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**SHORT COMMUNICATIONS**

# Synthesis of 5-Acetyl-6-hydroxyacenaphthylene

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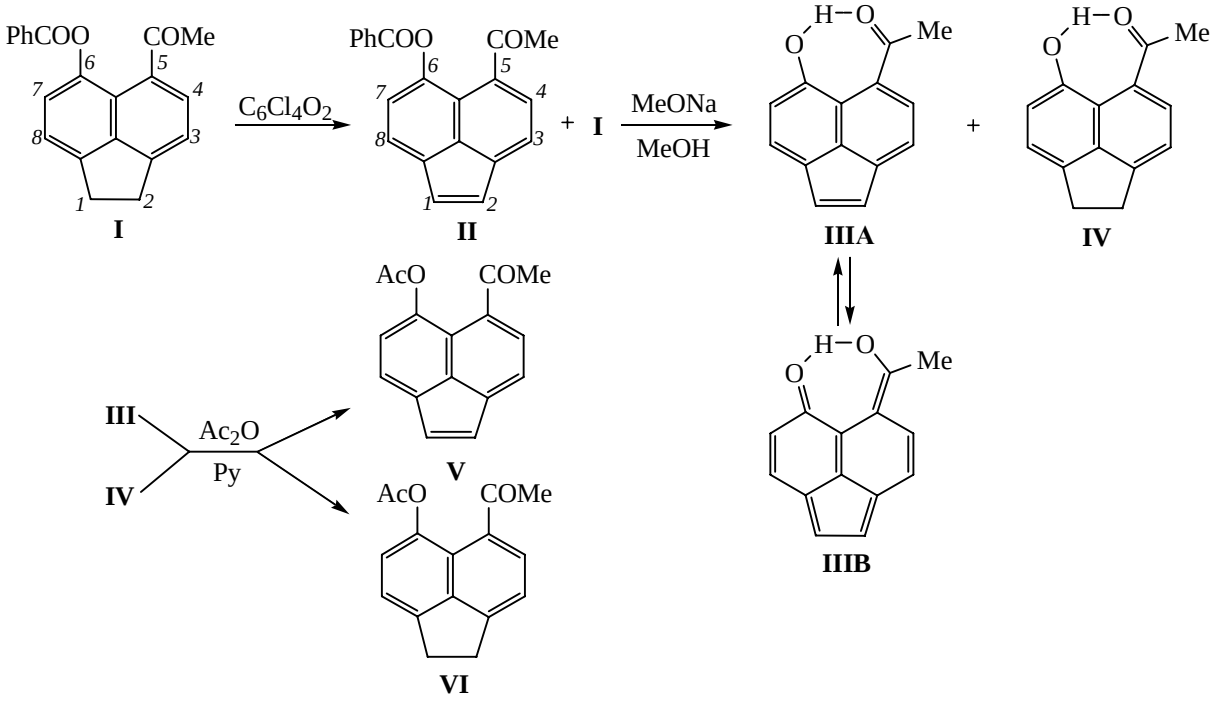
We reported recently [1] on the synthesis of the first representative of acenaphthylene *peri*-aminoketones and comprehensively discussed the importance for the theory and practice of the organic chemistry of acenaphthylene derivatives containing *peri*-hydroxy or *peri*-amino-carbonyl moiety.

The goal of this study was the preparation of 5-acetyl-6-hydroxyacenaphthylene, the first member of the unknown class of *peri*-hydroxyacylacenaphthylenes. The synthesis of the target compound was performed by dehydration with chloranil of 5-acetyl-6-benzoyloxy-acenaphthene (**I**) that we described before [2].

The reaction resulted in a mixture of the initial **I** and dehydrated **II** compounds in a ratio 1:1 ($^1$H NMR data) that remains unchanged at variation of the reagents ratio and reaction conditions (temperature, reaction time). We failed to separate this mixture into individual substances by chromatography on various carriers (aluminum oxide, silica gel) applying different eluents (benzene, chloroform), since the compounds possessed identical chromatographic mobility ($R_f$ 0.8).

After the cleavage of the ester group we obtained a mixture of the corresponding hydroxy derivatives of acenaphthylene **III** and of previously described [2]




**I** **II** **IIIA** **IV** **IIIB** **V** **VI**

acenaphthene **IV** that had different chromatographic mobility and consequently were isolated in an individual state by column chromatography on silica gel.

The structure of the target 5-acetyl-6-hydroxyacenaphthylene (**III**) was proved by spectral methods. Also a comparison of the spectral characteristics was performed for acenaphthylene **III** and acenaphthene **IV** *peri*-hydroxyketones and their O-acetates **V** and **VI** to estimate the variations in the structural and electronic parameters at the appearance of a double bond in the *peri*-position with respect to the hydroxyketo moiety. To this end we report here the IR and $^1$H NMR spectra of the formerly prepared [2] acenaphthene derivatives **IV** and **VI** alongside those of the corresponding newly synthesized acenaphthylene ketones **III** and **V**. The spectra were registered under identical conditions.

Thus, in the IR spectra of both *peri*-hydroxyketones **III** and **IV** the absorption band of the carbonyl group appeared similarly as a narrow band at 1635 cm$^{-1}$, whereas the position of the stretching vibrations band of the hydroxy group was different (2630 cm$^{-1}$ for compound **III** and 2713 cm$^{-1}$ for compound **IV**). In the $^1$H NMR spectrum of the acenaphthene derivative **IV** in deuterochloroform the bimethylene unit is observed as a four-proton centrosymmetrical multiplet centered at 3.4 ppm that is transformed into two one-proton doublets (6.82 and 7.20 ppm) with a small coupling constant (5.13 Hz) in going to acenaphthylene *peri*-hydroxyketone **III**, and the proton signals of the naphthalene framework in this case slightly (by 0.16 ppm) shift downfield. The hydroxy group protons give rise to sharp singlets at 11.6 and 12.9 ppm for acenaphthene **IV** and acenaphthylene **III** *peri*-hydroxyketones respectively indicating the strengthening of the intramolecular hydrogen bonds in going from compound **IV** to compound **III**. The signal of the hydroxy group proton of acenaphthylene *peri*-hydroxyketone **III** in solution of deuterodimethyl sulfoxide shifts from 12.9 to 11.5 ppm. The aromatic protons in positions *2* and *7* of the naphthalene framework of acenaphthene *peri*-hydroxyketone **IV** adjacent to the bimethylene unit and being in long-range coupling with the protons of the latter appear like broadened one-proton doublets (unresolved multiplets); therefore it is possible to unambiguously identify each signal of the aromatic protons.

IR and $^1$H NMR spectra of acenaphthylene **V** and acenaphthene **VI** [2] *peri*-acetoxyketones also are quite dissimilar.

**5-Acetyl-6-hydroxyacenaphthylene (III).** A mixture of 0.63 g (2 mmol) of 5-acetyl-6-benzoyloxyacenaphthene [2] and 0.49 g (2 mmol)of chloranil in 5 ml of *o*-dichlorobenzene was boiled for 2 h till disappearance of chloranil (TLC monitoring). Then the mixture was cooled, filtered from the separated precipitate of tetrachlorodihydroxybenzene, the filterate was concentrated and subjected to column chromatography on aluminum oxide (eluent chloroform) collecting the fraction with $R_f$ 0.8. On evaporating chloroform we obtained 270 mg of yellow powder which appeared as a single spot on a thin layer of aluminum oxide. $^1$H NMR spectrum revealed that the substance was a mixture of two compounds: Initial ketone **I** was present in the mixture with its oxidation product **II** in a 1:1 ratio. To a dispersion of 340 mg of this mixture in 3 ml of methanol was added 58 mg of dry sodium methylate, and the solid substance gradually dissolved. After 15 min the solution was diluted with water and acidified with a dilute (1:1) hydrochloric acid till the medium turned acid. The dispersion obtained was extracted with chloroform, washed with water, and dried with calcium chloride, then the solvent was evaporated, and the resulting mixture of *peri*-hydroxyketones **III** and **IV** was separated by column chromatography on silica gel (eluent chloroform). We isolated 100 mg (44%) of red fraction of $R_f$ 0.8 (target compound **III**) and 110 mg (48%) of orange fraction of $R_f$ 0.4 (*peri*-hydroxyketone **IV**). Acenaphthylene *peri*-hydroxyketone **III,** mp 91–92°C. IR spectrum, ν, cm$^{-1}$: 2630 (OH), 1635 (MeC=O), 1590. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.90 s (3H, COMe), 6.82 d (1H, H$^2$, $J_{2,1}$ 5.13 Hz), 6.98 d (1H, H$^7$, $J_{7,8}$ 7.62 Hz), 7.20 d (1H, H$^1$ , $J_{1,2}$ 5.13 Hz), 7.58 d (1H, H$^8$, $J_{8,7}$ 7.62 Hz), 7.72 d (1H, H$^3$, $J_{3,4}$ 7.40 Hz), 8.36 d (1H, H$^4$, $J_{4,3}$ 7.40 Hz), 12.9 s (1H, OH). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.60 s (3H, COMe), 6.83 d (1H, H$^7$, $J_{7,8}$ 7.45 Hz), 6.90 d (1H, H$^2$, $J_{2,1}$ 5.18 Hz), 7.12 d (1H, H$^1$ , $J_{1,2}$ 5.18 Hz), 7.58 d (1H, H$^3$, $J_{3,4}$ 7.12 Hz), 7.60 d (1H, H$^8$, $J_{8,7}$ 7.45 Hz), 7.70 d (1H, H$^4$, $J_{4,3}$ 7.12 Hz), 11.50 s (1H, OH).

**5-Acetyl-6-hydroxyacenaphthene (IV)**. IR spectrum, ν, cm$^{-1}$: 2713 (OH), 1635 (MeC=O). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.80 s (3H, COMe), 3.40 m (4H, $CH_2CH_2$), 7.14 d (1H, H$^7$, $J_{7,8}$ 7.65 Hz), 7.24 br.d (1H, H$^3$, $J_{3,4}$ 7.51 Hz), 7.32 br.d (1H, H$^8$ , $J_{8,7}$ 7.65 Hz), 8.20 d (1H, H$^4$, $J_{4,3}$ 7.51 Hz), 11.60 s (1H, OH).

**5-Acetyl-6-acetoxyacenaphthylene (V).** To a dark-red solution of 42 mg (0.2 mmol) of compound **III** in 1 ml of pyridine at 0°C was added 1 ml of acetic anhydride. The solvent gradually decolorized and was

afterwards maintained at room temperature for 1 h more. Then the solution was poured into a strongly diluted hydrochloric acid. The precipitate separated after 1.5–2 h was filtered off and dried in air to obtain 35 mg (70%) of target compound **V** that was purified by column chromatography on aluminum hydroxide (eluent chloroform), mp 68–69°C. IR spectrum, ν, $cm^{-1}$: 1767 (MeCOO), 1690 (MeC=O). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, MeCOO), 2.70 s (3H, MeC=O), 6.07 d (1H, $H^2$, $J_{2,1}$ 5.22 Hz), 7.05 d (1H, $H^1$, $J_{1,2}$ 5.22 Hz), 7.22 d (1H, $H^7$, $J_{7,8}$ 6.97 Hz), 7.47 d (1H, $H^8$, $J_{8,7}$ 6.97 Hz), 7.61 br.d (2H, $H^3$, $H^4$ *J* 7.31 Hz).

**5-Acetyl-6-acetoxyacenaphthene (VI).** IR spectrum, ν, $cm^{-1}$: 1780 (MeCOO), 1700 (MeC=O). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, MeCOO), 2.60 s (3H, MeC=O), 3.40 br.s (4H, $CH_2CH_2$), 7.22 d (1H, $H^7$, $J_{7,8}$ 7.44 Hz), 7.28 br.d (1H, $H^8$, $J_{8,7}$ 7.44 Hz), 7.31 br.d (1H, $H^3$, $J_{3,4}$ 7.12 Hz), 7.45 d (1H, $H^4$, $J_{4,3}$ 7.12 Hz).

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