

## Building up of a *peri*-Hydroxynaphthoyl Fragment on the Core of 2*H*-Naphtho[1,8-*bc*]furan

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**Abstract**—The reaction of 2-aryl-5-acetoxy-4,8-di-*tert*-butyl-2*H*-naphtho[1,8-*bc*]furan with dichloromethyl ethyl ether in the presence of aluminum chloride gave rise to 6-formyl derivatives of the title heterocyclic system, and at the use of aliphatic acids anhydrides in the presence of perchloric acid 6-acyl derivatives were obtained. The target products with a *peri*-hydroxycarbonyl group were obtained by the ester group elimination.

Naphthalene derivatives containing in contiguous *peri*-positions a hydroxy and a carbonyl functions are potential precursors in the synthesis of *peri*-annelated heterocycles [1]. When therewith the two other *peri*-positions of the naphthalene are closed into a ring, the newly constructed *peri*-hydroxycarbonyl moiety may underlie the building up of the second *peri*-annelated heterocycle. Hence we state one among the strategies of building up bis-*peri*-annelated heterocyclic systems. Nowadays only single examples of bis-*peri*-annelated heterocycles were described [2–5] whose synthesis and investigation of some reactions were of accidental character, and the studies in this field as a whole could not be regarded as systematic. At the same time the bis-*peri*-annelated heterocyclic systems should possess characteristics of interest both from theoretical (e.g., study of the aromaticity problems) and practical viewpoint. The highly annelated systems are known to be prone to radiation processes whose study in the last few years is among the most important problems in creating working medium in memory devices.

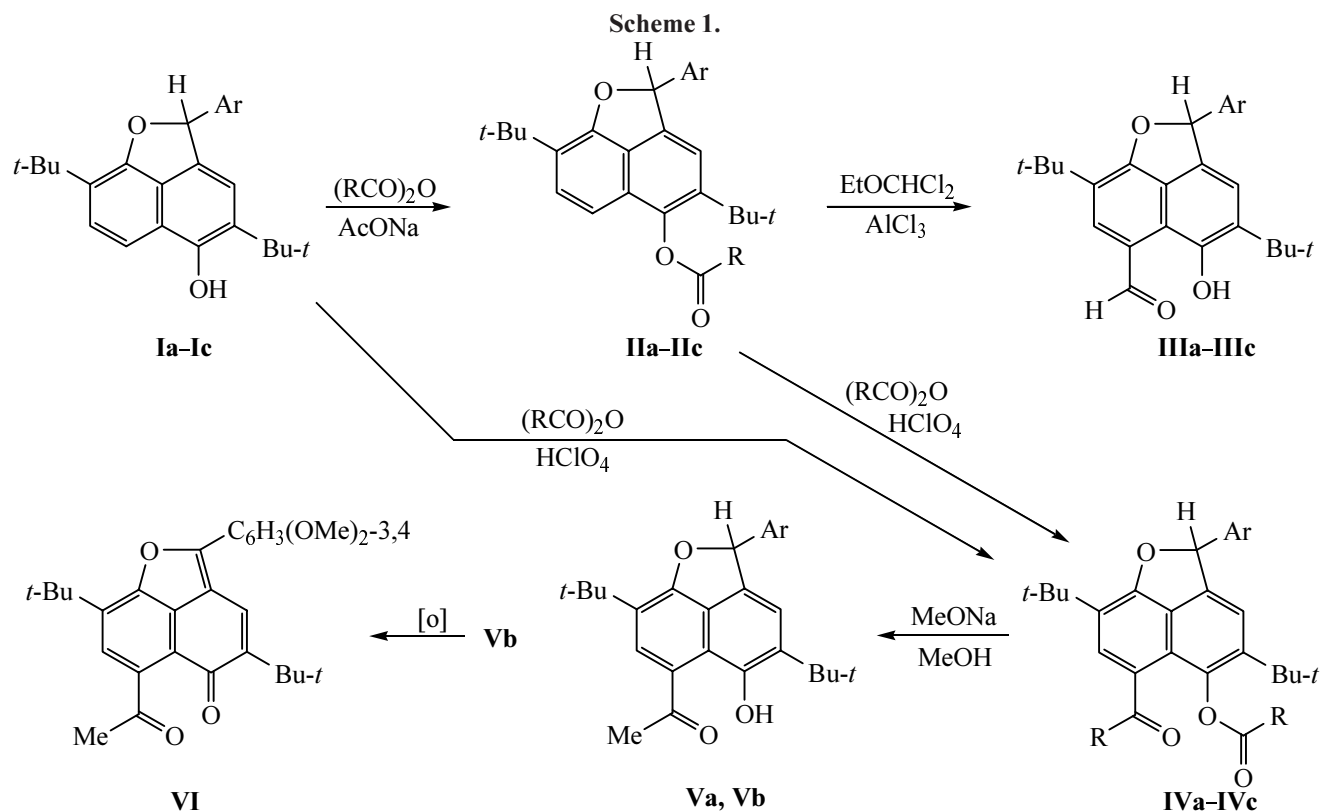
We believe that for designing bis-*peri*-annelated heterocycles of the naphthalene series 2-aryl-4,8-di-*tert*-butyl-5-hydroxy-2*H*-naphtho[1,8-*bc*]furans (**I**) may serve as useful syntheses. We reported on the synthesis of the latter in [6].

Actually, the electron-donor effect of the oxygen of the furane ring alongside the presence of a hydroxy group in position 5 and a *tert*-butyl substituents in positions 4 and 8 open up a possibility to introduce a carbonyl group just in the 6 position, i.e., to build up a *peri*-hydroxycarbonyl fragment.

In our previous studies we started from 1-acyloxy-5-methoxynaphthalenes in preparation of the *peri*-hydroxynaphthoyl moiety [7]. In the present work taking into account that the positions 4 and 8 (*ortho*-positions with respect to oxygen atoms) were blocked by *tert*-butyl substituents we hoped to construct the target *peri*-hydroxycarbonyl fragment omitting the stages of acylation and deacylation of the 5-hydroxy group. However both the formylation by Rieche reaction [8] and acylation with aromatic acyl chlorides by Friedel–Crafts reaction in the presence of the aluminum chloride [9] resulted in intractable products mixtures. We failed to isolate from these reaction mixtures individual substances in amounts sufficient for performing further synthetic attempts.

Better objects of Rieche reaction proved to be O-acetyl derivatives **II** prepared by boiling the corresponding naphtholes **I** in acetic anhydride in the presence of sodium acetate. For instance, bringing into the reaction 2-tolyl derivative of 5-acetoxynaphtho[1,8-*bc*]furan (**IIa**) we obtained in a high yield formylation product **IIIa**. Interestingly, under the formylation conditions a cleavage of the ester group occurred and thus we isolated at once from the reaction mixture the desired *peri*-hydroxyformyl derivative **IIIa** (Scheme 1).

On replacing in the 2-aryl substituent the *para*-methyl group by a more electron-donor *para*-methoxy group a bisformylation occurred into the position 6 of the naphthofuran ring and into position 3 of the aryl substituent. In this way from 2-(4-methoxyphenyl) derivative **IIb** we obtained dialdehyde **IIIb**. The formylation of 2-(3,4-dimethoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**IIc**) gave rise to a mixture of monoformyl **IIIc**



**B**, Ar = 4-MeC<sub>6</sub>H<sub>4</sub> (**a**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**b**), 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**c**); **II**, **IV**, R = Me, Ar = 4-MeC<sub>6</sub>H<sub>4</sub> (**a**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**b**), 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**c**); R = Et, Ar = 4-MeOC<sub>6</sub>H<sub>4</sub> (**d**); **III**, Ar = 4-MeC<sub>6</sub>H<sub>4</sub> (**a**), 3-CHO-4-MeOC<sub>6</sub>H<sub>3</sub> (**b**), 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**c**), 2-CHO-3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>2</sub> (**d**); **V**, Ar = 4-MeOC<sub>6</sub>H<sub>4</sub> (**a**), 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**b**).

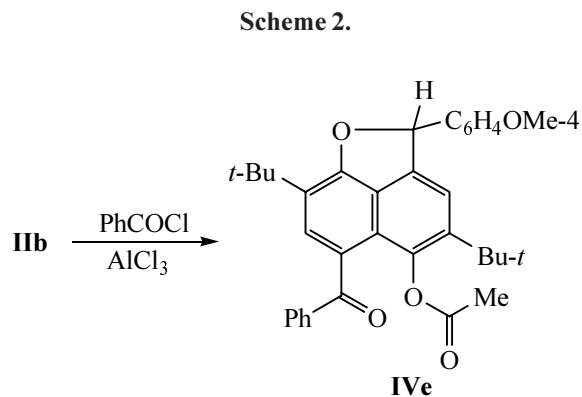
and bisformyl **III**d derivatives from which we succeeded to isolate by chromatography a certain amount of individual compound **III**c. The mixture of compounds **III**c and **III**d was characterized only by spectral methods.

The acylation of 6-acyloxynaphtho[1,8-*bc*]furans **II** with aliphatic acyl chlorides (acetyl and propionyl chlorides) catalyzed by perchloric acid afforded the corresponding *peri*-acyloxyketones **IV**. The acetylation of propionyloxy derivative **II**d under these conditions occurred with transesterification giving *peri*-acetyloxyketone **IV**a. It is of interest that *peri*-acyloxyketones **IV** can be obtained directly from 5-hydroxynaphtho[1,8-*bc*]furans **I** and aliphatic acyl chlorides in the presence of perchloric acid. In the latter reaction the C-acylation is preceded by the O-acylation of the naphthol hydroxy group.

We practically failed to prepare arylketones (**IV**, R = Ar) by C-arylation of 6-acetyloxynaphtho[1,8-*bc*]furans **II** with aromatic acids in polyphosphoric acid or with aroyl chlorides in the presence of aluminum chloride. In most cases intractable mixtures were obtained, and we could

not isolate any individual substances. Only in reaction of 6-acetyloxynaphtho[1,8-*bc*]furan (**II**b) with benzoyl chloride in the presence of aluminum chloride we separated in a 12% yield the corresponding *peri*-acetyloxyketone **IV**e (Scheme 2).

The deacylation of obtained *peri*-acyloxyketones **IV** effected by sodium methylate afforded the target *peri*-hydroxyketones **V** in good yields. The possibility of *peri*-hydroxyketones conversion into a methylenequinoid form



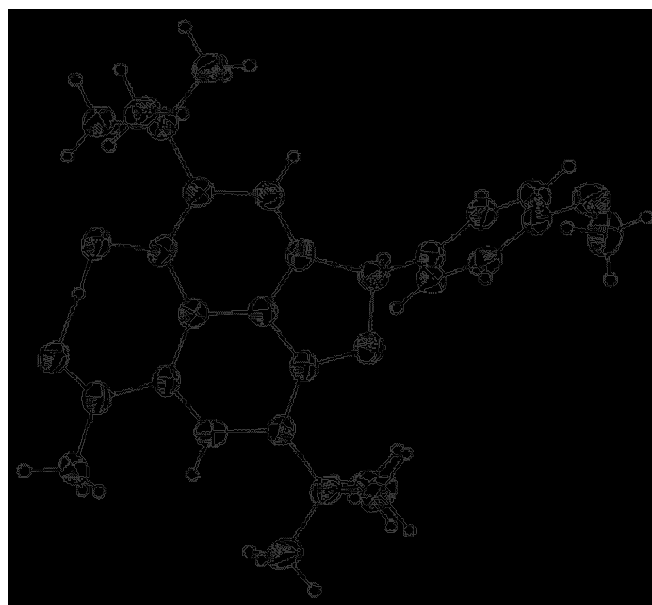
**VI** was shown by an example of treating compound **Vb** with potassium ferrocyanide.

The composition and structure of all compounds synthesized were proved by elemental analysis and spectral methods. The most of spectral characteristics given in the EXPERIMENTAL do not require further comments.

IR and  $^1\text{H}$  NMR spectra of dialdehyde **IIIb** require some elucidation. Two aldehyde groups of its molecule appear in the IR spectrum as two absorption bands of C=O bonds stretching vibrations at 1647 (formyl group involved into a hydrogen bond) and 1687  $\text{cm}^{-1}$ , and in the  $^1\text{H}$  NMR spectrum as two one-proton singlets at 9.5 and 10.5 ppm. The signal at 9.5 ppm obviously corresponds to the formyl group attached to the naphthalene ring. Its more upfield position is due to the intramolecular hydrogen bond with the proton of the *peri*-hydroxy group [10]. The latter is seen in the  $^1\text{H}$  NMR spectrum as a one-proton singlet at 12.8 ppm that disappears on deuteroexchange. The downfield signal at 10.5 ppm is well consistent with the proton chemical shifts in the *ortho*-substituted benzaldehydes [11].

The structure of *peri*-hydroxyketone (**Va**) was subjected to X-ray diffraction analysis (see figure). According to the X-ray diffraction data in the nearly planar molecule (the largest deviations from the plane do not exceed  $6^\circ$ ) exists an efficient intramolecular hydrogen bond between the hydroxy and the carbonyl groups present in the *peri*-position. For instance, the dihedral angle  $C^{13}O^{15}O^{24}C^{10}$  (here and hereinafter the crystallographic notation of atoms is given) is equal to  $7.68^\circ$ , the distance  $\text{O}-\text{H}\cdots\text{O}$  is 2.493 Å, the OHO angle is  $170.7^\circ$ . These parameters unambiguously show the presence of an intramolecular hydrogen bond. The bond angles in the naphthalene skeleton deviate significantly from the classic values ( $120^\circ$ ). The largest distortions are observed at the bridging carbon atoms: angles  $C^4C^{12}C^7$  and  $C^1C^{11}C^{10}$  equal respectively to  $109.81^\circ$  and  $132.54^\circ$ . These distortions result in alterations in the distances between the atoms located in the *peri*-position that in contrast to an ideal value (2.45 Å) become equal to 2.651 ( $C^1C^{10}$ ) and 2.285 ( $C^4C^7$ ) Å. The above deformations of the naphthalene skeleton are evidently due to the presence of the furan ring.

The published X-ray diffraction data [12–14] on the fine structure of nucleophile-substituted *peri*-naphthoyl derivatives **A**, among them those with  $\text{Nu} = \text{OH}$ , clearly demonstrate the attractive interaction  $\text{Nu}\cdots\text{C}=\text{O}$  resulting in the deformation of the bond angles of the exocyclic



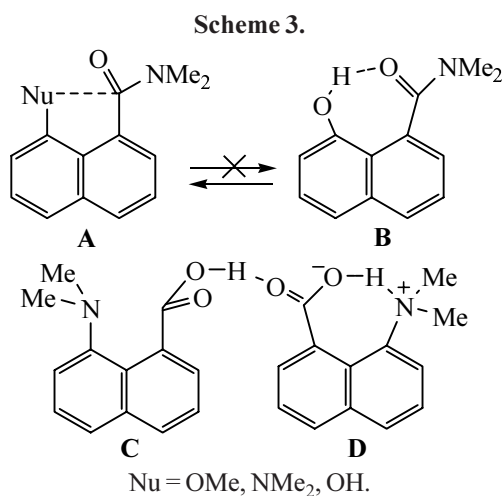
Crystal structure of 6-acetyl-4,8-di-*tert*-butyl-5-hydroxy-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**Va**).

naphthalene bonds but not touching the aromatic skeleton. In the *peri*-hydroxynaphthoyl derivative **B** the formation of the intramolecular hydrogen bond between the carbonyl oxygen and the hydroxy group proton is less favorable that the attractive interaction between the hydroxy group oxygen and the carbonyl carbon, and just the latter exists in the crystalline structure.

This fact may be understood considering that the involvement of the *peri*-carbons into the seven-membered ring arising at formation of the intramolecular hydrogen bond and the proper formation of this ring leading to repulsion of the nucleophilic and electrophilic substituent requires considerable distortion of the bond angles in the molecule. Apparently the energy gain at the intramolecular hydrogen bond formation is not sufficient to provide for the losses at the deformation of a stable aromatic system and at the counteraction against the attractive interaction (Scheme 3).

The known example of a compound with a hydrogen bond in a seven-membered ring between the substituents in positions 1 and 8 of naphthalene [12] whose geometry correlates well with that of our substance is the zwitterionic form of amino acid **D**. However it is stabilized in the crystal by formation of an intermolecular hydrogen bond between its carboxylate group and a carboxy group of amino acid **C** resulting in dimers in the molecular packing.

In our case the additional factor stabilizing the seven-membered ring with an intramolecular hydrogen bond



consists apparently in the forced deformation of the bond angles of the naphthalene skeleton because of the annelated furan ring. This observation once more supports our previous [15] assumptions that the formation of a seven-membered ring on the naphthalene *peri*-positions is facilitated by the presence in the molecule of a *peri*-annelated five-membered ring.

#### EXPERIMENTAL

IR spectra of compounds obtained were registered on a spectrophotometer Specord IR-71 from mulls in mineral oil. <sup>1</sup>H NMR spectra were obtained on spectrometers Bruker Avance DPX-250 and Varian Unity-300 from solutions in CDCl<sub>3</sub>; internal reference HMDS. Mass spectrum was measured on a Kratos instrument with a direct admission of a sample into the ionizing chamber, ionizing electrons energy 70 eV, controlling voltage 1.75 kV.

**X-ray diffraction analysis of compound Va** was carried out using a single crystal of linear dimensions 0.29×0.27×0.25 mm, C<sub>28</sub>H<sub>32</sub>O<sub>4</sub>, *M* 432.54, at 120(2) K on a diffractometer Bruker SMART CCD area detector (λMOK<sub>α</sub>-radiation, θ<sub>max</sub> 27.99°, spherical segment -9 ≤ *h* ≤ 9, -16 ≤ *k* ≤ 16, -16 ≤ *l* ≤ 17). Overall 11118 reflections were obtained, 4155 among them were symmetrically independent (*R*<sub>int</sub> 0.0442). Triclinic crystals, space group *P*-1, *a* 7.3820, *b* 12.3768, *c* 13.0135 Å, α 94.828(2), β 101.279(3), γ 100.343(3)°, *V* 1138.3(2) Å<sup>3</sup>, *Z* 2, *d*<sub>calc</sub> 1.262 g cm<sup>-3</sup>, μ 0.083 mm<sup>-1</sup>, *F*(000) 464.0. The structure was solved by the direct method, all nonhydrogen atoms were localized by difference synthesis of the electron density and refined by *F*<sup>2</sup><sub>*hkl*</sub> in the full-matrix anisotropic approximation. All hydrogen atoms were placed into the geometrically calculated positions and refined with the use of the *riding* model

with *U*(H) = 1.2*U*(C) [*U*(C) is the equivalent thermal factor of the carbon linked to the corresponding hydrogen atom]. The final values of the unreliability factors (301 refined parameter) accounting for 5413 reflections were calculated till *R*1 = 0.0639 [calculated along *F*<sub>*hkl*</sub> for 2329 reflections with *I* > 2σ(*I*)], *wR*2 0.1202, GOOF 0.982. The residual electron density from the difference Fourier series was 0.215 and -0.213 Å<sup>-3</sup>. The main geometrical parameters from the X-ray data are as follows: interatomic distances (Å), C<sup>1</sup>-C<sup>11</sup> (1.467), C<sup>10</sup>-C<sup>11</sup> (1.429), C<sup>4</sup>-C<sup>12</sup> (1.404), C<sup>7</sup>-C<sup>12</sup> (1.388), C<sup>1</sup>-C<sup>13</sup> (1.468), C<sup>10</sup>-O<sup>24</sup> (1.359), C<sup>13</sup>-O<sup>15</sup> (1.237), O<sup>15</sup>-O<sup>24</sup> (1.498), C<sup>4</sup>-O<sup>5</sup> (1.368), O<sup>5</sup>-C<sup>6</sup> (1.483), C<sup>6</sup>-C<sup>7</sup> (1.515); bond angles (deg), C<sup>4</sup>C<sup>12</sup>C<sup>7</sup> (109.81), C<sup>1</sup>C<sup>11</sup>C<sup>10</sup> (132.54), C<sup>11</sup>C<sup>1</sup>C<sup>13</sup> (126.12), C<sup>11</sup>C<sup>10</sup>O<sup>24</sup> (121.64), C<sup>4</sup>O<sup>5</sup>C<sup>6</sup> (108.81), O<sup>5</sup>C<sup>6</sup>C<sup>7</sup> (103.47), C<sup>6</sup>C<sup>7</sup>C<sup>12</sup> (107.29), C<sup>13</sup>O<sup>15</sup>H (111.18), C<sup>10</sup>O<sup>24</sup>H (170.70), C<sup>1</sup>C<sup>13</sup>O<sup>15</sup> (123.14), C<sup>4</sup>C<sup>12</sup>C<sup>11</sup> (125.02).

**5-Acetoxy-4,8-di-*tert*-butyl-2-(4-methylphenyl)-2*H*-naphtho[1,8-*bc*]furan (IIa).** A solution of 0.374 g (1 mmol) of 4,8-di-*tert*-butyl-5-hydroxy-2-(4-methylphenyl)-2*H*-naphtho[1,8-*bc*]furan (**Ia**) and 0.082 g (1 mmol) of sodium acetate in 2 ml of acetic anhydride was boiled for 15 min, cooled, and poured in water. On hydrolysis of excess anhydride the separated precipitate was filtered off and crystallized from hexane, yield 0.303 g (73%), light-yellow substance, mp 133–135°C. IR spectrum: ν 1767 cm<sup>-1</sup> (C=O). <sup>1</sup>H, δ, ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.4 s (3H, Me), 2.5 s (3H, OCOMe), 6.75 s (1H, furan), 6.9 d (1H, naphth.), 7.1 s (1H, naphth.), 7.2 d (2H, tolyl), 7.25 d (2H, tolyl), 7.45 d (1H, naphth.). Found, %: C 81.13; H 7.51. C<sub>28</sub>H<sub>32</sub>O<sub>3</sub>. Calculated, %: C 80.77; H 7.69.

Compounds **Iib**, **c** were prepared in a similar way.

**5-Acetoxy-4,8-di-*tert*-butyl-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (IIb).** Yield 70%, mp 160°C. IR spectrum: ν 1767 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR spectrum, δ, ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.4 s (3H, COMe), 3.8 s (3H, OMe), 6.85 d (1H, naphth.), 6.9 d (2H, anisyl), 7.1 s (1H, naphth.), 7.3 d (2H, anisyl), 7.4 d (1H, naphth.). Found, %: C 77.43; H 7.58. C<sub>28</sub>H<sub>32</sub>O<sub>4</sub>. Calculated, %: C 77.78; H 7.41.

**5-Acetoxy-4,8-di-*tert*-butyl-2-(3,4-dimethoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (IIc).** Yield 75%, mp 98°C. IR spectrum: ν 1767 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR spectrum, δ, ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.5 s (3H, COMe), 3.8 s (3H, OMe), 3.9 s (3H, OMe), 6.75 s (1H, furan), 6.9 m (3H, arom), 7.0 d (1H, veratr.), 7.1 s (1H, veratr.), 7.25 s (1H, naphth.), 7.45 d (1H, naphth.). Found, %: C 75.53; H 7.48. C<sub>29</sub>H<sub>34</sub>O<sub>5</sub>. Calculated, %: C 75.34; H 7.36.

**4,8-Di-*tert*-butyl-2-(4-methoxyphenyl)-5-propionyloxy-2*H*-naphtho[1,8-*bc*]furan (IIId).** A solution of 0.39 g (1 mmol) of 2-(4-methylphenyl)-4,8-di-*tert*-butyl-5-hydroxy-2*H*-naphtho[1,8-*bc*]furan (**Ib**) and 0.082 g (1 mmol) of sodium acetate in 2 ml of propionic anhydride was boiled for 15 min, cooled, and poured in water. On hydrolysis of excess anhydride the separated precipitate was filtered off and crystallized from hexane. Yield 0.3 g (67%), light-yellow substance, mp 92°C. IR spectrum:  $\nu$  1767  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 1.6 t (3H, CH<sub>2</sub>CH<sub>3</sub>), 2.7 q (2H, CH<sub>2</sub>CH<sub>3</sub>), 3.8 s (3H, OMe), 6.75 s (1H, furan), 6.8 d (1H, naphth.), 6.9 d (2H, anisyl), 7.1 s (1H, naphth.), 7.3 d (2H, anisyl), 7.4 d (1H, naphth.). Found, %: C 78.27; H 7.47. C<sub>29</sub>H<sub>34</sub>O<sub>4</sub>. Calculated, %: C 78.03; H 7.39.

**4,8-Di-*tert*-butyl-5-hydroxy-2-(4-methylphenyl)-6-formyl-2*H*-naphtho[1,8-*bc*]furan (IIIa).** To a cooled dispersion of 0.208 g (0.5 mmol) of 5-acetoxy-4,8-di-*tert*-butyl-2-(4-methylphenyl)-2*H*-naphtho[1,8-*bc*]furan (**IIa**) in 1 ml of 1,1,2,2-tetrachloroethane was added by portions while stirring 0.1 g (0.75 mmol) of anhydrous aluminum chloride, the mixture was maintained for 4 h and then poured in water. The precipitate obtained was filtered off, dried, and subjected to chromatography on alumina (eluent benzene), yield 0.109 g (54%), golden crystalline substance, mp 85–88°C. IR spectrum:  $\nu$  1635  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.3 s (3H, Me), 6.7–7.9 m (7H, arom) 9.5 s (1H, CHO), 12.35 s (1H, OH). Found, %: C 80.42; H 7.32. C<sub>27</sub>H<sub>30</sub>O<sub>3</sub>. Calculated, %: C 80.60; H 7.46.

Likewise were prepared compounds **IIIb**, **IIIc**.

**4,8-Di-*tert*-butyl-5-hydroxy-2-(3-formyl-4-methoxyphenyl)-6-formyl-2*H*-naphtho[1,8-*bc*]furan (IIIb),** yield 35%, mp 105–107°C. IR spectrum:  $\nu$  1647 (C=O), 1687  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 3.95 s (3H, OMe), 6.85 C (1H, furan), 7.0 d (1H, benz.), 7.2 C (1H, naphth.), 7.4 d (1H, benz.), 7.85 s (1H, benz.), 7.95 s (1H, naphth.), 9.6 s (1H, CHO), 10.4 s (1H, CHO), 12.4 s (1H, OH). Found, %: C 75.42; H 6.79. C<sub>28</sub>H<sub>30</sub>O<sub>5</sub>. Calculated, %: C 75.34; H 6.73.

**4,8-Di-*tert*-butyl-5-hydroxy-2-(3,4-dimethoxyphenyl)-6-formyl-2*H*-naphtho[1,8-*bc*]furan (IIIc),** yield 24%, mp 70–73°C. IR spectrum:  $\nu$  1635  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 3.8 s (3H, OMe), 3.9 s (3H, OMe), 6.75 s (1H, furan), 6.85–6.95 m (3H, benz.), 7.25 s (1H, naphth.), 7.9 s (1H, naphth.), 9.6 s (1H, CHO), 12.4 s (1H, OH). Found, %: C 75.24; H 7.31. C<sub>28</sub>H<sub>32</sub>O<sub>5</sub>. Calculated, %: C 75.0; H 7.14.

**5-Acetoxy-6-acetyl-4,8-di-*tert*-butyl-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (IVb).** To a cooled dispersion of 0.097 g (0.25 mmol) of 4,8-di-*tert*-butyl-5-hydroxy-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**Ib**) in 1 ml of acetic acid was added 0.01 ml of perchloric acid, the mixture was kept for 15 min and then poured in water. The precipitate obtained was filtered off and crystallized from ethanol to obtain 0.104 g (87%) of colorless substance, mp 149–151°C. IR spectrum:  $\nu$  1750 (C=O), 1673  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.4 s (3H, OCOMe), 2.6 s (3H, COMe) 3.8 s (3H, OMe), 6.75 s (1H, furan), 6.9 d (2H, anisyl), 7.2 m (3H, arom), 7.7 s (1H, veratr.). Found, %: C 75.68; H 7.32. C<sub>30</sub>H<sub>34</sub>O<sub>5</sub>. Calculated, %: C 75.95; H 7.17.

Likewise were obtained compounds **IVa**, **IVc**, **IVd**.

**5-Acetoxy-6-acetyl-4,8-di-*tert*-butyl-2-(4-methylphenyl)-2*H*-naphtho[1,8-*bc*]furan (IVa),** yield 80%, mp 106–108°C. IR spectrum:  $\nu$  1755 (C=O), 1673  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.35 s (3H, Me), 2.38 s (3H, OCOMe), 2.65 s (3H, COMe), 6.8 s (1H, furan), 7.25 m (5H, arom), 7.7 s (1H, naphth.). Found, %: C 78.81; H 7.32. C<sub>30</sub>H<sub>34</sub>O<sub>4</sub>. Calculated, %: C 78.60; H 7.42.

**5-Acetoxy-6-acetyl-4,8-di-*tert*-butyl-2-(3,4-dimethoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (IVc),** yield 77%, mp 104°C. IR spectrum:  $\nu$  1673 (C=O), 1747  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.35 s (3H, OCOMe), 2.62 s (3H, COMe), 4.8 s (3H, OMe), 4.9 s (3H, OMe), 6.7–7.0 m (4H, arom), 7.2 s (1H, arom), 7.7 d (1H, arom). Mass spectrum,  $m/z$ : 504  $M^+$ .

**4,8-Di-*tert*-butyl-2-(3,4-dimethoxyphenyl)-5-propionyloxy-6-propionyl-2*H*-naphtho[1,8-*bc*]furan (IVd).** To a cooled dispersion of 0.42 g (1 mmol) of 4,8-di-*tert*-butyl-5-hydroxy-2-(3,4-dimethoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**Ic**) in 2 ml of propionic anhydride was added 0.01 ml of perchloric acid, the mixture was kept for 30 min and then poured in water. The precipitate obtained was filtered off and subjected to chromatography on alumina (eluent chloroform) to isolate 0.104 g (87%) of colorless substance, mp 88°C. IR spectrum:  $\nu$  1753 (C=O), 1687  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.2 t [6H, (CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.7 br.m (2H, CH<sub>2</sub>CH<sub>3</sub>), 3.8 q (2H, CH<sub>2</sub>CH<sub>3</sub>), 3.9 s (3H, OMe), 6.75–7.6 m (7H, arom). Found, %: C 73.68; H 7.81. C<sub>32</sub>H<sub>40</sub>O<sub>6</sub>. Calculated, %: C 73.85; H 7.69.

**5-Acetoxy-6-benzoyl-4,8-di-*tert*-butyl-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (IVe).** To

a cooled dispersion of 0.268 g (0.5 mmol) of 5-acetoxy-4,8-di-*tert*-butyl-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**IIIb**) in 1 ml of 1,1,2,2-tetrachloroethane was added 0.196 ml (0.75 mmol) of benzoyl chloride and then by portions at stirring also 0.1 g (0.75 mmol) of anhydrous aluminum chloride. The mixture was kept for 4 h at room temperature and then poured in water. The precipitate obtained was filtered off, dried, and subjected to column chromatography on alumina (eluent benzene). Yield 0.064 g (12%), yellow substance, mp 128–130°C. IR spectrum:  $\nu$  1660 (C=O), 1760  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.36 s (3H, OCOMe), 3.8 s (3H, OMe), 6.8–7.9 m (12H, arom). Found, %: C 78.45; H 6.63. C<sub>35</sub>H<sub>36</sub>O<sub>5</sub>. Calculated, %: C 78.36; H 6.72.

**6-Acetyl-4,8-di-*tert*-butyl-5-hydroxy-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (Va).**

To a dispersion of 0.474 g (1 mmol) of 5-acetoxy-6-acetyl-4,8-di-*tert*-butyl-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**IVb**) in 3 ml of methanol was added 3 ml of sodium methylate saturated solution in methanol, and the mixture was stirred for 30 min. Then the solution was poured in water and acidified with a dilute hydrochloric acid to weakly acidic pH. The precipitate obtained was filtered off, dried, and subjected to column chromatography on alumina (eluent chloroform). The first fraction was collected. Yield 0.15 g (32.5%), yellow substance, mp 124–125°C. IR spectrum:  $\nu$  2500 (OH), 1625  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.8 s (3H, COMe), 3.8 s (3H, OMe), 6.8 s (1H, furan), 6.9 d (2H, anisyl), 7.2 m (3H, arom), 8.25 s (1H, naphth.), 12.8 s (1H, OH). Found, %: C 77.85; H 7.36. C<sub>28</sub>H<sub>32</sub>O<sub>4</sub>. Calculated, %: C 77.78; H 7.41.

Compound **Vb** was prepared in the same way.

**6-Acetyl-4,8-di-*tert*-butyl-5-hydroxy-2-(3,4-dimethoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (Vb),** yield 32.5%, mp 146–147°C. IR spectrum:  $\nu$  2500 (OH), 1620  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.4 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.8 s (3H, COMe), 3.75 s (3H, OMe), 3.9 s (3H, OMe), 6.7 s (1H, furan), 6.9 m (3H, veratr.), 7.2 s (1H, naphth.), 8.2 s (1H naphth.), 12.8 s (1H, OH). Found, %: C 75.39; H 7.21. C<sub>29</sub>H<sub>34</sub>O<sub>5</sub>. Calculated, %: C 75.33; H 7.36.

**6-Acetyl-4,8-di-*tert*-butyl-2-(3,4-dimethoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan-5-one (VI).**

To a solution of 0.462 g (1 mmol) of 6-acetyl-4,8-di-*tert*-

butyl-5-hydroxy-2-(3,4-dimethoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**Vb**) in 2 ml of benzene was added a solution of 0.251 g (1 mmol) of K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 0.075 g of NaOH in 4 ml of water, and the mixture was stirred with a magnetic stirrer at 70°C for 1 h. Then the benzene solution was evaporated, and the residue was subjected to column chromatography on alumina (eluent chloroform). The first fraction was collected. Yield 0.308 g (67%), yellow substance, mp 189–190°C. IR spectrum:  $\nu$  1700 (C=O), 1630  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.5 d [18H, (CMe<sub>3</sub>)<sub>2</sub>], 2.6 s (3H, COMe), 4.0 d (6H, OMe), 7.05 d (1H, veratr.), 7.2 s (1H, naphth.), 7.5 s (1H, veratr.), 7.65 d (1H, veratr.), 7.9 s (1H, naphth.). Found, %: C 75.81; H 7.04. C<sub>29</sub>H<sub>32</sub>O<sub>5</sub>. Calculated, %: C 75.65; H 6.96.

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