

Studies on Pyrazolones

XII. Alkaline Decomposition of Furlone Yellow

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Alkaline hydrolysis of furlone yellow¹ (I) at room temperature gives a salt of the base II, which on acidification splits off carbon dioxide to form the compound III.

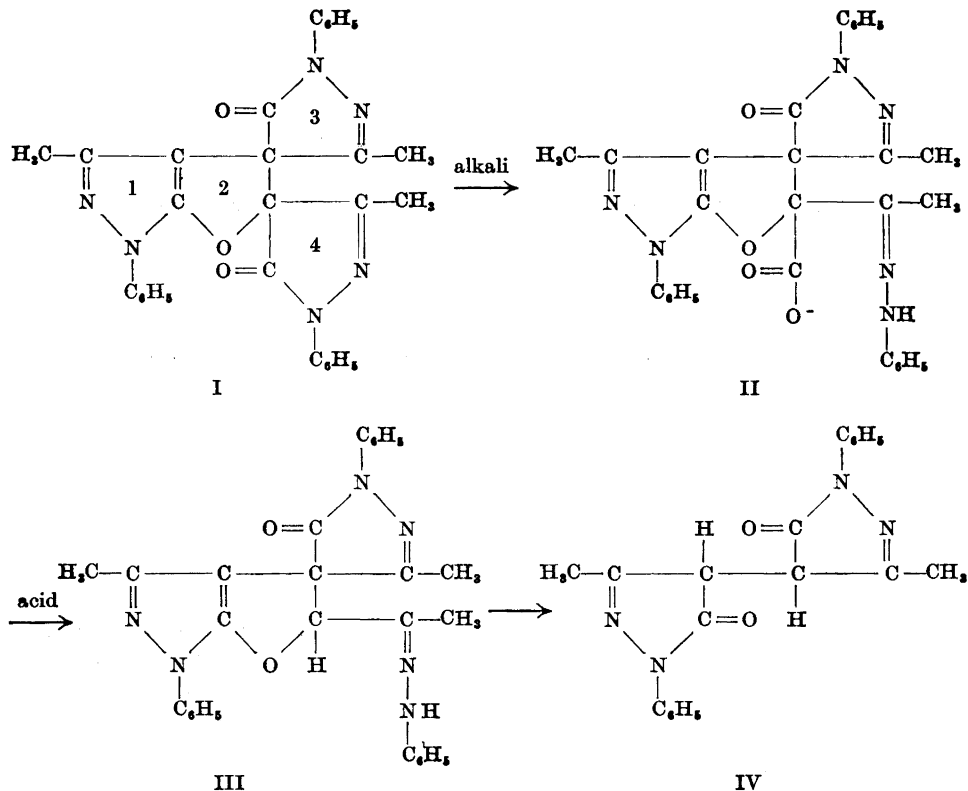
The pyrazolone ring of 1-phenyl-3-methyl-2-pyrazolin-5-ones is stable towards alkali, unless both the 4-hydrogen atoms are substituted, at least one of them by an electron-attracting group. Cleavages of pyrazolone rings by alkali have been described, *e.g.* for rubazonic acid² and for 1,1'-diphenyl-3,3'-dimethyl-4-cyano-[4,4'-bi-2-pyrazoline]-5,5'-dione³. In the present paper one of the alkaline cleavage products of furlone yellow¹ is studied.

From the acidified, alkaline hydrolysate of furlone yellow (I) a colourless compound can be isolated, the elemental analyses of which are in accordance with the structure III. The product is insoluble in aqueous alkali. In solution it decomposes in a couple of days with formation of 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione² (IV). This degradation, which is catalysed by acids and bases, excludes a cleavage of the pyrazolone ring 3 of I during the hydrolysis. As ring 1 has a stable pyrazole structure the ring 4 must have been split up in accordance with formula II. The intermediate II has not been isolated. On acidification it splits off carbon dioxide.

In addition coloured products of hydrolysis are formed from I. They have not been investigated and may involve cleavage of ring 3 of I.

EXPERIMENTAL

Preparation of III. Furlone yellow¹ (5.27 g) was dissolved in 300 ml of boiling ethanol, the solution was cooled to room temperature, and 2.5 N sodium hydroxide (75 ml) was added. After 2 h the solution was acidified with 2.5 N hydrochloric acid (75 ml) and immediately precipitated with water to prevent decomposition of the product III formed. The precipitate was collected by filtration, washed with water and air-dried (5.3 g). The product obtained was dissolved in ethyl acetate (150 ml, room temperature). Insoluble bispyrazolone (IV) was sometimes present and had to be removed by filtration. After evaporation of the excess of ethyl acetate at room temperature, colourless crystals of



III separated on scratching. They were filtered and washed with ethyl acetate (yield 3.35 g). For further purification the treatment with ethyl acetate may be repeated. M. p. about 155° (decomp.). (Found: C 70.9; H 5.3; N 17.1; O 6.6. Calc. for C₂₉H₂₆N₆O₂: C 71.0; H 5.3; N 17.1; O 6.5.)

Degradation of III with formation of IV. A solution of III (0.25 g) in chloroform (4 ml) was kept at room temperature for 24 h. The colourless precipitate formed (0.15 g) was filtered and washed with chloroform. It was almost insoluble in boiling ethanol, melted >300° (decomp.) and was oxidized by nitrous acid to form pyrazole blue. Accordingly it must be 1,1'-diphenyl-3,3'-dimethyl-[4,4'-bi-2-pyrazoline]-5,5'-dione* (IV). — When hydrogen chloride was passed through a benzene solution of III, the degradation to the bispyrazolone IV was rapid. Analogously the addition of alkali to an ethanol solution of III accelerated the formation of IV. (Found: C 69.1; H 5.2; N 16.4. Calc. for C₂₆H₁₈N₄O₂: C 69.3; H 5.2; N 16.2.)

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