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New Synthetic Approach to *peri*-Hydroxy-Substituted Carbonyl Acenaphthene Derivatives

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Abstract—A new approach to the synthesis of *peri*-hydroxyacenaphthoyl compounds has been developed on the basis of acylation (formylation) of 5-acyloxyacenaphthenes. The reactions are accompanied by formation of the corresponding 3- and 8-acyl-substituted isomers. In some cases, the latter can be isolated and identified by ^{1}H NMR spectroscopy.

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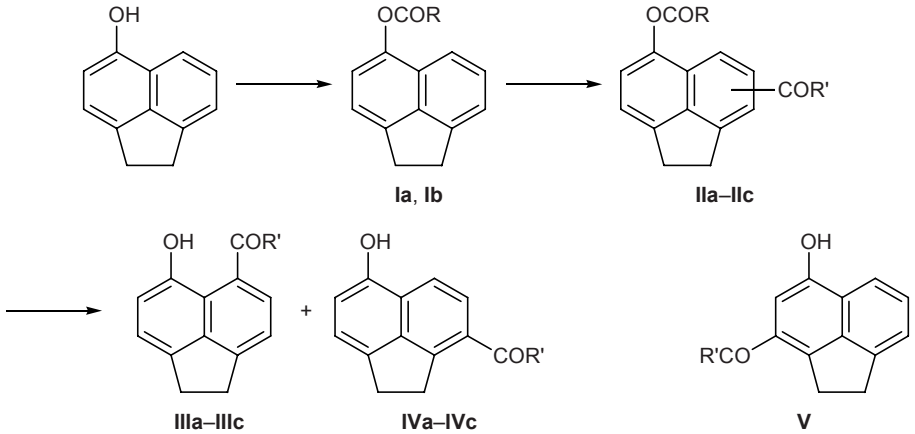
peri-Hydroxyacenaphthoyl compounds attract interest as potential precursors of *peri*-fused heterocyclic systems having an ethylene bridge [1–3] and starting materials for the preparation of *peri*-hydroxy-substitued carbonyl acenaphthylene derivatives; the latter are obtained by dehydrogenation of the ethylene unit [4].

A traditional procedure for the synthesis of the above acenaphthene compounds implies acylation of acenaphthene, nitration, catalytic reduction of the nitro group with hydrazine over Raney nickel, diazotization of the amino group, and its replacement by hydroxy group [2]. The main disadvantage of this procedure is the necessity of performing the whole transformation sequence for each of desired acenaphthene. Furthermore, we failed to obtain in this way *peri*-hydroxyacenaphthenecarbaldehyde because of side reactions of intermediate *peri*-amino aldehyde, which gave rise to an inseparable product mixture as a result of condensation of the aldehyde group with hydrazine (with formation of azines) and intermolecular self-condensation involving two and more *peri*-amino aldehyde molecules (with formation of cyclic and linear Schiff bases).

The procedure proposed in the present work is based on acid-catalyzed acylation (formylation) of esters derived from 5-hydroxyacenaphthene. The use of esters is necessary to avoid acylation at the *ortho*-position with respect to the hydroxy group. The corresponding methyl ketones were synthesized by acyla-

Scheme 1.



I, R = Me (**a**), Ph (**b**); **II**, R = R′ = Me (**a**); R = R′ = Ph (**b**); R = Ph, R′ = Me (**c**); **III**, **IV**, R′ = Me (**a**), Ph (**b**), H (**c**); **V**, R′ = Ph.

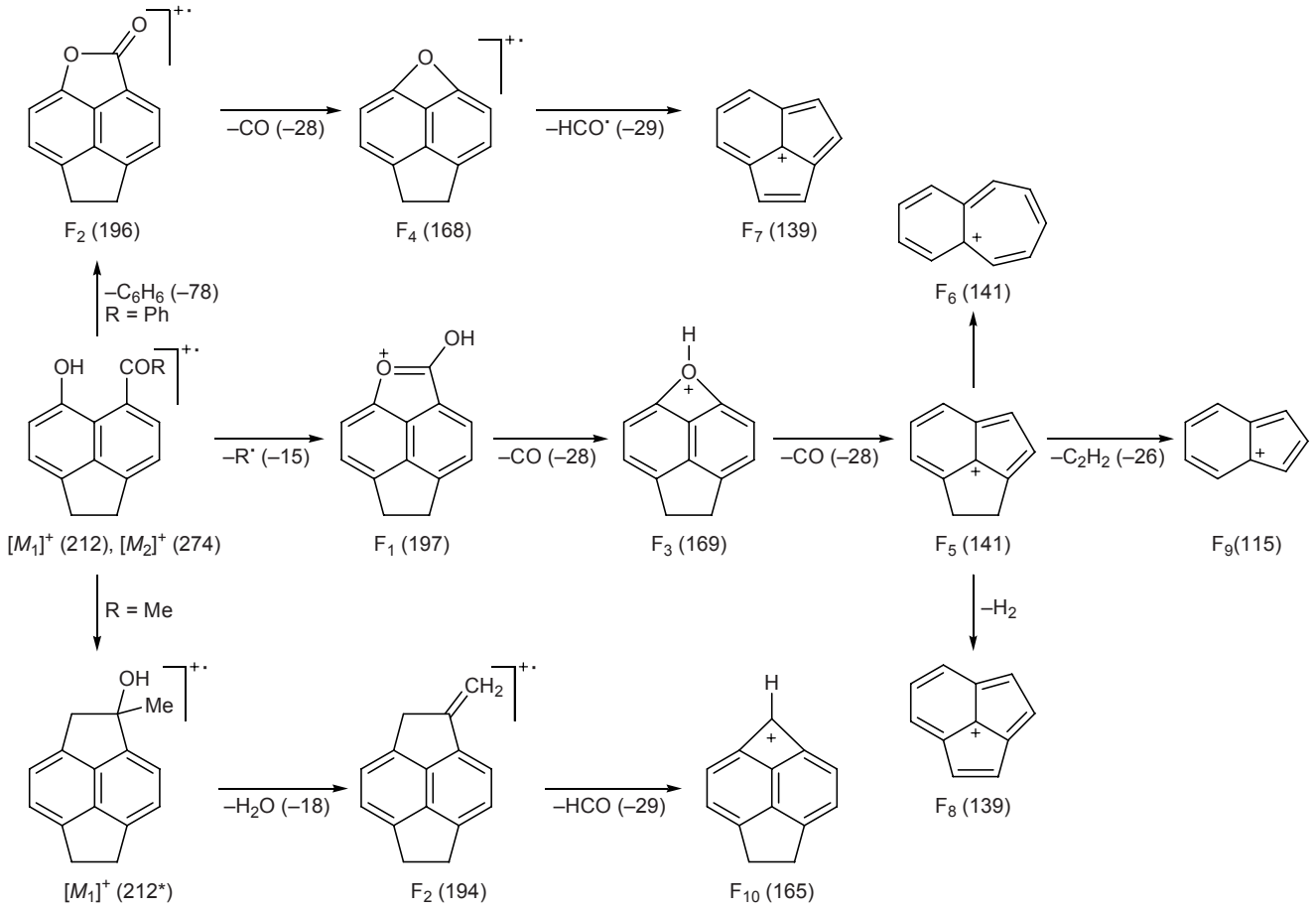
tion with acetic anhydride in the presence of perchloric acid or aluminum chloride, phenyl ketones were obtained by acylation with benzoyl chloride in tetrachloroethane in the presence of aluminum chloride, and $AlCl_3$-catalyzed formylation with dichloromethyl ethyl ether gave formyl-substituted derivatives. In the latter case, the reactions led to the formation of mixtures of O-acylated ketones and aldehydes **II**, which cannot be separated by chromatography. However, after hydrolysis of the ester group, the resulting hydroxy derivatives had different chromatographic mobilities, and the target *peri*-hydroxy compounds **III** were isolated from the multicomponent reaction mixtures. The benzoylation of 5-acetoxyacenaphthene (**Ia**) in the presence of aluminum chloride was accompanied by partial, and the formylation, by complete removal of the ester group (Scheme 1).

In the formylation of phenyl ketone **Ib**, apart from *peri*-hydroxy aldehyde **IIIc** we isolated another isomer which was assigned the structure of 6-hydroxyacenaphthene-3-carbaldehyde (**IVc**). The corresponding 3-substituted isomer **IVb** was also isolated in the benzoylation reaction (R′ = Ph); according to the ^{1}H NMR data, it contained about ~20% of one more isomer, presumably 8-benzoyl-6-hydroxyacenaphthene (**V**). We failed to purify compound **IVb** from **V** by chromatography or recrystallization. In the ^{1}H NMR spectrum of mixture **IVb**/**V** a singlet was present between two triplets in the δ region 3.2–3.6 ppm belonging to the ethylene bridge. This singlet is likely to arise from the corresponding protons of 8-benzoyl isomer **V**. The hydroxy protons in both isomers give rise to two broadened singlets at δ 5.3–5.5 ppm. The aromatic region of the spectrum contains a singlet and a doublet from the 8-benzoyl isomer with an intensity of ~20% of the intensity of the one-proton signals from 3-benzoyl isomer **IVb**.

Among the acetylation products, we succeeded in isolating only *peri*-hydroxyacetylacenaphthene **IIIa** as individual substance.

Unlike isomers **III**, compounds **IV** lack intramolecular hydrogen bond which affects the position of the hydroxy proton signal in the ^{1}H NMR spectra. Compounds **III** are characterized by a downfield signal in

Scheme 2.



the region δ 10–11.5 ppm, while the hydroxy proton in isomers **IV** resonates at δ 5–5.5 ppm. The structure of compounds **IV** as 3- rather than 8-acyl-substitued isomers **V** is confirmed by the presence in their ^{1}H NMR spectra of four one-proton doublets; compounds like **V** should display a one-proton singlet, two one-proton doublets, and one-proton triplet.

The structure of **IIIa** and **IIIb** was also confirmed by mass spectrometry. Probable fragmentation pathways of their molecules under electron impact are shown in Scheme 2. The main fragmentation pathway of molecular ions $[M_1]^+$ and $[M_2]^+$ derived from compounds **IIIa** and **IIIb**, respectively, includes initial elimination of methyl or phenyl radical with formation of stable fragment ion F_1 (I_{rel} = 70, 98%) which undergoes further decomposition to give stable ($I_{rel} \geq 50\%$) ions F_5, F_6, F_8, and F_9 (except for F_3, I_{rel} = 3, 15%). Some alternative decomposition pathways are also possible.

EXPERIMENTAL

The IR spectra were recorded on a Specord 71IR spectrophotometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Varian Unity-300 instrument in $CDCl_3$ using hexamethyldisiloxane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Varian MAT-44 instrument.

Acenaphthen-5-yl acetate (Ia). A solution of 0.63 g (3.7 mmol) of acenaphthen-5-ol in 3 ml of acetic anhydride containing a catalytic amount of sodium acetate was heated under reflux for 30 min. The mixture was cooled and poured into water, and the precipitate was filtered off and washed with water. Yield 0.73 g (92%), colorless powder, mp 90–91°C (from ethanol). IR spectrum, ν, cm^{-1}: 1767 (C=O), 1607. ^{1}H NMR spectrum, δ, ppm: 2.4 s (3H, CH_3), 3.30–3.45 m (4H, CH_2), 7.16 d (1H, 4-H, $J_{4,3}$ = 7.50 Hz), 7.24 d (1H, 3-H, $J_{3,4}$ = 7.50 Hz), 7.30 br.d (1H, 8-H, $J_{8,7}$ = 5.05 Hz), 7.43–7.51 m (2H, 6-H, 7-H). Found, %: C 79.52; H 5.51. $C_{14}H_{12}O_2$. Calculated, %: C 79.23; H 5.70.

Acenaphthen-5-yl benzoate (Ib). Benzoyl chloride, 0.9 ml (7.81 mmol), was added at 0°C to a solution of 0.45 g (2.6 mmol) of acenaphthen-5-ol in 2 ml of anhydrous pyridine, the mixture was kept for 1 h at room temperature, acidified with dilute hydrochloric acid to pH ~3, and diluted with water, and an oily material separated and was ground with ethanol. Yield 0.58 g (80%), colorless powder, mp 94–96°C (from ethanol). IR spectrum, ν, cm^{-1}: 1740 (C=O), 1590. ^{1}H NMR spectrum, δ, ppm: 3.35–3.50 m (4H, CH_2), 7.20–8.30 m (10H, H_{arom}). Found, %: C 83.36; H 4.92. $C_{19}H_{14}O_2$. Calculated, %: C 83.19; H 5.14.

1-(6-Hydroxyacenaphthen-5-yl)ethanone (IIIa). *a*. Acetic anhydride, 0.5 ml (5.3 mmol), was added to a solution of 0.22 g (1 mmol) of compound **Ia** in 2 ml of tetrachloroethane, the mixture was cooled to 0°C, and 0.3 g (2.2 mmol) of anhydrous $AlCl_3$ was added in portions under stirring. The mixture was kept for 24 h at room temperature and poured into water, the solvent was removed by steam distillation, and the precipitate, 0.145 g, was filtered off. It was dispersed in 3 ml of methanol, and the suspension was treated with 0.031 g of sodium methoxide over a period of 1 h at room temperature, acidified with dilute hydrochloric acid to pH ~3, and diluted with water. The precipitate was filtered off, dried, and dissolved in chloroform, and the solution was applied to a column charged with Al_2O_3. The column was eluted with chloroform to isolate 0.04 g (33%) of compound **IIIa** as an orange powder with mp 98–99°C; published data [1]: mp 96°C. IR spectrum, ν, cm^{-1}: 2670, 1635 (C=O), 1590. ^{1}H NMR spectrum, δ, ppm: 2.80 s (3H, CH_3), 3.35 m (2H, 1-H), 3.43 m (2H, 2-H), 7.14 d (1H, 7-H, $J_{7,8}$ = 7.65 Hz), 7.24 br.d (1H, 3-H, $J_{3,4}$ = 7.47 Hz), 7.32 br.d (1H, 8-H, $J_{8,7}$ = 7.62 Hz), 8.20 d (1H, 4-H, $J_{4,3}$ = 7.55 Hz), 11.60 s (1H, OH). Mass spectrum, *m*/*z* (I_{rel}, %): 212 (100) $[M]^+$, 197 (98) F_1, 194 (18) F_2*, 169 (15) F_3, 165 (22) F_4*, 141 (75) F_5 or F_6, 139 (55) F_8, 115 (60) F_9, 43 (35) $[MeCO]^+$. Found, %: C 78.89; H 5.47. $C_{14}H_{12}O_2$. Calculated, %: C 79.23; H 5.70.

b. Two drops of 72% perchloric acid were added to a solution of 0.22 g (1 mmol) of compound **Ia** in 2 ml of acetic anhydride, and the mixture was kept for 3 h at room temperature and poured into water. An oily material separated and was extracted into chloroform, and the extract was concentrated and subjected to column chromatography on Al_2O_3 using chloroform as eluent. A fraction with R_f 0.6 was collected. The eluate was evaporated, the oily residue was dissolved in 3 ml of methanol, 0.03 g of sodium methoxide was added, and the mixture was kept for 30 min at room temperature, acidified with dilute hydrochloric acid to pH ~3, and diluted with water. Yield 0.05 g (23%), orange powder, mp 98–99°C (from ethanol).

(6-Hydroxyacenaphthen-5-yl)phenylmethanone (IIIb) and (6-hydroxyacenaphthen-3-yl)phenylmethanone (IVb). *a*. Benzoyl chloride, 0.4 ml

(3.47 mmol), was added to a solution of 0.5 g (1.8 mmol) of compound **Ib** in 4.5 ml of tetrachloroethane, the mixture was cooled to 0°C, and 0.62 g (4.6 mmol) of anhydrous $AlCl_3$ was added in portions under stirring. The mixture was kept for 4.5 h at room temperature, poured into water, and subjected to steam distillation. The solid residue, 0.32 g was subjected to chromatography on aluminum oxide using chloroform as eluent to isolate 0.22 g of a mixture of isomeric benzoates **IIb**. The isomer mixture was dispersed in 3 ml of methanol, 0.031 g of sodium methoxide was added, and the mixture was kept for 30 min at room temperature, acidified with dilute hydrochloric acid to pH ~3, and diluted with water. The precipitate was filtered off, dried, and dissolved in chloroform, and the solution was subjected to column chromatography on Al_2O_3 using chloroform as eluent to isolate compound **IIIb** (R_f 0.75) and a mixture of compounds **IVb** and **V** (R_f 0.25).

(6-Hydroxyacenaphthen-5-yl)phenylmethanone (IIIb). Yield 0.04 g (25%), red plates, mp 117–118°C; published data [1]: mp 115°C. IR spectrum, ν, cm^{-1}: 1633 (C=O), 1590. ^1H NMR spectrum, δ, ppm: 3.4 m (4H, CH_2), 7.2–7.9 m (9H, H_{arom}), 9.6 s (1H, OH). Mass spectrum, *m*/*z* (I_{rel}, %): 274 (80) $[M]^+$, 197 (70) F_1, 196 (85) F_2, 169 (3) F_3, 168 (27) F_4, 141 (52) F_5 or F_6, 139 (25) F_7, 139 (63) F_8, 115 (55) F_9, 105 (45) $[PhCO]^+$, 77 (100) $[Ph]^+$. Found, %: C 83.47; H 4.93. $C_{19}H_{14}O_2$. Calculated, %: C 83.19; H 5.14.

(6-Hydroxyacenaphthen-3-yl)phenylmethanone (IVb) and (5-hydroxyacenaphthen-3-yl)phenylmethanone (V) (isomer mixture). Yield 0.04 g (25%), yellow powder, mp 183–186°C. IR spectrum, ν, cm^{-1}: 3394 (OH), 1650 (C=O). Found, %: C 82.82; H 5.33. $C_{19}H_{14}O_2$. Calculated, %: C 83.19; H 5.14.

b. Benzoyl chloride, 0.4 ml (3.47 mmol), was added to a solution of 0.32 g (1.5 mmol) of compound **Ia** in 4 ml of tetrachloroethane, the mixture was cooled to 0°C, and 0.62 g (4.6 mmol) of anhydrous $AlCl_3$ was added in portions under stirring. The mixture was kept for 4.5 h at room temperature, poured into water, and subjected to steam distillation. The oily residue was dissolved in chloroform, and the solution was subjected to column chromatography on silica gel using hexane as eluent to isolate 0.03 g of compound **IIIb** (orange product, mp 115°C, R_f 0.75) and 0.15 g of a mixture of ketones **IIIb** and **IVb** (R_f 0.4). Isomer mixture **IIIb**/**IVb** was treated with 0.03 g of sodium methoxide in 3 ml of methanol, and the mixture was acidified with dilute hydrochloric acid to pH ~3 and diluted with water. The precipitate was filtered off, dried, and dissolved in chloroform, and the solution was subjected to column chromatography on Al_2O_3 using chloroform as eluent to isolate 0.025 g (19%) of compound **IIIb** as orange powder with mp 115°C, R_f 0.75. Overall yield of **IIIb** 0.055 g.

6-Hydroxyacenaphthene-5-carbaldehyde (IIIc) and 6-hydroxyacenaphthene-3-carbaldehyde (IVc). *a*. Compound **Ib**, 0.27 g (1 mmol), was dissolved in 3 ml of tetrachloroethane, 0.3 ml of dichloromethyl ethyl ether was added, the mixture was cooled to 0°C, and 0.2 g (1.5 mmol) of anhydrous $AlCl_3$ was added in portions under stirring. The mixture was left to stand overnight at room temperature, poured into water, and subjected to steam distillation. The residue was dissolved in chloroform, and the solution was subjected to column chromatography on Al_2O_3 using chloroform as eluent to isolate 0.17 g of an aldehyde mixture which was dispersed in 3 ml of methanol. Sodium methoxide, 0.03 g, was added to the suspension, and the mixture was kept for 30 min at room temperature, acidified with dilute hydrochloric acid to pH ~3, and diluted with water. The precipitate was filtered off, dried, and dissolved in chloroform, and the solution was subjected to column chromatography on Al_2O_3 using chloroform as eluent to isolate compounds **IIIc** (R_f 0.7) and **IVc** (R_f 0.2).

6-Hydroxyacenaphthene-5-carbaldehyde (IIIc). Yield 0.04 g (36%), orange plates, mp 128–130°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1607. ^1H NMR spectrum, δ, ppm: 3.31–3.38 m (2H, 1-H), 3.38–345 m (2H, 2-H), 7.13 d (1H, 7-H, $J_{7,8}$ = 7.69 Hz), 7.32 d (1H, 3-H, $J_{3,4}$ = 7.04 Hz), 7.34 d (1H, 8-H, $J_{8,7}$ = 7.62 Hz), 7.93 d (1H, 4-H, $J_{4,3}$ = 7.09 Hz), 9.8 s (1H, CHO), 11.5 s (1H, OH). Found, %: C 78.52; H 5.40. $C_{13}H_{10}O_2$. Calculated, %: C 78.77; H 5.09.

6-Hydroxyacenaphthene-3-carbaldehyde (IVc). Yield 0.015 g (14%), yellow powder, mp 168–170°C. IR spectrum, ν, cm^{-1}: 3300, 1660 (C=O), 1590. ^1H NMR spectrum, δ, ppm: 3.41 t (2H, 1-H, J_1 = 4.55, J_2 = 5.86 Hz), 3.77 t (2H, 2-H, J_1 = 6.01, J_2 = 5.72 Hz), 5.21 s (1H, OH), 6.98 d (1H, 7-H, $J_{7,8}$ = 7.47 Hz), 7.22 d (1H, 8-H, $J_{8,7}$ = 7.40 Hz), 7.84 d (1H, 5-H, $J_{5,4}$ = 8.65 Hz), 7.87 d (1H, 4-H, $J_{4,5}$ = 8.60 Hz), 10.3 s (1H, CHO). Found, %: C 78.51; H 4.83. $C_{13}H_{10}O_2$. Calculated, %: C 78.77; H 5.09.

b. Dichloromethyl ethyl ether, 0.3 ml, was added to a solution of 0.22 g (1 mmol) of acetate **Ia** in 2 ml of

tetrachloroethane, the mixture was cooled to 0°C, and 0.3 g (2.2 mmol) of anhydrous $AlCl_3$ was added in portions under stirring. The mixture was left to stand overnight at room temperature and poured into water, and the solvent was removed by steam distillation. The product was extracted into chloroform, and the extract was washed with water, dried, and subjected to column chromatography on Al_2O_3 using chloroform as eluent. Yield of compound **IIIc** 0.07 g (29%), orange plates, mp 125–126°C.

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