SYNTHESIS OF 6-OXA-8-AZA-6,7,8,9,11,12,13,14,16,17-DECAHYDROCYCLOPENTA[a]PHENANTHRENE

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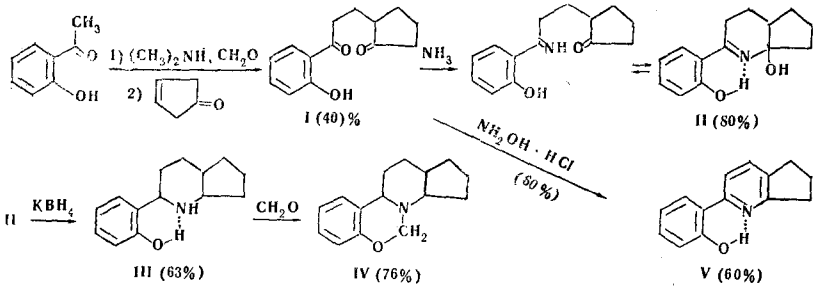
UDC 547.677.2'867.2.07

In a study of the possibility of the syntheses of heterocyclic analogs of steroids from 1,5-diketones, we have established that 1,5-diketones of the I type may be a convenient base for the synthesis of a system with a 6-oxa-8-azasteroid skeleton. Starting with the 1-(2-hydroxyphenyl)-3-(2-oxocyclohexyl)-1-propanone (I) that we obtained, we synthesized 6-oxa-8-aza-6,7,8,9,11,12,13,14,16,17-decahydrocyclopenta[a]phenanthrene (IV):



We obtained I by the method for the synthesis of 1,5-diketones described in [1]. Its IR spectrum shows absorption of both aliphatic-aromatic (1660 cm^{-1}) and alicyclic (1730 cm^{-1}) ketones. The closing of the pyridine ring that is characteristic for 1,5-diketones occurs by the action of hydroxylamine hydrochloride on I via the Stobbe variant [2], and V is formed. Compound II is readily formed by treatment of an alcohol solution of I with 25% ammonium hydroxide. In the crystalline state it exists in the cyclic form, since its IR spectrum, recorded in mineral oil, does not contain absorption above 1630 cm^{-1}, while in the IR spectrum recorded in $CHCl_3$ there is an intense band at 1730 cm^{-1} (alicyclic C=O) as well as absorption at 3620 cm^{-1} (unassociated OH), which makes it possible to assume that a tautomeric equilibrium between the cyclic and open form exists in solution. Diketone I is regenerated on treatment of II with dilute HCl. Reduction of II with KBH_4 in dioxane–water at 30-40° gives, according to thin-layer-chromatographic data, one isomer of III with m/e 217^+. The latter very readily reacts with 40% formalin at room temperature to form IV with m/e 229^+. Compounds II (in cyclic form), III, and V are "quasisteroid" chelates: their IR spectra contain a broad band at 2600-3200 cm^{-1} (chelate OH). This band is absent in the IR spectrum of IV; moreover, there is no absorption at 3200-3700 cm^{-1}. This indicates the absence of O–H and N–H bonds in IV. At the same time, a narrow peak at 2780 cm^{-1} (O–CH_2–N) appears in the spectrum.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrophotometer, while the mass spectra were recorded with an MKh-1303 spectrometer.

1-(2-Hydroxyphenyl)-3-(2-oxocyclopentyl)-1-propanone (I). This was obtained as white crystals with mp 38-39° (by freezing out from petroleum ether). Found: C 72.7; H 6.9%. $C_{14}H_{16}O_3$. Calculated: C 72.4; H 6.9%.

Far-Eastern State University, Vladivostok. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, p. 1149, August, 1971. Original article submitted December 13, 1970

8-Hydroxy-2-(2-hydroxyphenyl)perhydropyrindine (II). This was obtained as yellow crystals with mp 142-143° (from benzene). Found: C 73.1; H 7.3; N 6.2%. $C_{14}H_{17}NO_2$. Calculated: C 72.7; H 7.4; N 6.1%.

2-(2-Hydroxyphenyl)perhydropyrindine (III). This was obtained as white crystals with mp 59-61° (sublimation). Found: C 77.7; H 8.9; N 6.5%. $C_{14}H_{19}NO$. Calculated: C 77.4; H 8.8; N 6.4%.

6-Oxa-8-aza-6,7,8,9,11,12,13,14,16,17-decahydrocyclopenta[a]phenanthrene (IV). This was obtained as white crystals with mp 53-54° (sublimation). Found: C 78.7; H 8.5; N 6.0%. $C_{15}H_{19}NO$. Calculated: C 78.6; H 8.29; N 6.12%.

2-(Hydroxyphenyl)-6,7-dihydropyrindine (V). This was obtained as pale-yellow crystals with mp 95-96° (sublimation). Found: C 79.5; H 6.3; N 6.7%. $C_{14}H_{13}NO$. Calculated: C 79.6; H 6.2; N 6.6%.

LITERATURE CITED

1. N. S. Gill, K. B. James, F. Lions, and K. T. Potts, J. Am. Chem. Soc., 74, 4923 (1952).
2. H. Stobbe, Ber., 35, 3978 (1902).