here a mixture of 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione (pyrazole blue) and 1-phenyl-1''-*p*-bromophenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione is obtained. This proves that in the adducts C—C bonds exist between the three carbon atoms at the 4-positions and consequently that the formulas I a and b are correct. The light absorption spectrum (Fig. 1) and the equivalent weight (258) of 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione are in agreement with this view.

The mechanism of the reaction between the terpyrazolone and nitrous acid is supposed to be the following:



Decoloration of a chloroform solution of pyrazole blue by 1-phenyl-3-methyl-4-bromo-5-pyrazolone is possible only with an excess of the bromopyrazolone. Attempts to purify the adduct have not been successful as they cause partial decomposition with recovery of pyrazole blue.



The velocities of both addition and decomposition are increased by alkalis, diminished by acids.

\* Py is used to represent the radicals

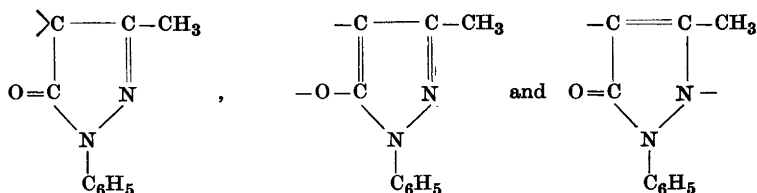
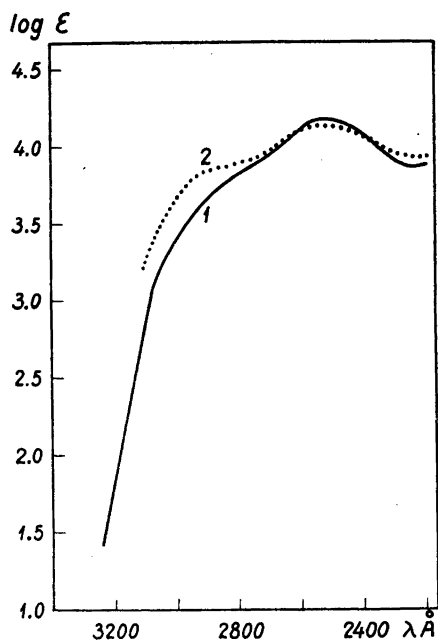


Fig. 1.  $\log \epsilon = \log \log \frac{I_0}{I} - \log c \cdot l$  is plotted against the wave length. The concentration,  $c$ , of the substances is expressed in pyrazolone units per liter. 1) 1,1',1''-Triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione in ethanol ( $3.2 \cdot 10^{-3}$ ,  $3.2 \cdot 10^{-4}$  and  $3.2 \cdot 10^{-5}$  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).



It is likely that 1-phenyl-3-methyl-4-bromo-5-pyrazolone should add to pyrazole blue in the same way as does 1-phenyl-3-methyl-5-pyrazolone, especially as 1-phenyl-3,4-dimethyl-4-halo-5-pyrazolones and 1-phenyl-3-methyl-4,4-dihalo-5-pyrazolones do not decolorize a pyrazole blue solution. Furthermore, when a solution of 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione is brominated with the equimolar amount of bromine in buffered ( $p_H \sim 9$ ) solution, pyrazole blue precipitates immediately. It follows that a PyHPyPyBr compound of the structure II c dissociates in the same way as does the adduct from 1-phenyl-3-methyl-4-bromo-5-pyrazolone and pyrazole blue. This supports the view that they are identical. A reduced stability of the bromo compound is to be expected for the substitution diminishes the opportunities for resonance.

#### EXPERIMENTAL

1,1',1''-Triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione (I a) from 1-Phenyl-3-methyl-5-pyrazolone and Pyrazole Blue. Py = Py (2.0 g) and  $PyH_2$  (1.05 g) in chloroform (25 ml) were boiled about ten minutes. A white precipitate and a colourless solution resulted. With excess  $PyH_2$  the reaction took place rapidly also at room temperature. The precipitate was filtered from the cooled mixture and washed with chloro-

form and ether. Yield 2.95 g (97 %). The last traces of solvents were removed by heating the product several hours *in vacuo* (100° C, 0.5 mm Hg) over silica gel. It was then a hygroscopic powder. Found: C 69.3, H 5.0, N 16.20, equiv. wt. 259 on titration against phenolphthalein.  $C_{30}H_{26}O_3N_6$  (518.6) requires C 69.5, H 5.0, N 16.21, equiv. wt. 259. Light absorption curve, see Fig. 1. M.p. about 200° C with decomposition.

From the solution in alcohol of 1,1',1''-triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione a stabler crystal form separates when the walls of the beaker are scratched. Also this stable form is more soluble in ethanol than is 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione.

*1,1'-Diphenyl-1''-p-bromophenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione (I b) from 1-p-Bromophenyl-3-methyl-5-pyrazolone and Pyrazole Blue.* HPyPyPy<sub>p-Br</sub>H was prepared and dried analogously to HPyPyPyH. From 0.246 g of Py<sub>p-Br</sub>H<sub>2</sub> and 0.331 g of Py = Py in 10 ml of chloroform, 0.543 g of HPyPyPy<sub>p-Br</sub>H was obtained (95 % yield). The colourless, hygroscopic product melted at about 200° C with decomposition. It is only slightly soluble in alcohol, insoluble in ether. Found: C 60.2, H 4.1, N 14.05, Br 13.3, equiv. wt. 299. Calc. for  $C_{30}H_{25}BrO_3N_6$  (597.5): C 60.3, H 4.2, N 14.07, Br 13.4, equiv. wt. 299.

*Reaction between 1,1',1''-Triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione and Nitrous Acid.* HPyPyPyH (1.40 g) and excess sodium nitrite were dissolved in 2.5 N sodium hydroxide solution and poured into 5 N sulphuric acid with stirring. A few ml of ether were added to prevent foaming. The blue precipitate formed was filtered by suction, washed with water and extracted with boiling ethanol for half a minute. Pyrazole blue (0.92 g, 99 %) remained and was collected by filtration, washed with ethanol and air-dried. It was purified by solution in chloroform and precipitation with ether. (Found: N 16.3. ( $C_{10}H_8ON_2$ )<sub>2</sub> (344.4) requires N 16.3.) Evaporation of the ethanolic extract gave 0.55 g of yellow needles from which almost colourless 1-phenyl-3-methyl-4-nitro-5-pyrazolone (m.p. 129° C with decomposition; cf. Knorr<sup>4</sup>) was isolated (extraction of impurities with ether, recrystallization from ethanol). Found: C 55.1, H 4.3.  $C_{10}H_9O_3N_3$  (219.2) requires C 54.8, H 4.1.

*Reaction between 1,1'-Diphenyl-1''-p-bromophenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione and Nitrous Acid.* PyHPyPy<sub>p-Br</sub>H (5.5 g) was dissolved in 2.5 N sodium hydroxide solution containing an excess of sodium nitrite, and the solution was added to 5 N sulphuric acid with stirring. The blue reaction product was filtered by suction and washed with water, alcohol and ether. Yield 3.2 g (91 % calculated according to the equation p. 356). The substance was purified by precipitation with ether from its solution in chloroform. Found: C 63.0, H 4.1, Br 8.8. Calc. for Py = Py, ( $C_{10}H_8ON_2$ )<sub>2</sub>, (344.4): C 69.7, H 4.7. Calc. for Py = Py<sub>p-Br</sub>,  $C_{20}H_{15}BrO_2N_4$ , (423.3): C 56.7, H 3.6, Br 18.9.

#### SUMMARY

1,1',1''-Triphenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione and 1,1'-diphenyl-1''-p-bromophenyl-3,3',3''-trimethyl-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione have been prepared for the first time. The analogous 1,1',1''-triphenyl-3,3',3''-trimethyl-4-bromo-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione is unstable and dissociates into pyrazole blue and 1-phenyl-3-methyl-4-bromo-5-pyrazolone in not too acid solutions.

## REFERENCES

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