SYNTHESIS OF 2-PHENYL-5-ALKOXYNAPHTHO[1,8-b,c]FURYLIUM SALTS

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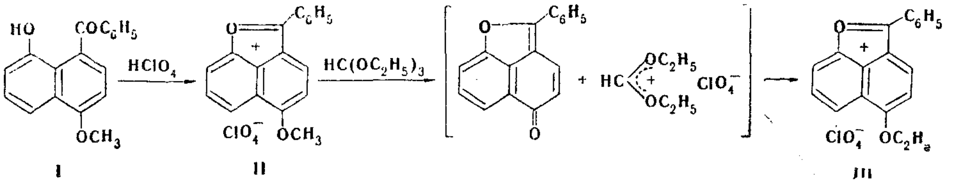
We have found that 2-phenyl-5-methoxynaphtho[1,8-b,c]furylium perchlorate (II), with mp 165-166°C (from acetic acid), is formed in 75% yield in the reaction of a mixture of 72% perchloric acid and acetic anhydride (1:3) with 4-methoxy-8-hydroxybenzoylnaphthalene (I). PMR spectrum (in CF_3COOH), δ: 4.02 (s, OCH_3) and 7.2-8.8 ppm (m, 10H, aromatic). In contrast to the IR spectrum of the starting peri-hydroxy ketone I, the absorption bands of hydroxyl and carbonyl groups vanish in the IR spectrum (in mineral oil) of salt II, and bands appear at 1100 (ClO_4^-) and 1630 cm^{-1}; this constitutes evidence for cyclization of the peri-hydroxy ketone.

2-Phenyl-5-ethoxynaphtho[1,8-b,c]furylium perchlorate (III), with mp 171°C (from acetic acid), was obtained in 67% yield by heating peri-hydroxy ketone I with $HClO_4$ in ethyl orthoformate. IR spectrum (in mineral oil): 1630, 1550, 1520, and 1100 cm^{-1}. PMR spectrum (in CF_3COOH), δ: 1.32 (3H, t, $CH_2\underline{CH_3}$), 4.37 (2H, q, $\underline{CH_2}CH_3$), and 7.2-8.5 ppm (m, 10H, aromatic.

The formation of 5-ethoxy derivative III instead of 5-methoxy derivative II, which was established by comparison of their PMR spectra (from the appearance of characteristic signals of a C_2H_5 group and the disappearance of the singlet of the OCH_3 group), occurs as a result of the rather unusual transalkylation of salt II, which evidently proceeds through a methylenequinone intermediate.



The synthesized naphtho[1,8-b,c]furylium salts contain a new heterocyclic cation that differs qualitatively from the known furylium cation with respect to the presence of a closed 12π-electron system.

The highest frequency bands in the IR spectra of salts II and III are the low intensity bands at 1630 cm^{-1}, which can evidently be regarded as characteristic for this heterocyclic cation.

The hydrolysis of salts II and III in aqueous acetone proceeds rapidly at room temperature to give, respectively, peri-hydroxy ketone I, with mp 238-239°C (from dimethylformamide), in 97% yield [IR spectrum (in mineral oil): 3230 and 1650 cm^{-1}] and 4-ethoxy-8-hydroxybenzoylnaphthalene, with mp 195-197°C (from ethanol), in 96% yield [IR spectrum (in mineral oil): 3100 and 1640 cm^{-1}]. PMR spectrum (in deuterodimethyl sulfoxide), δ: 1.37 (3H, t, $CH_2\underline{CH_3}$), 4.1 (2H, q, $\underline{CH_2}CH_3$), 6.65-7.75 (m, 10H, aromatic), and 10.1 ppm (s, OH).

The individuality of the peri-hydroxy ketones was confirmed by chromatography in a thin layer of Silochrome S-120. Satisfactory results of analysis for carbon and hydrogen were obtained for all of the compounds.

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