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Synthesis of 4,8-Dibenzoyl-1,5-dihydroxynaphthalene and of Some Derivatives Thereof[*]

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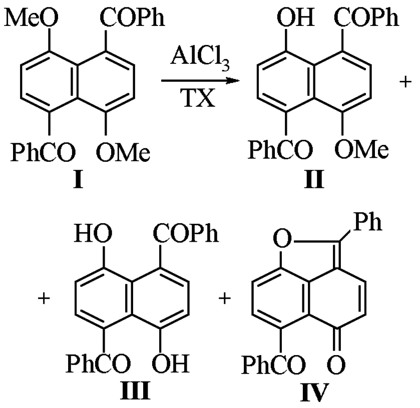
Abstract—Demethylation of 4,8-dibenzoyl-1,5-dimethoxynaphthalene was carried out to afford the corresponding bis-peri-hydroxydiketone and its derivatives. The acylation and alkylation was performed with one among these derivatives, 6-benzoyl-2-phenylnaphtho[bc]furan-5-one.

peri-Hydroxysubstituted naphthaldehydes and naphthyl ketones are known to be potential precursors of the *peri*-annealed heterocycles [1]. In the same way bis-*peri*-hydroxynaphthoyl compounds can become key initial substances in the synthesis of various representatives from the virtually unknown series of bis-*peri*-anneled heterocyclic systems.

We lately obtained 4,8-dihydroxy-1,5-diformylnaphthalene [2]. This study is aimed to look for new approaches in the synthesis of the first bis-*peri*-hydroxynaphthyldiketones and their simple derivatives.

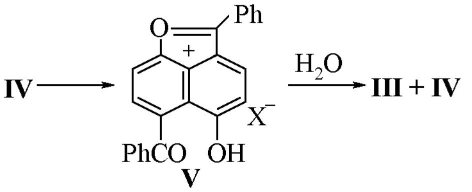
One of possible ways to prepare the desired compounds can be a dealkylation of the appropriate bis-*peri*-methoxydiketones. To this end the formerly reported [3] 1,5-dibenzoyl-4,8-dimethoxynaphthalene (**I**) was treated with anhydrous aluminum chloride at heating in tetrachloroethane.



(1)

As a result of the reaction forms a mixture of dimethylation products **II**–**IV** in a ratio depending on the temperature of the process.

At room temperature the main product is the partially demethylated hydroxymethoxydiketone **II** whereas at 90°C prevails exhaustive demethylation yielding methylenequinone **IV**. Dihydroxydiketone **III** is present in traces at both temperature modes. Its presence is qualitatively indicated by a characteristic blot at the start during chromatography of the reaction mixture on the thin layer of alumina. Methylenequinone **IV** arises due to acid-catalyzed dehydration of the dihydroxydiketone **III**. The reversed conversion **IV** → **III** is achieved by treating methylenequinone **IV** with perchloric acid in acetic acid solution with subsequent addition of water. Here the precursor of dihydroxyketone **III** is the corresponding naphtho[*bc*]furylium salt **V** that can be isolated in crystalline state and that is quickly hydrolyzed with air moisture at standing in air.



(2)

The attempt to prepare and isolate crystalline 5-ethoxy- (**VI**) or 5-acetoxy- (**VIII**) substituted salts of the naphtho[*b,c*]furylium by reacting quinone **VI** with triethyl orthoformate or acetic anhydride respectively in the presence of boron trifluoride etherate or acetate did not give the desired result. On diluting the reaction mixtures with ether the expected salts did not precipitate but their formation is evidenced by the

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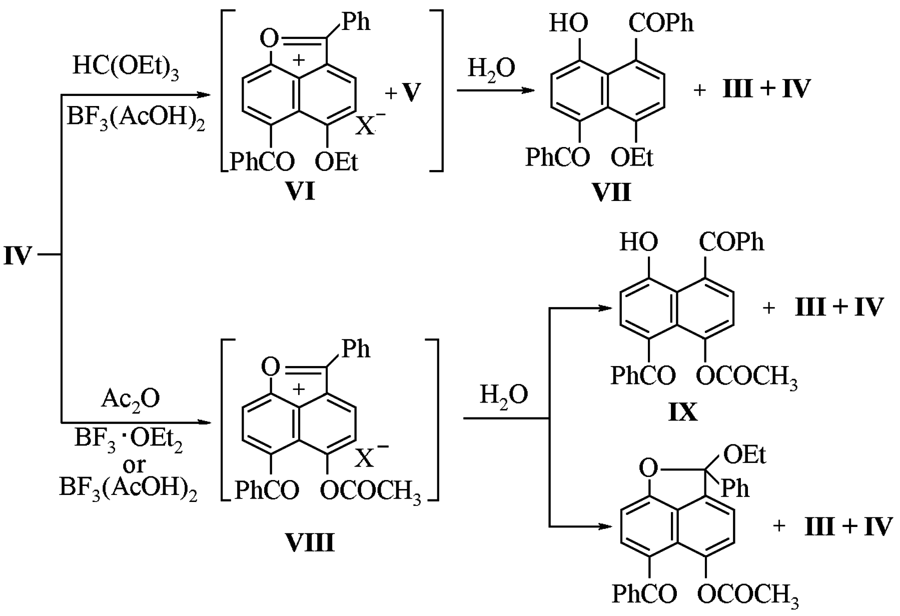
Scheme.



hydrolysis products of the reaction mixtures. The reaction of quinone **IV** with triethyl orthoformate (see scheme) apparently gives rise to *o*-ethylated **VI** and O-protonated **V** cations with considerable prevalence of the former. The reaction with water of cation **VI** takes a single route consisting in opening of the heterocycle to afford diketone **VII**, whereas the hydrolysis of cation **V** occurs according to Scheme 2 yielding a mixture of hydroxydiketone **III** and quinone **IV**.

The result of hydrolysis of acetoxycation **VIII** depends on reaction conditions. For instance, dilution with water of the salt **VIII** solution in the acetic anhydride affords a mixture of hydroxyacetoxydiketone **IX** and quinone **IV** with prevalence of the former. In other words the attack of water molecules playing the role of a nucleophile is directed to the carbon atoms in position 2 of the heteroring of naphtho[*bc*]furylium cation **VIII** or to the carbon of the ester group in the cation.

The hydrolysis of the reaction mixture containing cation **VIII** preliminary diluted with ethyl ether takes place at the phase boundary between the ether and water layer and results in a mixture of 2-ethoxynaphtho[*bc*]furan (**X**) (main product) and quinone **IV**. We presume that the formation of the ethoxy derivative **X** occurs by reaction of acetoxycation **VIII** with ethanol contained in the ethyl ether for the same compound was obtained by hydrolysis of the reaction mixture with ethanol.

In all experiments the hydrolysis products were separated by column chromatography on alumina, eluent chloroform. The weighted ratios of the separated products are listed in EXPERIMENTAL.

EXPERIMENTAL

IR spectra of compounds obtained were recorded on spectrophotometer Specord IR-71 from mulls in mineral oil. ^{1}H NMR spectra were registered on spectrometer Varian Unity-300, solvent CDCl$_3$, internal reference HMDS. The purity of compounds obtained was checked by TLC on alumina, eluent chloroform.

Spectral characteristics of compounds synthesized are presented in Table 1, elemental analyses in Table 2.

Demethylation of 1,5-dibenzoyl-4,8-dimethoxynaphthalene (I). (a) Into a heated to 30–35°C dispersion of 1.2 g (0.003 mol) of 1,5-dibenzoyl-4,8-dimethoxynaphthalene (**I**) in 30 ml of tetrachloroethane was added by portions 2 g of anhydrous aluminum chloride. The mixture was heated under reflux on a water bath for 40 min, cooled, and poured into ice water. The solvent was removed by steam distillation. The yellow solid was twice crystallized from dimethylformamide to obtain 0.65 g (85%) of 6-benzoyl-2-phenyloxynaphtho[*bc*]furan-5-one (**IV**), mp 245°C.

Filtrate was poured into water, the precipitate was collected and treated with 5% solution of NaOH. The alkaline solution was acidified with diluted (1 : 1) HCl to obtain 30 mg (3%) of colorless 4,8-dibenzoyl-1,5-dihydroxynaphthalene (**III**), mp 275°C (from ethanol).

The residue was crystallized from ethanol to obtain 115 mg (10%) of 4,8-dibenzoyl-1-hydroxy-5-methoxynaphthalene (**II**), mp 261°C.

(b) Into a heated to 30–35°C dispersion of 1.75 g (0.0045 mol) of 1,5-dibenzoyl-4,8-dimethoxynaphthalene (**I**) in 35 ml of tetrachloroethane was added by portions 3 g of anhydrous aluminum chloride. The mixture was stirred for 1 h at room temperature, then the reaction mixture was poured into ice water. The solvent was removed by steam distillation. The solid was twice crystallized from ethanol to obtain 1.3 g (77%) of compound **II**, mp 261°C.

Filtrate was poured into water, the precipitate was collected and treated with 5% solution of NaOH. The alkaline solution was acidified with diluted (1 : 1) HCl to obtain 52 mg (4%) of colorless 4,8-dibenzoyl-1,5-dihydroxynaphthalene (**III**), mp 275°C (from ethanol).

The residue was crystallized from dimethylformamide to obtain 150 mg (10%) of compound **IV**, mp 245°C.

6-Benzoyl-5-hydroxy-2-phenylnaphtho[bc]furylium perchlorate (V). To a dispersion of 50 mg (0.0014 mol) of quinone **IV** in 1 ml of acetic acid was added dropwise 0.14 ml of 72% perchloric acid, and the mixture was boiled for 5–7 min. On cooling separated a red precipitate that was filtered off, washed with ether, and dried. We obtained 60 mg (96%) of compound **V**, mp 235°C.

Hydrolysis of perchlorate V. To a dispersion of 43 mg (0.0001 mol) of perchlorate **V** in 1 ml of acetone was added dropwise water (3–4 ml). The yellow precipitate was filtered off, washed with water, dried, treated with 5% solution of NaOH, acidified with diluted (1 : 1) HCl. We obtained 7 mg of compound **III**. The residue was crystallized from dimethylformamide to afford 24 mg (69%) of quinone **IV**.

2,6-Dibenzoyl-1-hydroxy-5-ethoxynaphthalene (VII). A dispersion of 90 mg (0.00025 mol) of quinone **IV** in 2 ml of triethyl orthoformate and 0.2 ml of boron trifluoride acetate was stirred with a magnetic stirrer for 2 h, then the mixture was diluted with water, and the precipitate formed was filtered off. We obtained 60 mg (59%) of colorless compound **VII**, mp 267°C (from ethanol).

Table 1. Spectral characteristics of compounds **II**–**X**

Compd. no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm
II	3220, 1647, 1607	
III	3498, 1656, 1635, 1607	4.05 s (éH, OCH_3); 7.2–7.85 m (14H, arom.); 8.65 s (1H, OH)
IV	1660, 1633, 1580, 1554	7.36–8.1 m (14 H, arom.)
VII	3180, 1660 1647, 1593 1580	0.97 t (3H, $\underline{CH}_3CH_2$); 3.8–4 m (2H, $CH_3\underline{CH}_2$); 6.7–8.1 m (14 H, arom.); 8.7 s (1H, OH)
IX	3193, 1780, 1673, 1647, 1593	1.9 s (éH, CH_3CO); 6.9–7.9 m (14H, arom.); 9.0 s (1H, OH)
X	1767, 1660, 1633, 1607, 1595	1.25 t (3H, $\underline{CH}_3CH_2$); 2 m (3H, CH_3CO); 3.25–3.6 s (2H, $CH_3\underline{CH}_2$); 6.8–7.9 m (14H, arom.)

Table 2. Elemental analyses of compounds **II**–**X**

Compd. no.	Found, %		Formula	Calculated, %	
	C	H		C	H
II	78.49	4.65	$C_{25}H_{18}O_4$	78.53	4.71
III	78.35	4.28	$C_{24}H_{16}O_4$	78.26	4.35
IV	82.40	4.15	$C_{24}H_{14}O_3$	82.29	4.00
VII	78.81	5.21	$C_{26}H_{20}O_4$	78.79	5.05
IX	76.26	4.45	$C_{26}H_{18}O_5$	76.10	4.39
X	76.59	5.28	$C_{28}H_{22}O_5$	76.71	5.02

The ethanol solution was diluted with water, the separated precipitate was filtered off, dried, and subjected to chromatography on a column packed with alumina (eluent chloroform). We obtained 12 mg (13%) of quinone **IV** and 7 mg (7%) of compound **III**.

5-Acetoxy-6-benzoyl-2-phenyl-2H-2-ethoxynaphtho[bc]furan (X). To a hot dispersion of 0.18 g (0.0005 mol) of quinone **IV** in 2 ml of acetic anhydride was added 0.15 ml (0.001 mol) of boron trifluoride etherate, the red solution was heated for 2–3 min, cooled, diluted with ether, and poured into water. The thick viscous substance formed was twice crystallized from ethanol to obtain 98 mg (80%) of colorless crystals of compound **X**, mp 136°C.

The ethanol solution was diluted with water, the separated precipitate was filtered off, dried, and subjected to chromatography on a column packed with alumina (eluent chloroform). We obtained 24 mg (13%) of quinone **IV** and 10 mg (5%) of compound **III**.

5-Acetoxy-2,6-dibenzoyl-1-hydroxynaphthalene (IX). To a hot dispersion of 90 mg (0.00025 mol) of quinone **IV** in 1.5 ml of acetic anhydride was added 0.06 ml (0.0005 mol) of boron trifluoride etherate. The mixture was maintained at the room temperature for 20–30 min, and then diluted with water. We obtained 78 mg (74%) of compound **IX**, mp 263°C (from alcohol).

The ethanol solution was diluted with water, the separated precipitate was filtered off, dried, and subjected to chromatography on a column packed with alumina (eluent chloroform). We obtained 10 mg (11%) of quinone **IV**.

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