

DEHYDRATIONAL CYCLISATION OF 2,2'-DIACETYLAMINO-1,1'-DIANTHRAQUINONYL TO FLAVANTHRONE*

V. KRATOCHVÍL, V. SLAVÍK and M. NEPRAŠ

Research Institute of Organic Syntheses,
532 18 Pardubice - Rybitví

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Formation of flavanthrone by the dehydrational cyclisation of 2,2'-diacetyl-amino-1,1'-dianthraquinonyl in sulfuric acid has been examined with a special respect to the influence of temperature and concentration of the acid.

In the present time, flavanthrone has lost the importance as a vat dye but shows excellent colouristic properties in the pigment form, *i.e.*, it is *inter alia* highly light fast even in very low dilutions. Flavanthrone may be produced by two methods. One synthesis¹ starts from 2-aminoanthraquinone which is chlorinated with sulfuryl chloride and the resulting 1-chloro-2-aminoanthraquinone is acylated with phthalic anhydride at 230°C. The acyl derivative is subjected to the Ullmann reaction and the resulting 2,2'-diphthaloylamino-1,1'-dianthraquinonyl is cyclised to flavanthrone by refluxing in 5% aqueous sodium hydroxide for a long period of time. The other synthesis^{2,3} starts with the Ullmann reaction of 1-chloro-2-acetylaminanthraquinone in a dipolar aprotic solvent at a low temperature and the resulting 2,2'-diacetyl-amino-1,1'-dianthraquinonyl is cyclised to flavanthrone in sulfuric acid (80% to concentrated) at temperatures below 100°C. The thus-obtained flavanthrone exhibits a higher purity than the product of the former method.

As shown by preliminary experiments, the above dehydrational cyclisation takes also place under other conditions than those reported in the literature^{2,3}. It was therefore of interest to examine in detail the effect of the concentration of sulfuric acid and of the temperature on the course of the reaction. In this paper, we wish to present results of kinetic measurements of the dehydrational cyclisation of 2,2'-diacetyl-amino-1,1'-dianthraquinonyl and activation energy values for the experimental concentrations of sulfuric acid.

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EXPERIMENTAL

2,2'-Diacetylamino-1,1'-dianthraquinonyl was obtained by the reported² procedure and crystallised from nitrobenzene; the chromatographically homogeneous substance forms yellow needles which do not melt up to 360°C. 2,2'-Diamino-1,1'-dianthraquinonyl was prepared from the dipthaloylamino derivative by deacylation with hydrazine hydrate in pyridine at room temperature. During the preparation and the purification process, the diamino derivative is readily converted to flavanthrone. The crude product was therefore not purified but directly used in spectrophotometrical measurements. As shown by analysis, the crude product contained 78% of 2,2'-diamino-1,1'-dianthraquinonyl and 22% of flavanthrone. Aqueous solutions of sulfuric acid were prepared from Analytical Grade 96% sulfuric acid and their concentration was determined acidimetrically using the Tashiro mixed indicator.

Absorption spectra were measured on a recording Unicam SP 700 spectrophotometer. Kinetic measurements were performed on an one-beam Hilger Uvispek spectrophotometer with a photo-multiplier adaptor and thermostatted cell block. Quartz cells were used in both cases (optical layer, 10 mm; ground caps).

Kinetics measurements of the dehydrational cyclisation of 2,2'-diacetylamino-1,1'-dianthraquinonyl to flavanthrone were carried out in freshly prepared $2 \cdot 10^{-5}$ mol solutions of sulfuric acid in the 510 nm region where only the resulting flavanthrone absorbed. Temperature of reaction mixtures during the kinetic measurements were maintained with the accuracy of $\pm 0.1^\circ\text{C}$. The results were evaluated statistically by means of a standard program and calculations were performed on a Hewlet Packard 2116B computer. Calculations of rate constants were effected using the relation of a pseudomonomolecular reaction⁴. The activation energy E^\ddagger data for the experimental solutions of sulfuric acid were determined graphically from the slope of the $\log k$ versus $1/T \cdot 10^3$ (K^{-1}) plot.

RESULTS AND DISCUSSION

In order to explain the dehydrational cyclisation of 2,2'-diacetylamino-1,1'-dianthraquinonyl in sulfuric acid with the formation of flavanthrone, it was necessary to examine the behaviour of reactants and products in 80% to 96% sulfuric acid. Fig. 1

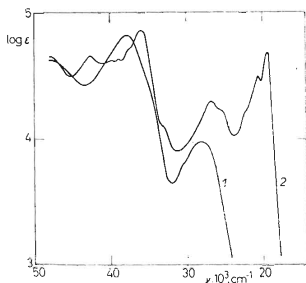


FIG. 1
Absorption Curves of 2,2'-Diacetylamino-1,1'-dianthraquinonyl (1) and Flavanthrone (2) in 80.3% Sulfuric Acid

shows absorption curves of 2,2'-diacetyl-amino-1,1'-dianthraquinonyl 1 and flavantrone 2 in 80.3% sulfuric acid. The absorption spectrum of flavantrone was measured at various concentrations of sulfuric acid (from 80% to 96%); it did not practically change within this concentration range. In view of the spectral character of the two compounds, it was possible to examine the cyclisation rate dependence on the concentration of sulfuric acid and on the temperature by spectrophotometrical measurements of the extinction of the resulting flavantrone at $1.96 \mu\text{m}^{-1}$ (510 nm), *i.e.*, in the region where 2,2'-diacetyl-amino-1,1'-dianthraquinonyl does not absorb at all. The absorption spectrum of 2,2'-diamino-1,1'-dianthraquinonyl was impossible to measure since the addition of this substance into sulfuric acid is immediately

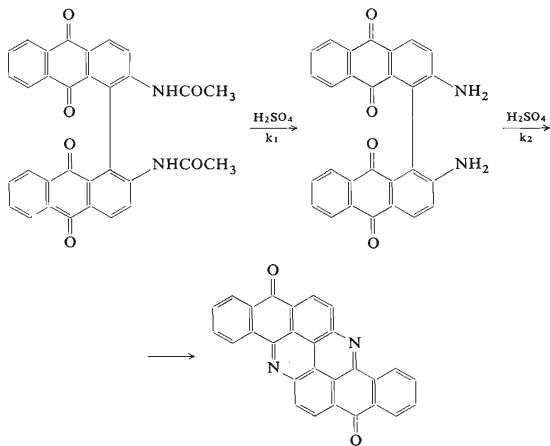
TABLE I

Effect of Sulfuric Acid Concentration and Temperature on the Cyclisation Rate of 2,2'-Diacetyl-amino-1,1'-dianthraquinonyl with the Formation of Flavantrone

t , °C	k_1 , $\text{mol l}^{-1} \text{min}^{-1}$	E^\ddagger , kcal mol^{-1}
80.26% sulfuric acid		
$t_1 = 60$	$k_1 = 2.03 \cdot 10^{-3}$	33.9
$t_2 = 70$	$k_2 = 7.77 \cdot 10^{-3}$	
$t_3 = 80$	$k_3 = 2.02 \cdot 10^{-2}$	
$t_4 = 90$	$k_4 = 5.81 \cdot 10^{-2}$	
85.07% sulfuric acid		
$t_1 = 50$	$k_1 = 2.25 \cdot 10^{-3}$	26.2
$t_2 = 60$	$k_2 = 7.36 \cdot 10^{-3}$	
$t_3 = 70$	$k_3 = 2.43 \cdot 10^{-2}$	
$t_4 = 80$	$k_4 = 7.09 \cdot 10^{-2}$	
89.96% sulfuric acid		
$t_1 = 40$	$k_1 = 2.55 \cdot 10^{-3}$	24.8
$t_2 = 50$	$k_2 = 9.08 \cdot 10^{-3}$	
$t_3 = 60$	$k_3 = 2.84 \cdot 10^{-2}$	
$t_4 = 70$	$k_4 = 7.78 \cdot 10^{-2}$	
96.1% sulfuric acid		
$t_1 = 30$	$k_1 = 4.70 \cdot 10^{-3}$	21.8
$t_2 = 40$	$k_2 = 1.78 \cdot 10^{-2}$	
$t_3 = 50$	$k_3 = 4.12 \cdot 10^{-2}$	
$t_4 = 60$	$k_4 = 0.14$	

followed by cyclisation with the formation of flavanthrone. Table I shows rate constants of the cyclisation of 2,2'-diacetyl-amino-1,1'-dianthraquinonyl to flavanthrone; the experimental data clearly indicate the influence of the sulfuric acid concentration and temperature on the course of the cyclisation.

The experimental data make possible to identify the rate determining step in the formation of flavanthrone. Conversion of the starting 2,2'-diacetyl-amino-1,1'-dianthraquinonyl to flavanthrone proceeds by an at least two-step reaction. The first step, hydrolytical removal of acetyl groups, is followed by the cyclisation of the resulting diamino derivative to flavanthrone. The second step proceeds considerably more fastly and thus the reaction rate is determined by the rate of hydrolysis. On the basis of the above observations, the formation of flavanthrone may be illustrated by Scheme 1 ($k_1 \ll k_2$).



SCHEME 1

From the practical point of view it is of importance that the reaction rate is sufficient even under conditions that are less vigorous than those reported in the patent literature^{2,3}. The temperature and sulfuric acid concentration may be varied in dependence on the purity of the starting compound on the one hand and the required purity and yield of the product on the other. The cyclisation conditions also affect the size and character of the resulting flavanthrone particles. In the case of low concentrations of sulfuric acid, flavanthrone is deposited in a fine crystalline form and

in a high yield. With increasing concentrations of sulfuric acid larger crystals are formed and a portion of flavanthrone along with the contaminants remains in the solution (particularly at elevated temperatures). Cyclisations in concentrated sulfuric acid usually afford a solution of flavanthrone from which the product is isolated by precipitation with water or pouring into excess water.

REFERENCES

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