ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 10, pp. 1576–1577. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.N. Antonov, R.V. Tyurin, L.G. Minyaeva, V.V. Mezheritskii, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 10, pp. 1585–1586.

SHORT COMMUNICATIONS

First *peri*-Amino Ketone of the Acenaphthylene Series

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Received August 1, 2006

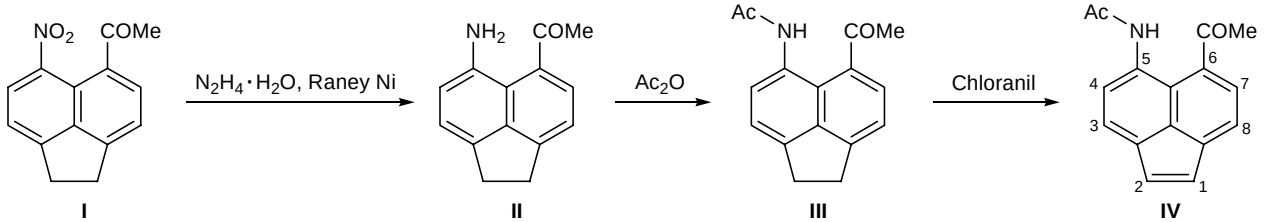
DOI: 10.1134/S1070428006100319

The properties of a hydroxy or amino group in the *peri* position with respect to a carbonyl group differ from the properties of the same substituents in the *ortho* position owing to the lack of conjugation through the aromatic π system. This specificity of *peri*-substituted compounds prevents them from participating in fundamental transformations intrinsic to aromatic systems, such as benzoid–quinoid tautomerism, electrocyclic ring closure, chelation of metals, etc. Therefore, design of structures in which the above functional groups would be conjugated through the aromatic bond system despite their *peri* arrangement with respect to each other should open new prospects in theoretical studies and practical organic synthesis.

The present communication reports on the synthesis of the first representative of such compounds, 5-acetyl-6-acetylaminoacenaphthylene, according to the scheme shown below. Compounds **II** and **III** were prepared by modified procedures [1]. No spectral parameters of these compounds were given in [1]. Therefore, we thought it reasonable to adduce the synthetic procedures and analyze spectral parameters of compounds **II** and **III** and newly synthesized amino ketone **IV**.

In the ^{1}H NMR spectrum of *peri*-amino ketone **II**, protons of the amino group give rise to a broadened two-proton singlet at δ 4.5 ppm due to formation of a weak intramolecular hydrogen bond between one proton of that group and carbonyl oxygen atom; this hydrogen bond allows free rotation about the C–N bond, and the observed signal is the result of coalescence at room temperature. Protons in the two methylene groups constitute a strongly coupled *AA'BB'* system which appears in the ^{1}H NMR spectrum ($CDCl_3$) as a complex centrosymmetric four-proton multiplet at δ 3.34 ppm. Aromatic protons in positions *3* and *8* of the acenaphthene ring, i.e., in the positions neighboring to the ethylene bridge, give broadened one-proton doublets at δ 7.18 and 7.22 ppm. The IR spectrum of amino ketone **II** contained two well resolved absorption bands due to stretching vibrations of the amino group (3407 and 3327 cm^{-1}) and carbonyl absorption band at 1660 cm^{-1}.

The presence of an electron-withdrawing acetyl group on the nitrogen atom in compound **III** strongly enhances the intramolecular hydrogen bond, and the signal from the NH proton in the acetylamino group shifts strongly downfield (a sharp singlet at 9.7 ppm in DMSO-d_6). Signals from the methylene protons appear as a complex multiplet at δ 3.4 ppm, and aromatic protons give rise to two one-proton doublets with equal coupling coupling constants (J = 7.17 Hz) and a two-proton singlet. In the IR spectrum of **III** we observed two carbonyl absorption bands at 1650 and 1670 cm^{-1} and N–H stretching vibration band at 3300 cm^{-1}.



I **II** **III** **IV**

Unlike acenaphthene precursor **III**, the ^{1}H NMR spectrum of *peri*-acetylamino ketone **IV** in $CDCl_3$ lacks signals from methylene protons, and two one-proton doublets appear at δ 6.88 and 7.10 ppm (^3J = 5.31 Hz) due to 1-H and 2-H. Aromatic protons in the naphthalene fragment give four one-proton doublets, which were assigned on the basis of the corresponding coupling constants. The signal from the NH proton in the acetylamino group shifts even more downfield (δ 10.7 ppm), presumably due to strengthening of the intramolecular hydrogen bond. The signal from the same proton in the spectrum recorded in DMSO-d_6 is located in a slightly stronger field (δ 10.1 ppm), but it appears as a sharp singlet. This means that the intramolecular hydrogen bond (7-membered H-chelate ring) is sufficiently strong to remain unbroken even in such a strongly polar aprotic solvent as dimethyl sulfoxide. In going to DMSO-d_6, the spectral pattern in the region corresponding to resonance of the aromatic naphthalene protons becomes more complex: one of the doublets is retained, while signals from the remaining three protons give rise to a difficultly interpretable multiplet consisting of five peaks. The IR spectrum of **IV** contains sharp peaks belonging to stretching vibrations of the N–H bond (3270 cm^{-1}) and two carbonyl groups (1687 and 1660 cm^{-1}).

Studies on specific physical, spectral, and chemical properties of the new *peri*-acetylamino ketone of the acenaphthylene series are now in progress. Their results, as well as the synthesis of new related compounds, will be reported elsewhere.

1-(6-Aminoacenaphthen-5-yl)ethanone (II). 1-(6-Nitroacenaphthen-5-yl)ethanone (**I**), 5 g (20 mmol), was dispersed in 83 ml of methanol, 2.1 g of Raney nickel was added, and 8.3 ml of hydrazine hydrate was then added in portions at 20–25°C. When gas evolution was over, the catalyst was filtered off, the filtrate was poured into a 4-fold volume of water, and the precipitate was filtered off and dried at room temperature. Yield 4 g (91%), yellow powder, mp 121–122°C (from ethanol–water, 1:3); published data [1]: mp 121.5–122°C. IR spectrum, ν, cm^{-1}: 3407, 3327 (NH); 1660 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.8 s (3H, COMe), 3.34 m (4H, CH_2CH_2), 4.45 br.s (2H, NH_2), 6.84 d (1H, 7-H, ^3J = 7.41 Hz), 7.18 br.d (1H, 8-H, ^3J = 7.41 Hz), 7.22 br.d (1H, 3-H, ^3J = 7.22 Hz), 7.78 d (1H, 4-H, ^3J = 7.22 Hz). Found, %: C 79.35; H 6.26; N 6.87. $C_{14}H_{13}NO$. Calculated, %: C 79.62; H 6.16; N 6.64.

***N*-(6-Acetylacenaphthen-5-yl)acetamide (III).** A suspension of 0.568 g (2.7 mmol) of amino ketone **II** in 5 ml of water was heated to 40–50°C, and 1 ml of acetic anhydride was added. The mixture became homogeneous, and a solid material separated in 3–5 min. The precipitate was filtered off. Yield 0.554 g (81%), pale yellow powder, mp 161–162°C (from ethanol); published data [1]: mp 160.2–161°C. IR spectrum, ν, cm^{-1}: 3300 (NH), 1647 (C=O), 1673 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.96 s (3H, $COCH_3$), 2.6 s (3H, $NCOCH_3$), 3.36 m (4H, CH_2CH_2), 7.34 d (1H, 4-H, ^3J = 7.17 Hz), 7.4 s (2H, 7-H, 8-H), 7.5 d (1H, 3-H, ^3J = 7.17 Hz), 9.7 br.s (1H, NH). Found, %: C 75.51; H 6.12; N 5.75. $C_{16}H_{15}NO_2$. Calculated, %: C 75.89; H 5.93; N 5.53.

***N*-(6-Acetylacenaphthylen-5-yl)acetamide (IV).** Chloranil, 0.438 g (1.8 mmol), was added to a solution of 0.3 g (1.2 mmol) of compound **III** in 2 ml of *o*-dichlorobenzene, and the mixture was heated for 2 h under reflux (using a Vigreaux column). The solvent was removed, and the dry residue was dissolved in chloroform and subjected to chromatography on Al_2O_3. Yield 0.04 g (13%), yellow powder, mp 107–108°C. IR spectrum, ν, cm^{-1}: 3274 (NH), 1660 (C=O, amide), 1687 (C=O, ketone). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 2.23 s (3H, COMe), 2.84 s (3H, NCOMe), 6.88 d (1H, 1-H, ^3J = 5.3 Hz), 7.1 d (1H, 2-H, ^3J = 5.3 Hz), 7.62 d (1H, 4-H, ^3J = 7.6 Hz), 7.66 d (1H, 7-H, ^3J = 7.2 Hz), 8.1 d (1H, 8-H, ^3J = 7.2 Hz), 8.3 d (1H, 3-H, ^3J = 7.6 Hz), 10.7 br.s (1H, NH); in DMSO-d_6: 2.0 s (3H, COMe), 2.6 s (3H, NCOMe), 7.05 d (1H, 1-H, ^3J = 5.3 Hz), 7.15 d (1H, 2-H, ^3J = 5.3 Hz), 7.47 d (1H, 4-H, ^3J = 7.3 Hz), 7.7–7.83 m (3H, 3-H, 7-H, 8-H), 10.1 s (1H, NH). Found, %: C 76.15; H 5.41; N 5.77. $C_{16}H_{13}NO_2$. Calculated, %: C 76.49; H 5.18; N 5.58.

The ^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer at 300 MHz relative to HMDS as internal reference. The IR spectra were measured in mineral oil on a Specord 71IR instrument.

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