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TRANSFORMATION OF PYRYLIUM ACETATES INTO BENZENE DERIVATIVES

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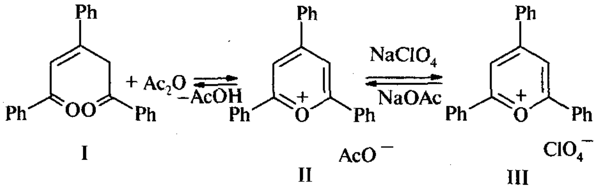
Transformation of a pyrylium cation into benzene derivatives can be accomplished by creating high concentrations of C-nucleophiles, which is possible when strong bases are used as catalysts [1]. Previously [2], we have proposed a method of CH-acid activation, according to which the process can be also catalyzed by weak bases such as sodium acetate.

Similar results can be obtained by using 1,3,5-triphenyl-1,5-pentene-2-dione (I) instead of pyrylium salt [1]. This fact is indicative of equilibrium processes involving pyrylium acylates:



According to this scheme, dione I converts into benzene derivatives on heating in acetic anhydride without adding sodium acetate. This transformation is provided by the formation of contacting ion pairs of pyrylium cation and acetate anion.

In order to confirm the existence of pyrylium acetate (II) in the ionic form, we have studied the electronic absorption spectra of 2,4,6-triphenylpyrylium perchlorate (III) and dione I in acetic anhydride. The UV spectrum of perchlorate III in acetic anhydride displays two intense absorption bands peaked at 407 and 357 nm (Fig. 1, curve *1*). The shape of this spectrum remains unchanged when an equimolar amount of sodium acetate is added to this solution. However, the presence of excess sodium acetate in the reaction medium results in decreasing intensity of the absorption peaks at 357 and 407 nm, which is characteristic of ionic structures [3]. The intensity drop ceases after 20 min, which is evidence of attaining an equilibrium (isosbestic point at $\lambda = 320$ nm).

The UV spectrum of 1,3,5-triphenyl-1,5-pentene-2-dione (I) in acetic anhydride at room temperature exhibits a single pronounced maximum at 310 nm and is stable in time (Fig. 2, curve *1*). However, the spectrum dramatically changes on heating the sample to 80°C, whereby two additional absorption bands appear at 360 and 408 nm that ca be assigned to pyrylium cation (Fig. 2, curve *2*). Upon keeping at this temperature for 20-min, the intensity of these absorption peaks attains a constant level (Fig. 2, curve *3*). Coincidence of this spectrum with that of pyrylium cation leads to the conclusion that pyrylium acetate exists in acetic anhydride in the form of an ionic compound.

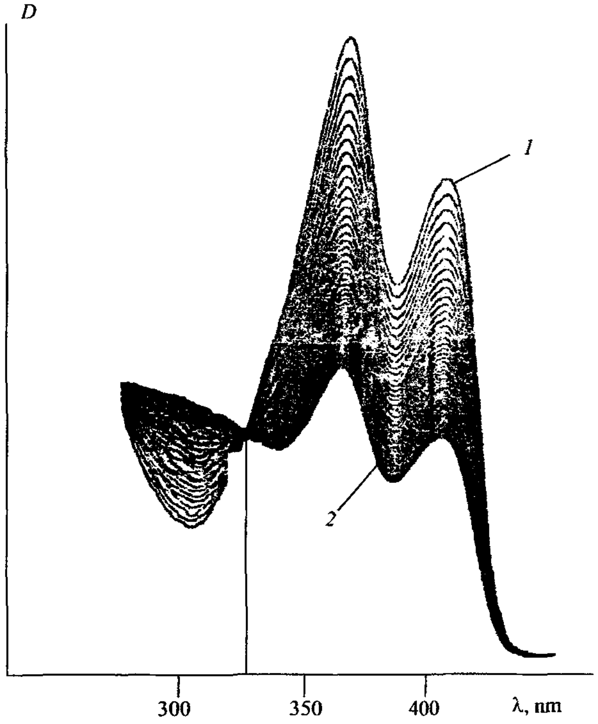


Fig. 1. The electronic absorption spectra of 2,4,6-triphenylpyrylium perchlorate III in pure acetic anhydride (curve *1*) and in the presence of excess sodium acetate (curve *2*, after a 20-min contact).

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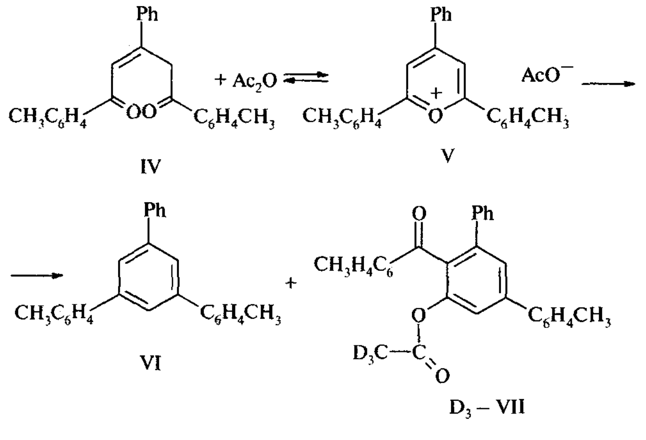
Further transformation was followed with the aid of ^1H NMR spectroscopy. The room-temperature spectrum of 1,5-bis(4′-methylphenyl)-3-phenyl-1,5-pentene-2-dione (IV) in deuterated acetic anhydride displays, besides a multiplet of 14 aromatic protons, a two-proton singlet ($\delta = 4.38$ ppm) from a methylene group and signals from two nonequivalent methyl groups (2.32 and 2.34 ppm). On heating the reaction mixture to 80°C, the intensity of the signal from methylene group drops by half, while the number of signals from methyl groups increases. A 30-min treatment at 80°C leads to no further changes in the NMR spectrum. We may suggest that not all diketone IV is converted into pyrylium acetate V and that only a *cis*-form of diketone IV exhibits cyclization under these conditions.

Increasing the temperature up to 120°C gives rise to new changes in the ^1H NMR spectrum. A 20-min treatment at this temperature results in disappearance of the signal of methylene group and the appearance of signals from three nonequivalent methyl groups (2.26, 2.35, and 2.37 ppm). Vanishing of the former signal indicates that all of diketone IV has entered into reaction. The signals of methyl groups reflect the presence of compounds VI and D_3 – VII in the mixture. These compounds were obtained from 4-phenyl-2,6-ditolylpyrylium [1] and independently synthesized from diketone IV (see the experimental chemical part below).



Thus, the results of UV and ^1H NMR spectroscopic measurements confirm the existence of pyrylium acetate in the reaction medium and show evidence of the ionic character of this compound.

EXPERIMENTAL PART

The ^1H NMR spectra were measured on a Tesla B-487 (80 MHz) instrument (Czech Republic) using 0.3 – 0.5 M solutions in deuterated acetic anhydride and TMS as the internal standard. The electronic absorption spectra were automatically recorded on a Specord spectrophotometer using 1-cm quartz cells in a temperature-controlled compartment. The samples were dissolved in acetic anhydride to a concentration of $2 \times 10^{-5} - 1 \times 10^{-5}$ M.

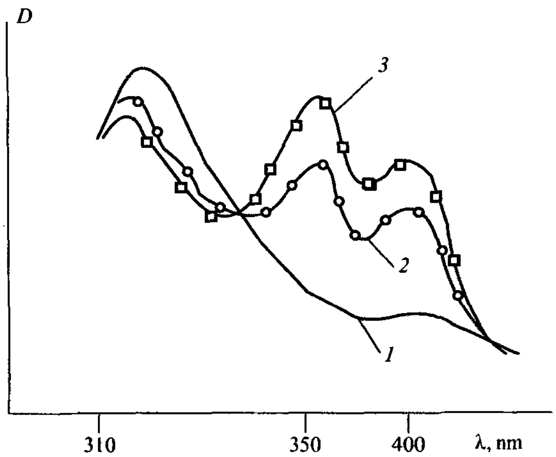


Fig. 2. The electronic absorption spectra of 1,3,5-triphenylpyrylium perchlorate I in acetic anhydride measured at *1*) 20°C and *2*, *3*) 80°C.

3,5-Di(4′-methylphenyl)diphenyl (VI) and 3-acetoxy-2-(4′-methylbenzoyl)-4-(4″-methylphenyl)diphenyl (VII). A solution of 1 mmole of 1,5-bis(4′-methylphenyl)-3-phenyl-1,5-pentene-2-dione (IV) in 0.02 mole of acetic anhydride was boiled for 30 min, cooled, and extracted with 10 – 15 ml of diethyl ether. The ether fraction was separated and evaporated. The residue was washed with 2 ml of ethanol to obtain 0.08 g of compound VI. Compound VII (0.18 g) was precipitated with water from ethanol mother liquor.

Compound VI: yield, 0.08 g (22 %); m.p., 205°C; IR spectrum (ν_{max}, cm^{-1}): 1580, 1567 (C=C$_{arom}$). Compound VII: yield, 0.18 g (45 %); m.p., 80°C; IR spectrum (ν_{max}, cm^{-1}): 1540, 1593 (C=C$_{arom}$), 1620 (C=O).

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