

## Studies on Pyrazolones

### IV. Condensation Reactions with Certain 1-Aryl-3-methyl-4-halo-5-pyrazolones

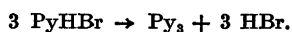
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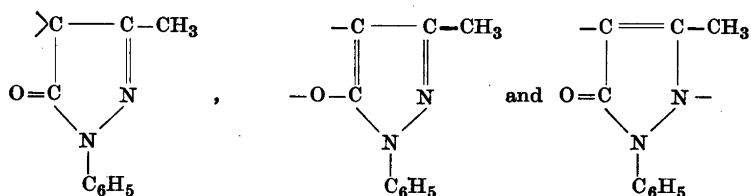
In 1887 Knorr<sup>1</sup> prepared pyrazole blue by the coupling of two molecules of 1-phenyl-3-methyl-4-bromo-5-pyrazolone. In the present investigation the formation of another condensation product (here called furlone yellow) has been achieved by interaction of three molecules of the same bromo-compound.

When an alcoholic solution of 1-phenyl-3-methyl-4-bromo-5-pyrazolone is neutralized with sodium hydroxide solution, crystals of furlone yellow soon precipitate. Furlone yellow can also be obtained from buffered solutions of 1-phenyl-3-methyl-4-halo-5-pyrazolones. Small amounts of cupric ions catalyze the reaction, hydrogen ions retard it (*cf.* Smith<sup>2</sup>). A solubility curve according to Kunitz and Northrup<sup>3</sup> (Fig. 1) indicates that the product is a single compound.

Furlone yellow has the same C-, H- and N-content as pyrazole blue. It is free from bromine and active hydrogen atoms. Ebullioscopic measurements of the molecular weight suggest a  $\text{Py}_3^x$ -formula. Because of these facts it is a ring product formed according to the equation



\* Py represents the radicals



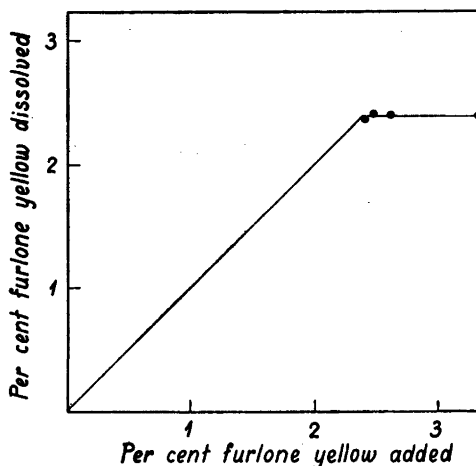


Fig. 1. Solubility diagram of furlone yellow in benzene-petroleum ether (1:1).

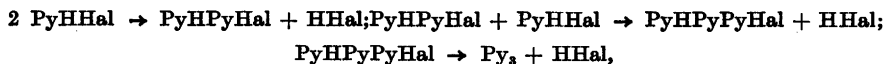
It is soluble in benzene, acetone, chloroform and ether but only slightly soluble in ethanol at room temperature. When heated it melts with decomposition at 158° C. Consequently it is not identical with the yellow substance prepared by Smith<sup>2,p.7</sup>.

Furlone yellow decomposes rapidly in alkaline solution yielding an orange-red colour. With concentrated sulphuric acid and ferric chloride it gives a red colour. With zinc chloride, hydrogen chloride and water a colourless, very unstable double compound of the composition  $\text{Py}_3 \cdot \text{ZnCl}_2 \cdot 2\text{HCl} \cdot 2\text{H}_2\text{O}$  is formed.

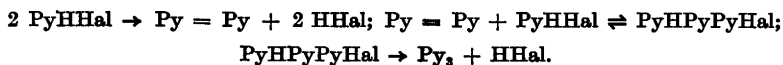
Furlone yellow reacts slowly with hydrogen chloride in ether solution with formation of the slightly soluble salt  $\text{PyHPyH} \cdot 2\text{HCl}$ . The reaction proceeds via several steps. Initially a colourless addition product from furlone yellow and hydrogen chloride is formed, from which unchanged furlone yellow is easily regained. After a while white crystals separate, which are probably the hydrochloride of  $\text{PyHPyCl}$ . The chloro-compound is then slowly reduced to  $\text{PyHPyH} \cdot 2\text{HCl}$ . The mother liquor from the filtration of  $\text{PyHPyH} \cdot 2\text{HCl}$  gives pyrazole blue when diluted with alcohol.

From the decomposition with hydrogen chloride, it is evident that two of the three pyrazolone groups of furlone yellow are coupled together at their C-4 positions, but *a priori* very little can be deduced about the way the third pyrazolone unit is attached to the rest. A study of the intermediate products in the formation of furlone yellow will give further information.

At first sight it seems probable that furlone yellow is formed according to the equations:



1,1'-diphenyl-3,3'-dimethyl-4-halo-[4,4'-bi-2-pyrazoline]-5,5'-dione being an intermediate. However, repeated attempts to prepare PyHPyBr only resulted in rapid precipitation of pyrazole blue. PyHPyCl was obtained by addition of hydrogen chloride to pyrazole blue in ether, but on dilution pyrazole blue was recovered. Thus PyHPyCl, which is undoubtedly more stable than PyHPyBr, can exist only in an environment too acid to allow a reaction with PyHHal. Accordingly, the velocity of the splitting off of HHal from PyHPyHal is very great in not too acid medium and must far exceed the velocity of the condensation with PyHHal. This indicates that furlone yellow is not formed by a reaction between PyHPyHal and PyHHal but via pyrazole blue and consequently by reaction between pyrazole blue and 1-phenyl-3-methyl-4-halo-5-pyrazolone.

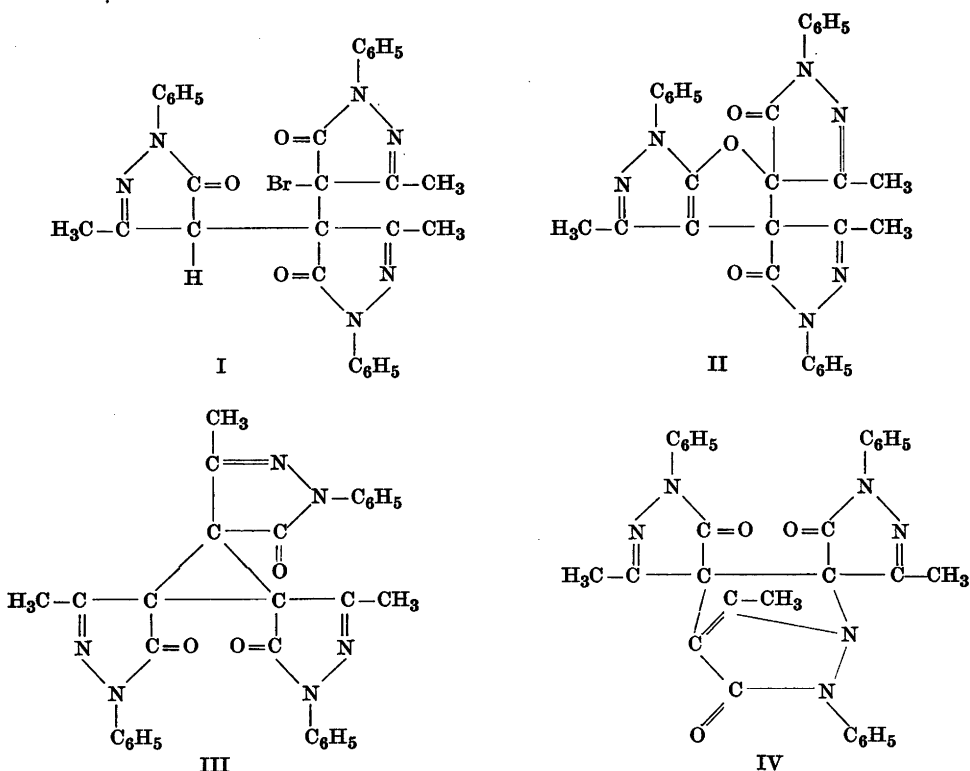


With some precautions — addition of chloroform to dissolve the pyrazole blue, alkaline solution to get the addition reaction sufficiently catalyzed — it was possible to prepare furlone yellow from pyrazole blue and 1-phenyl-3-methyl-4-bromo-5-pyrazolone in 70 per cent yield (calculated on the total amount of pyrazolone). This yield is too great to have had its origin from the PyHBr alone.

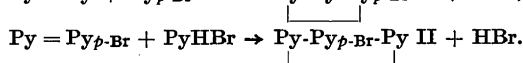
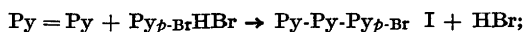
In a previous paper (Westöö<sup>4</sup>) it was shown that the adduct PyHPyPyBr is a 1,1',1''-triphenyl-3,3',3''-trimethyl-4-bromo-[4,4',4''-ter-2-pyrazoline]-5,5',5''-trione (I). Consequently C—C-bonds must exist between all three pyrazolone units in furlone yellow.

The formulas II, III and IV represent potential structures for furlone yellow. Formula IV can be rejected at once for it violates Bredt's rule<sup>5</sup> and does not explain the decomposition reactions with alkali or acid. In favour of III is the fact that in the case of other substances prepared by similar reactions, such as pyrazole blue and 1,1'-diphenyl-3,3',4,4'-tetramethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione<sup>6</sup>, only C—C-bonds are formed. On the other hand formula II is preferable for steric reasons.

A possible way of distinguishing between the formulas II and III is to prepare a furlone yellow product substituted in one of the pyrazolone groups



in two ways so as to place the substituent in different pyrazolone nuclei in the two preparations. If formula III is correct for furlone yellow, identical products or *cis-trans* isomers will be obtained from the two syntheses. Otherwise, two structural isomers will be formed. As substituent bromine in *para* position of the phenyl group was chosen. Thus the two syntheses to be achieved are



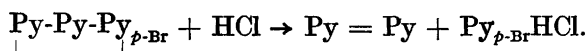
From pyrazole blue and 1-*p*-bromophenyl-3-methyl-4-bromo-5-pyrazolone a yellow compound of the expected properties (decomposition by alkali with orange colour, moderate solubility in benzene, slight solubility in alcohol) could be prepared. The  $\text{Py-Py-Py}_{p\text{-Br}}$  I was contaminated with the corresponding tri-*p*-bromophenyl-compound, from which it was partly separated by fractional precipitation from benzene solution, using alcohol as precipitant. Final purification was accomplished by chromatography on silica gel.

PyHBr and a mixture of  $\text{Py} = \text{Py}$  and  $\text{Py} = \text{Py}_{p\text{-Br}}$  obtained by reaction between  $\text{HPyPyPy}_{p\text{-Br}}\text{H}$  and nitrous acid<sup>4</sup> were used as starting material for  $\text{Py-Py-Py}_{p\text{-Br}}$  II. In the mixture of  $\text{Py-Py-Py}_{p\text{-Br}}$  and  $\text{Py}_3$  obtained, the bromo-compound was the less soluble and could be enriched by dissolution in benzene and precipitation with alcohol. Final purification involved chromatography on silica gel.

The two mono-*p*-bromo-furlone yellows prepared are not identical. This is obvious from the fact that although they have the same composition, they have different decomposition temperatures, 147° C and 161° C respectively, and also different light absorption curves (Fig. 2). Their solubilities in ethanol are different as well. Thus of the latter compound 0.5 mg dissolves per ml of ethanol, of the former four times as much.

*Cis-trans* isomers of III might well show different decomposition temperatures and solubilities, but their light absorption curves should not differ very much. However, the conclusive proof of the relation between the two isomers is given by their decomposition reactions with hydrogen chloride.

When  $\text{Py-Py-Py}_{p\text{-Br}}$  I prepared from pyrazole blue and 1-*p*-bromophenyl-3-methyl-4-bromo-5-pyrazolone was decomposed with hydrogen chloride,  $\text{Py} = \text{Py}$  and  $\text{PyHPyH} \cdot 2\text{HCl}$  were obtained. After oxidation of  $\text{PyHPyH} \cdot 2\text{HCl}$  to give  $\text{Py} = \text{Py}$ , the total yield of pyrazole blue was 60 per cent calculated according to the equation

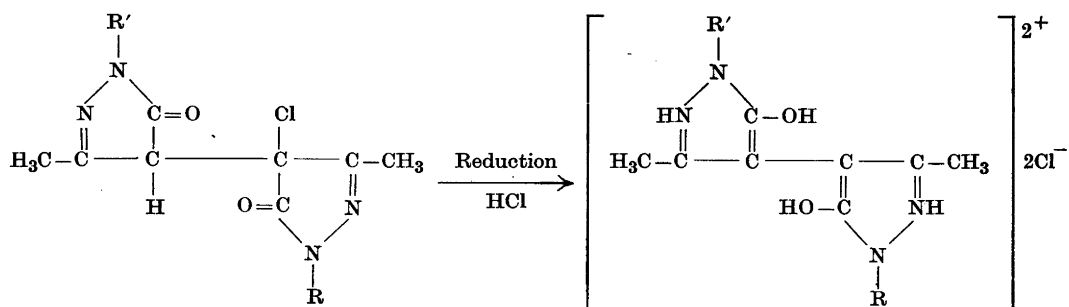
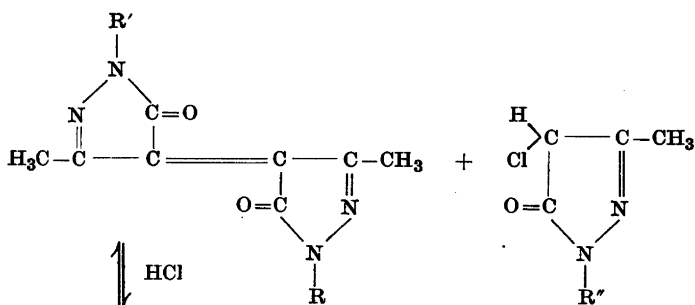
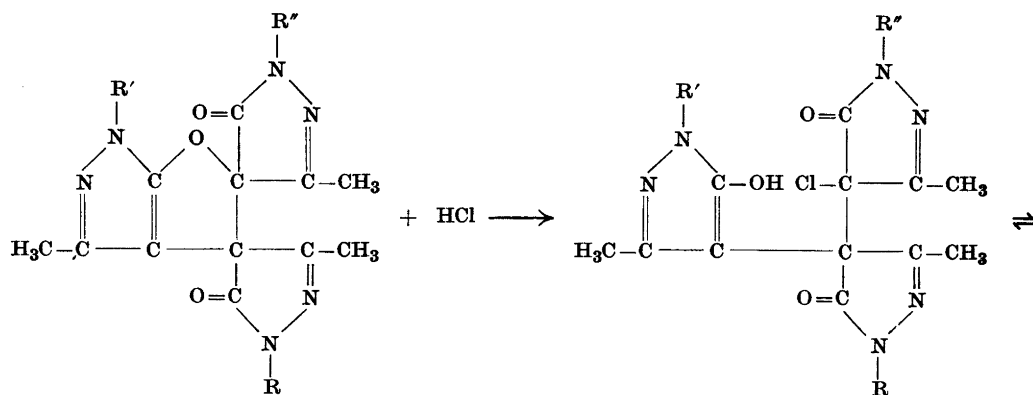


$\text{Py-Py}_{p\text{-Br}}\text{-Py}$  II from  $\text{Py} = \text{Py}_{p\text{-Br}}$  and PyHBr was treated in the same way. Here  $\text{Py} = \text{Py}_{p\text{-Br}}$  and the hydrochloride of  $\text{PyHPy}_{p\text{-Br}}\text{H}$  were obtained in 70 per cent yield.

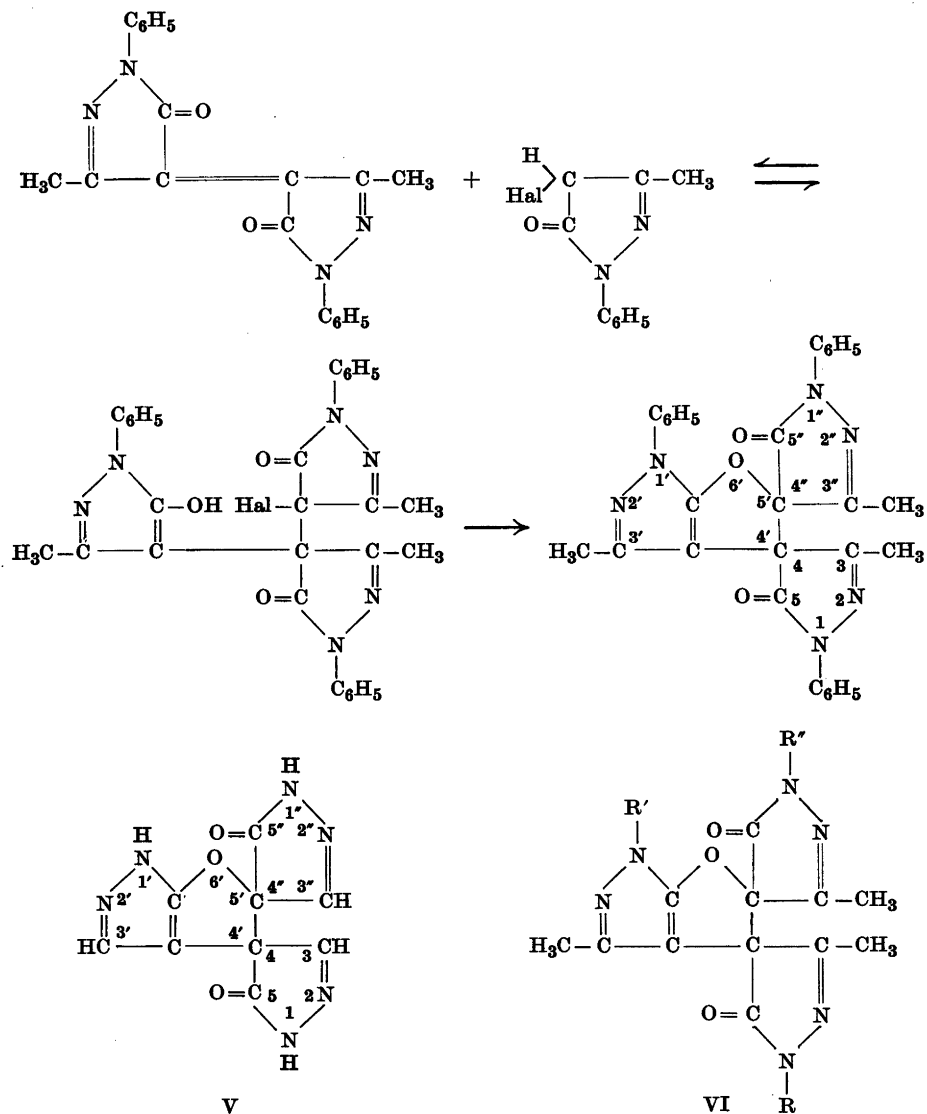
The different products of pyrazole blue type obtained at the decomposition reactions indisputably show that the two mono-*p*-bromo-furlone yellows are neither identical nor *cis-trans* isomers of formula III, but are structural isomers. Consequently formula II is valid for furlone yellow. However, formula II allows the existence of a *cis* and a *trans* form of furlone yellow. Whether only one of them or a mixture of both has been obtained is still in the process of research.

The decomposition of furlone yellow by alkali (p. 361) does not prejudice formula II, for an analogy is found in the behaviour of 1-phenyl-3,4-dimethyl-4-halo-5-pyrazolones. These compounds have the same structure as part of formula II for furlone yellow with a polarizable atom in the 4-position and are destroyed by alkali with the appearance of an orange-red colour.

The chief reactions of furlone yellows with hydrogen chloride can now be written:



Equations for the formation of furlone yellow can be written as follows:

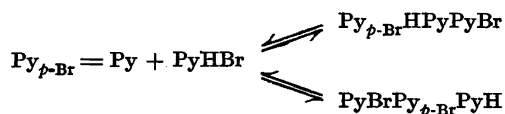


- a)  $R=R'=\text{C}_6\text{H}_5$ ;  $R'=\textit{p}\text{-BrC}_6\text{H}_4$   
 b)  $R=R'=\text{C}_6\text{H}_5$ ;  $R'=\textit{p}\text{-BrC}_6\text{H}_4$   
 c)  $R=\textit{p}\text{-BrC}_6\text{H}_4$ ;  $R'=R'=\text{C}_6\text{H}_5$   
 d)  $R=R'=\text{C}_6\text{H}_5$ ;  $R'=\textit{o}\text{-CH}_3 \cdot \text{C}_6\text{H}_4$   
 e)  $R=R'=\text{C}_6\text{H}_5$ ;  $R'=\textit{p}\text{-C}_6\text{H}_4$   
 f)  $R=R'=\textit{p}\text{-BrC}_6\text{H}_4$ ;  $R'=\textit{o}\text{-CH}_3 \cdot \text{C}_6\text{H}_4$

The systematic name of furlone yellow is 1,1',1''-triphenyl-3,3',3''-trimethyl-dispiro [pyrazole-4(5*H*),4'(5'*H*)-1*H*-furo [2,3-*c*] pyrazole-5',4''(5''*H*)-pyrazole]-5,5''-dione. In order to simplify the nomenclature, the diketone V will be called furlone. Thus furlone yellow is a 1,1',1''-triphenyl-3,3',3''-trimethylfurlone and the bromo-derivative prepared from pyrazole blue and 1-*p*-bromophenyl-3-methyl-4-bromo-5-pyrazolone is 1,1'-diphenyl-1''-*p*-bromophenyl-3,3',3''-trimethylfurlone (VI a).

#### STRUCTURE OF MONO-*p*-BROMO-FURLONE YELLOW II

Although the structures of furlone yellow (II) and of 1,1'-diphenyl-1''-*p*-bromophenyl-3,3',3''-trimethylfurlone (VI a) are settled, the constitution of the bromo-compound prepared from mono-*p*-bromo-pyrazole blue and 1-phenyl-3-methyl-4-bromo-5-pyrazolone is still unknown. Here the addition to the reactive double bond can take place in two ways:



This makes possible the formation of two structural isomers, VI b and c.

By comparing the light absorption curves of some substituted furlone yellows, 1,1'-diphenyl-1''-*o*-tolyl-3,3',3''-trimethylfurlone (VI d), 1,1'-diphenyl-1''-*p*-tolyl-3,3',3''-trimethylfurlone (VI e), 1,1'-diphenyl-1''-*p*-bromophenyl-3,3',3''-trimethylfurlone (VI a) and 1,1'-di-*p*-bromophenyl-1''-*o*-tolyl-3,3',3''-trimethylfurlone (VI f), with the curve of the mono-*p*-bromo-furlone yellow II obtained, it is possible to arrive at the probable structure of this compound. It is evident from the curves (Fig. 2) that the shoulder at 2 600—3 200 Å changes very little on variation of the 4-bromopyrazolone that is added to pyrazole blue to give the furlone yellow compound. Thus the shoulder is the same when Py = Py has reacted with PyHBr, Py<sub>*o*-Me</sub>HBr, Py<sub>*p*-Me</sub>HBr or Py<sub>*p*-Br</sub>HBr. Hence a moderate change of the aryl group in the structure VII has no influence on the shoulder, the intensity of which is nevertheless sure to be influenced by the structure VII as a whole.

The light absorption curves of 1,1'-di-*p*-bromophenyl-1''-*o*-tolyl-3,3',3''-trimethylfurlone (VI f) and mono-*p*-bromofurlone yellow II have shoulders similar to each other, but distinctly different from the corresponding shoulders of all the curves of furlone yellow products prepared from unsubstituted pyrazole blue (VI a, d, e and II). Knowing that the light absorption curves of



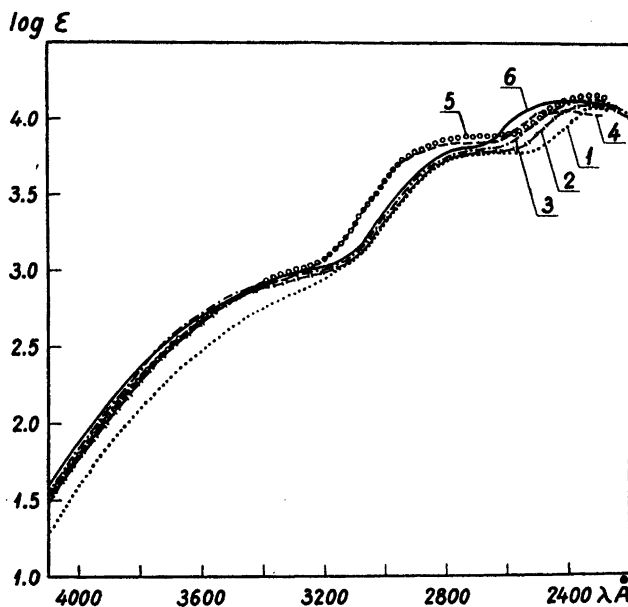
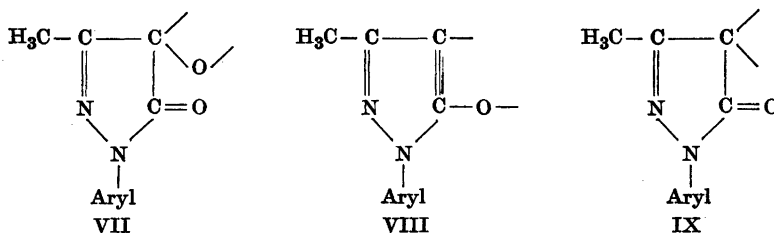


Fig. 2. All the products have been measured in ethanol solution. 1) 1,1'-Diphenyl-1''-o-tolyl-3,3',3''-trimethylfurlone (VI d) ( $2.4 \cdot 10^{-3}$ ,  $2.4 \cdot 10^{-4}$  and  $2.4 \cdot 10^{-5}$  M solutions). 2) 1,1',1''-Triphenyl-3,3',3''-trimethylfurlone (II) ( $1.4 \cdot 10^{-3}$ ,  $1.4 \cdot 10^{-4}$  and  $1.4 \cdot 10^{-5}$  M solutions). 3) 1,1'-Diphenyl-1''-p-tolyl-3,3',3''-trimethylfurlone (VI e) ( $2.7 \cdot 10^{-3}$ ,  $2.7 \cdot 10^{-4}$  and  $2.7 \cdot 10^{-5}$  M solutions). 4) 1,1'-Di-p-bromophenyl-1''-o-tolyl-3,3',3''-trimethylfurlone (VI f) ( $1.3 \cdot 10^{-3}$ ,  $2.6 \cdot 10^{-4}$  and  $2.6 \cdot 10^{-5}$  M solutions). 5) 1-p-Bromophenyl-1''-diphenyl-3,3',3''-trimethylfurlone (VI c) ( $1.9 \cdot 10^{-3}$ ,  $1.9 \cdot 10^{-4}$  and  $1.9 \cdot 10^{-5}$  M solutions). 6) 1,1'-Diphenyl-1''-p-bromophenyl-3,3',3''-trimethylfurlone (VI a) ( $1.9 \cdot 10^{-3}$ ,  $1.9 \cdot 10^{-4}$  and  $1.9 \cdot 10^{-5}$  M solutions).

substances with stable pyrazole structure (VIII) like 1-phenyl-3-methyl-5-methoxypyrazole (Valyashko and Bliznyukov<sup>7</sup>) show only one absorption band of appreciable intensity (at about 2400 Å) and no trace of shoulder or band at 2600–3200 Å, it is reasonable to suppose that the one third of the furlone yellow with that structure does not influence the shoulder either. The part of the molecule with the structure IX remains as a possibility. Substances of this type present shoulders at the wave length considered, e. g.  $\text{Py}(\text{CH}_3)_2$  (Biquard and Grammaticakis<sup>8</sup>) and  $\text{Py}(\text{CH}_3)\text{PyCH}_3$  (Westöo<sup>9</sup>). These facts favour the belief that the latter compound has the constitution VI c and is thus 1-p-bromophenyl-1',1''-diphenyl-3,3',3''-trimethylfurlone.



## EXPERIMENTAL

*1-p-Bromophenyl-3-methyl-4-bromo-5-pyrazolone*, *1-p-Tolyl-3-methyl-4-bromo-5-pyrazolone* and *1-o-Tolyl-3-methyl-4-bromo-5-pyrazolone*. They were prepared analogously to 1-phenyl-3-methyl-4-bromo-5-pyrazolone<sup>9</sup>. However, the hydrobromide of 1-*p*-bromophenyl-3-methyl-4-bromo-5-pyrazolone could not be decomposed into free pyrazolone and acid by water in acetic acid on account of its slight solubility in dilute acetic acid. Hence it was dissolved in alcohol with an excess of 2.5 *N* sodium hydroxide, acidified with dilute sulphuric acid (bromophenol blue as indicator) and precipitated with water. The free pyrazolone precipitated was filtered by suction and washed with water and small amounts of alcohol and ether. It was purified by extraction with chloroform (boiling half a minute) where it is only slightly soluble, followed by crystallization from alcohol. Found: equiv. wt.: 331 (on titration with sodium hydroxide against phenolphthalein).  $\text{C}_{10}\text{H}_8\text{Br}_2\text{ON}_2$  (332.0) requires equiv. wt. 332.

According to Dains, O'Brien and Johnsson<sup>10</sup>, 1-*o*-tolyl-3-methyl-4-bromo-5-pyrazolone is a yellow substance which melts at 116° C. The product obtained here was colourless after one crystallization from chloroform and then melted at 147–149° C with decomposition. Found: C 49.4, H 4.1, Br 29.95, N 10.56, equiv. wt. 267.4.  $\text{C}_{11}\text{H}_{11}\text{BrON}_2$  (267.1) requires C 49.5, H 4.15, Br 29.91, N 10.49, equiv. wt. 267.1.

1-*p*-Tolyl-3-methyl-4-bromo-5-pyrazolone could not be purified by recrystallization from chloroform, unlike PyHBr and  $\text{Py}_{o\text{-Me}}\text{HBr}$ , on account of the small temperature coefficient of its solubility in that solvent. Crystallization from alcohol gave a colourless product which melted with decomposition at 144° C. Found: equiv. wt. 267.3.  $\text{C}_{11}\text{H}_{11}\text{BrON}_2$  (267.1) requires equiv. wt. 267.1.

*1,1'-Di-p-bromophenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione*. This compound was obtained by oxidation of 1-*p*-bromophenyl-3-methyl-5-pyrazolone with phenylhydrazine in the same way that Knorr<sup>1</sup> prepared PyHPyH from  $\text{PyH}_2$ .

*1,1'-Di-p-bromophenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione*. This compound was prepared by oxidation of 1,1'-di-*p*-bromophenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione with nitrous acid in the same way that Knorr<sup>1</sup> prepared pyrazole blue; m.p. 248° C (decomposes). Found: C 47.8, H 2.8, Br 31.7, N 11.12.  $\text{C}_{20}\text{H}_{14}\text{Br}_2\text{O}_2\text{N}_4$  (502.2) requires C 47.8, H 2.8, Br 31.8, N 11.16.

*Furlone Yellow (II)*, *1,1',1''-Triphenyl-3,3',3''-trimethylfurlone*, from 1-Phenyl-3-methyl-4-bromo-5-pyrazolone. 1-Phenyl-3-methyl-4-bromo-5-pyrazolone (5 g) was dissolved in ethanol (150 ml), and sodium acetate (50 ml of 1.8 *N* solution), acetic acid (50 ml of 1.8 *N* solution) and a 0.01 % solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (2 ml) were added. The amount of acetic acid may be diminished or even omitted. The solution was allowed to stand overnight at room temperature, during which time yellow crystals precipitated. They

were filtered by suction and washed successively with 60 % and 95 % alcohol. Yield 65 %. The product, already quite pure, melted with decomposition at 158° C after recrystallization from ethanol. Found: C 69.7, H 4.7, N 16.30.  $(C_{10}H_8ON_2)_3$  (516.6) requires C 69.7, H 4.7, N 16.27. Ebullioscopic measurements of the molecular weight in benzene:  $M = 512$  (1 % solution),  $M = 507$  (2 % solution).

$Py_3 \cdot ZnCl_2 \cdot 2HCl \cdot 2H_2O$ . Furlone yellow was dissolved in concentrated hydrochloric acid and an excess of zinc chloride in the same solvent was added. Scratching the side of the beaker caused white crystals to precipitate. The very unstable product was filtered by suction, washed successively with small amounts of concentrated hydrochloric acid and ether, and air-dried overnight. Found C 46.6, H 4.1, Zn 8.6 (determined as sulphate ash), HCl 9.58 (titration against bromophenol blue),  $Cl^-$  18.62 (potentiometric titration with silver nitrate). Calc. for  $(C_{10}H_8ON_2)_3 \cdot ZnCl_2 \cdot 2HCl \cdot 2H_2O$  (762): C 47.3, H 4.0, Zn 8.6, HCl 9.57,  $Cl^-$  18.62.

*Decomposition of Furlone Yellow with Hydrogen Chloride.* Furlone yellow was dissolved in ether, and the solution was saturated with hydrogen chloride. A colourless solution was obtained. On immediate dilution with ether, the colour changed to yellow. Likewise in concentrated hydrochloric acid and in alcohol containing much hydrochloric acid, colourless solutions were obtained from which unchanged furlone yellow could be regained by dilution with water. When furlone yellow was allowed to remain in the acidic ether for some hours, white crystals precipitated. They were stable in the strongly acid solution, but when the mother liquor was diluted or when the crystals were collected and washed with ether, they rapidly turned into pyrazole blue. The unstable product is probably a hydrochloride of PyHPyCl (cf. p. 362). However, after remaining in the mother liquor four days, the crystals could be filtered, washed with ether and air-dried without change. The stable product was almost insoluble in alcohol. With nitrous acid it gave pyrazole blue. Found: C 56.2, H 4.8, Cl 16.74, 0.46 equiv. of weak acid, 0.92 equiv. of total acid per 100 g of substance on titration in acetone-alcohol solution. PyHPyH.2HCl (419.3) requires C 57.3, H 4.8, Cl 16.91, 0.477 equiv. of weak acid and 0.954 equiv. of total acid per 100 g of substance.

From the mother liquor pyrazole blue was obtained on dilution with alcohol.

*Furlone Yellow, 1,1',1''-Triphenyl-3,3',3''-trimethylfurlone, (II) from Pyrazole Blue and 1-Phenyl-3-methyl-4-bromo-5-pyrazolone.* PyHBr (0.669 g) and Py = Py (0.202 g) were shaken 20 hours with alcohol (20 ml), chloroform (20 ml), sodium acetate (13 ml of 1.8 N solution) and catalyst (0.25 ml of 0.01 %  $CuSO_4 \cdot 5H_2O$  solution).

The chloroform and alcohol were distilled off under reduced pressure. The precipitate formed (wt. 0.621 g) was filtered by suction, washed with water and air-dried. It was recrystallized from alcohol (5 ml), filtered by suction and washed with 5 ml of alcohol. Yellow crystals (0.464 g), which melted with decomposition at 152° C, were obtained. Another crystallization from alcohol (20 ml) resulted in 0.445 g of pure furlone yellow (70 % yield); m.p. 157° C with decomposition.

To prove that the pyrazole blue was really responsible for a considerable amount of the yield, this synthesis was checked by another one with PyHBr alone (0.654 g) as starting material. The procedure was exactly the same as above. A yellow substance weighing 0.420 g was obtained. From the first recrystallization there was obtained 0.296 g of product which melted with decomposition at 152° C. A second recrystallization from 10 ml of alcohol gave 0.259 g of furlone yellow, m.p. 157° C with decomposition.

The comparison of the yields of the two syntheses, 0.445 g and 0.259 g, is significant. The light absorption curves of the two products were identical.

*1,1'-Diphenyl-1''-p-bromophenyl-3,3',3''-trimethylfurlone (VI a) from Pyrazole Blue and 1-p-Bromophenyl-3-methyl-4-bromo-5-pyrazolone.*  $\text{Py}_{p\text{-Br}}\text{HBr}$  (2.05 g),  $\text{Py} = \text{Py}$  (2.55 g), chloroform (600 ml), alcohol (600 ml), sodium acetate (360 ml of 1.80 N solution) and catalyst (12 ml of 0.01 %  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution) were shaken over night. Decoloration occurred. The organic solvents were distilled off under reduced pressure. The precipitate formed during the evaporation was filtered by suction, washed with water and air-dried. After crystallization from alcohol the yield of yellow substance, partially  $(\text{Py}_{p\text{-Br}})_3$ , was 2.55 g. It was fractionated by solution in benzene and precipitation with alcohol, the tribromo-compound being less soluble than the monobromo-compound. The last fraction was dissolved in benzene and chromatographed on silica gel several times.  $(\text{Py}_{p\text{-Br}})_3$  was eluted by benzene + ether (20 : 1),  $\text{PyPy}_{p\text{-Br}}\text{Py}$  with ether. M. p. of the monobromo-compound 147° C with decomposition. Light absorption: Fig. 2. Found: C 60.5, H 3.8, Br 13.1, N 14.1.  $\text{C}_{30}\text{H}_{23}\text{BrO}_3\text{N}_6$  (595.5) requires C 60.5, H 3.9, Br 13.4, N 14.1.

*1-p-Bromophenyl-1''-diphenyl-3,3',3''-trimethylfurlone (VI c) from 1-Phenyl-3-methyl-4-bromo-5-pyrazolone and 1-Phenyl-1''-p-bromophenyl-3,3'-dimethyl-[4,4-bi-2-pyrazoline]-5,5'-dione.* Three and a half g of a mixture of  $\text{Py} = \text{Py}_{p\text{-Br}}$  and  $\text{Py} = \text{Py}$  prepared by oxidation of  $\text{PyHPyPy}_{p\text{-Br}}\text{H}$  with nitrous acid <sup>4</sup> and 2.9 g of  $\text{PyHBr}$  were shaken with chloroform (340 ml) and alcohol (45 ml) for 10 minutes. More alcohol (295 ml), sodium acetate (210 ml of 1.8 N solution) and catalyst (6 ml of 0.01 %  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution) were added, and the mixture was shaken overnight. Concentration of the decolorized solution *in vacuo*, filtration and crystallization from ethanol resulted in 3.15 g of a mixture of  $\text{Py}_3$  and  $\text{PyPy}_{p\text{-Br}}\text{Py}$ . It was dissolved in benzene and precipitated with ethanol.

Fraction	Weight, g	% C	Fraction	Weight, g	% C
1	0.68	63.5	3	0.35	67.1
2	0.62	63.8	4	0.75	67.6

Calc. for  $\text{PyPy}_{p\text{-Br}}\text{Py}$ : C 60.5. Calc. for  $\text{Py}_3$ : C 69.7.

The table shows that the bromo-compound was enriched in the first two fractions. These were dissolved in benzene and chromatographed several times on silica gel. The yellow monobromo-compound was eluted with benzene + ether (20 : 1). M. p. 161° C with decomposition. Light absorption: Fig. 2. Found: C 60.7, H 4.0, Br 13.4, N 14.1.  $\text{C}_{30}\text{H}_{23}\text{BrO}_3\text{N}_6$  (595.5) requires C 60.5, H 3.9, Br 13.4, N 14.1.

*Decomposition of 1,1'-Diphenyl-1''-p-bromophenyl-3,3',3''-trimethylfurlone and 1-p-Bromophenyl-1''-diphenyl-3,3',3''-trimethylfurlone (VI a and c) with Hydrogen Chloride.* 1,1'-Diphenyl-1''-p-bromophenyl-3,3',3''-trimethylfurlone (VI a) (0.367 g) was treated with hydrogen chloride in ether solution for three days. The crystals formed were filtered by suction, washed with ether and air-dried. From the bispyrazolone hydrochloride obtained unsubstituted pyrazole blue was prepared by oxidation with nitrous acid (the hydrochloride and excess sodium nitrite were dissolved in 2.5 N sodium hydroxide solution and poured into 5 N sulphuric acid). Yield 0.070 g (33 %). From the ether solution another 33 % of pyrazole blue was obtained by dilution with ether and alcohol. The products were mixed and purified by solution in boiling chloroform followed by precipitation with

ether, a procedure which does not separate different pyrazole blue substances from each other but eliminates ether-soluble impurities. Found: C 69.5, H 4.5.  $(C_{10}H_8ON_2)_2$  (344.4) requires C 69.7, H 4.7. A Beilstein test indicated that the substance was free from bromine.

1-*p*-Bromophenyl-1',1''-diphenyl-3,3',3''-trimethylfurlone (VI c) was treated in the same way. Here Py = Py<sub>*p*-Br</sub> was obtained in about 70 % yield. M.p. 219° C with decomposition. Found: C 56.9, H 3.45, Br 19.0, N 13.2.  $C_{20}H_{15}BrO_2N_4$  (423.3) requires C 56.7, H 3.6, Br 18.9, N 13.2.

1,1'-Diphenyl-1''-*o*-tolyl-3,3',3''-trimethylfurlone (VI d) from Pyrazole Blue and 1-*o*-Tolyl-3-methyl-4-bromo-5-pyrazolone. Py = Py (0.80 g) and Py<sub>*o*-Me</sub>HBr (0.632 g) were shaken for 1 hour with chloroform (75 ml), alcohol (75 ml) and sodium acetate (45 ml of 1.8 *N* solution) to establish equilibrium with the addition compound. Then a 5 %  $CuSO_4 \cdot 5H_2O$  solution (2 ml) was added, and the flask was shaken overnight. Despite the fact that the solution was bluish-brown next morning, the organic solvents were distilled off under reduced pressure. The precipitate formed during the evaporation was filtered by suction, washed with water and air-dried. It was repeatedly crystallized from alcohol. As a green colour was not removed by that procedure, a small crystal of Py<sub>*o*-Me</sub>HBr was added followed by another crystallization. Now a faintly yellow, almost white substance (20 % yield) was obtained, m.p. 151° C with decomposition. Light absorption: Fig. 2. Found: C 70.1, H 5.0, N 15.79.  $C_{31}H_{26}O_3N_6$  (530.6) requires C 70.2, H 4.9, N 15.84. As the product has not been purified by chromatography, some 1,1',1''-tri-*o*-tolyl-3,3',3''-trimethylfurlone is probably present.

1,1'-Diphenyl-1''-*p*-tolyl-3,3',3''-trimethylfurlone (VI e) from Pyrazole Blue and 1-*p*-Tolyl-3-methyl-4-bromo-5-pyrazolone. Pyrazole blue and an excess of Py<sub>*p*-Me</sub>HBr were treated as in the preceding synthesis, but only a very small yield was obtained. Hence an excess of Py = Py was tried.

Py = Py (0.66 g) and Py<sub>*p*-Me</sub>HBr (0.37 g) were shaken with alcohol (75 ml), chloroform (75 ml) and sodium acetate (45 ml of 1.8 *N* solution) during one hour. Then cupric catalyst (1 ml of 0.01 %  $CuSO_4 \cdot 5H_2O$  solution) was added, and the system was shaken overnight. In spite of the deficiency in Py<sub>*p*-Me</sub>HBr, complete decoloration took place. Evaporation, filtering and crystallization from alcohol as in the preceding synthesis gave 0.30 g of yellow product (41 % yield); m.p. 134° C with decomposition. The light absorption curve is shown in Fig. 2. Found: C 70.0, H 5.1, N 15.94.  $C_{31}H_{26}O_3N_6$  (530.6) requires C 70.2, H 4.9, N 15.84. The presence of some tri-*p*-tolyl-compound is probable.

1,1'-Di-*p*-bromophenyl-1''-*o*-tolyl-3,3',3''-trimethylfurlone (VI f) from 1-*o*-Tolyl-3-methyl-4-bromo-5-pyrazolone and Di-*p*-bromo-Pyrazole Blue. Py<sub>*p*-Br</sub> = Py<sub>*p*-Br</sub> (1.86 g) Py<sub>*o*-Me</sub>HBr (1.54 g), chloroform (430 ml) and alcohol (55 ml) were shaken for 10 minutes. After addition of more alcohol (375 ml) and 1.80 *N* sodium acetate solution (250 ml), the mixture was shaken for 2 hours. Then catalyst (35 ml of 3 %  $CuSO_4 \cdot 5H_2O$  solution) was added, and finally the flask was shaken overnight. Concentration of the decolorized solution in vacuo, filtration and crystallization from alcohol resulted in 1.20 g of the faintly yellow  $Py_{p-Br}Py_{p-Br}Py_{o-Me}$  (47 % yield) melting at 164° C with decomposition. Light absorption: Fig. 2. Found: C 54.0, H 3.6, Br 23.0, N 12.3.  $C_{31}H_{24}Br_2O_3N_6$  (688.4) requires C 54.1, H 3.5, Br 23.2, N 12.2. Some 1,1',1''-tri-*o*-tolyl-3,3',3''-trimethylfurlone is present as impurity.

*Light Absorption Measurements.* The light absorption was measured with a Beckmann spectrophotometer model DU. In the diagrams  $\log \epsilon = \log \log \frac{I_0}{I} - \log c \cdot l$  is plotted

against the wave length,  $\lambda$ , in Ångström units. The concentration,  $c$ , of the substances is not expressed in moles per liter but in pyrazolone units per liter.

## SUMMARY

Furlone yellow, a substance formed by the intermolecular dehydrohalogenation of three molecules of 1-phenyl-3-methyl-4-bromo-5-pyrazolone, has been prepared for the first time. The structure II containing a dihydrofuran ring is proposed for it. Several bromo- and methyl-substituted furlone yellows have also been prepared.

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