

## Studies on Pyrazolones

VI. 1,1',1''-Tri-*p*-tolyl-3,3',3''-trimethylfurlone and  
1,1',1''-Tri-*o*-tolyl-3,3',3''-trimethylfurlone

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The present paper describes the synthesis of two new furlone yellows, 1,1',1''-tri-*p*-tolyl-3,3',3''-trimethylfurlone and 1,1',1''-tri-*o*-tolyl-3,3',3''-trimethylfurlone. They were prepared from 1-*p*- and 1-*o*-tolyl-3-methyl-4-bromo-5-pyrazolone, respectively, by the procedure used for furlone yellow<sup>1</sup> itself except that the reaction medium was acetone instead of alcohol. This change improves the yield of furlone yellows, as shown by an experiment in which the yield of 1,1',1''-triphenyl-3,3',3''-trimethylfurlone was increased from 65 per cent to 87 per cent by substituting acetone for alcohol. The cause of lower yields in alcoholic media is that pyrazole blues are transient intermediates, and these, as was recently shown<sup>2</sup>, can react with alcohols to give other products.

The light absorption spectra of the two new furlone yellows are shown in Fig. 1. The spectrum of the *ortho* compound is shifted to lower wave-lengths and has smaller extinction coefficients than that of the *para* compound, which is similar to spectra of known unsubstituted and *para*-substituted furlone yellows<sup>1</sup>. The light absorption spectrum of 1-*o*-tolyl-3-methyl-4-bromo-5-pyrazolone differs similarly from the spectra of 1-phenyl-3-methyl-4-bromo-5-pyrazolone<sup>3</sup> and 1-*p*-tolyl-3-methyl-4-bromo-5-pyrazolone (Fig. 2).

## EXPERIMENTAL

*1,1',1''-Triphenyl-3,3',3''-trimethylfurlone.* 1-Phenyl-3-methyl-4-bromo-5-pyrazolone (1.36 g) was dissolved in acetone (90 ml), and acetic acid (30 ml of 1.8 *N* solution), sodium acetate (30 ml of 1.8 *N* solution) and copper sulphate (1.6 ml of 0.01 % CuSO<sub>4</sub> · 5H<sub>2</sub>O solution) were added. The next day the yellow crystals formed (0.70 g) were filtered by

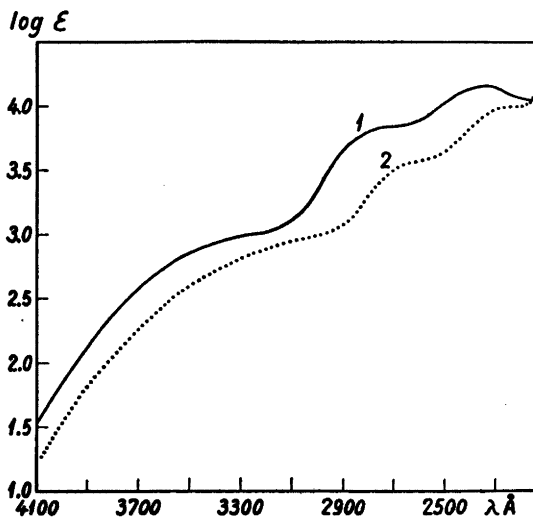


Fig. 1. 1) *1,1',1''-Tri-p-tolyl-3,3',3''-trimethylfurlone in ethanol* ( $2.0 \cdot 10^{-3}$ ,  $2.0 \cdot 10^{-4}$  and  $2.0 \cdot 10^{-5}$  M solutions). 2) *1,1',1''-Tri-o-tolyl-3,3',3''-trimethylfurlone in ethanol* ( $1.7 \cdot 10^{-3}$ ,  $1.7 \cdot 10^{-4}$  and  $1.7 \cdot 10^{-5}$  M solutions).

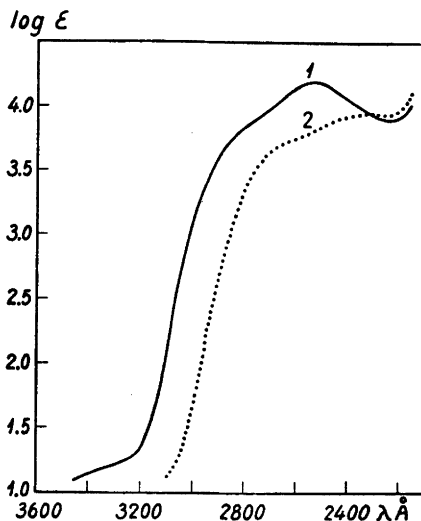


Fig. 2. 1) *1-p-Tolyl-3-methyl-4-bromo-5-pyrazolone in ethanol* ( $8.5 \cdot 10^{-3}$ ,  $8.5 \cdot 10^{-4}$  and  $8.5 \cdot 10^{-5}$  M solutions). 2) *1-o-Tolyl-3-methyl-4-bromo-5-pyrazolone in ethanol* ( $5.7 \cdot 10^{-3}$ ,  $5.7 \cdot 10^{-4}$  and  $5.7 \cdot 10^{-5}$  M solutions).

suction and washed with water and alcohol. From the combined filtrate and washings an additional 0.11 g of furlone yellow was obtained by precipitation with water, filtration, washing with water and recrystallization from alcohol. Yield 87 %. M. p. 158° C with decomposition. (Found: C 69.7; H 4.7. Calc. for  $(C_{10}H_8ON_2)_3$  (516.6): C 69.7; H 4.7.)

*1,1',1''-Tri-p-tolyl-3,3',3''-trimethylfurlone.* *1-p-Tolyl-3-methyl-4-bromo-5-pyrazolone* (1.91 g) in acetone (100 ml) was buffered with acetic acid (30 ml of 1.8 N solution) and sodium acetate (30 ml of 1.8 N solution). Cupric catalyst (2 ml of 0.01 %  $CuSO_4 \cdot 5H_2O$  solution) was added. The solution deposited 1.05 g of yellow crystals in the course of 12 hours at room temperature. These were filtered by suction, washed with water and alcohol, and air-dried. From the combined filtrate and washings another 0.05 g was obtained by precipitation with water and recrystallization from alcohol. Yield 83 %. M. p. 172° C (decomposes) after crystallization from alcohol. (Found: C 70.8; H 5.3; N 15.02. Calc. for  $(C_{11}H_{10}ON_2)_3$  (558.6): C 70.95; H 5.4; N 15.05.)

*1,1',1''-Tri-o-tolyl-3,3',3''-trimethylfurlone.* *1-o-Tolyl-3-methyl-4-bromo-5-pyrazolone* (1.02 g) in acetone (50 ml) was buffered with 30 ml of a solution 0.9 N in acetic acid and sodium acetate. Copper catalyst (3 ml of 0.01 %  $CuSO_4 \cdot 5H_2O$  solution) was added, and the solution was left at room temperature over night. Faintly-yellow crystals deposited. They were purified as described in the preceding synthesis. Yield 0.36 g (51 %). M. p. 162.5–163.5° C (decomposes) after crystallization from alcohol. (Found: C 70.7; H 5.3; N 15.00. Calc. for  $(C_{11}H_{10}ON_2)_3$  (558.6): C 70.95; H 5.4; N 15.05.)

*Light Absorption Measurements.* In the diagrams  $\log \epsilon = \log \log \frac{I_0}{I} - \log l \cdot c$  is plotted against the wave-length  $\lambda$ . The concentration,  $c$ , is counted in pyrazolone units per liter solution.

## REFERENCES

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