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Abstract

Full Text

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SYNTHESIS OF N-BENZOYL DERIVATIVES OF 1,2-DIHYDROQUINOLINES

(Presented by Academician M. I. Kabachnik, 10 VII 1963)

The synthesis of dihydroquinoline (I) and its derivatives is a rather difficult problem ([1]). Compounds of this type are very unstable; they readily polymerize and are oxidized by atmospheric oxygen, whereas their N-monobenzoyl derivatives are substances stable under ordinary conditions.

(I) (II)

We have developed a very simple method for obtaining N-benzoyl derivatives of the indicated type from readily available 2-methyl-4-hydroxy-1,2,3,4-tetrahydroquinolines with substituents in the benzene ring, existing in two stereoisomeric forms (II α and β).

As starting materials we used readily available N-monobenzoyl derivatives described in the literature ([2], [3]).

The elimination of water proceeds according to the scheme:

$$\text{(III)} \xrightarrow[\text{heating}]{\text{KHSO}_4} \text{(IV)} + \text{H}_2\text{O}$$

IIIa $R_1 = \text{CH}_3$, $R_2 = \text{H}$ IVa $R_1 = \text{CH}_3$, $R_2 = \text{H}$
IIIb $R_1 = R_2 = \text{CH}_3$ IVb $R_1 = R_2 = \text{CH}_3$

The procedure and the proof of structure are illustrated by two examples: 2,6-dimethyl- and 2,6,8-trimethyl-4-hydroxy-1,2,3,4-tetrahydroquinolines.

Experimental Part

1. 1-Benzoyl-2,6-dimethyl-1,2-dihydroquinoline (IVa). The monobenzoyl derivative of the β-isomer of 2,6-dimethyl-4-hydroxy-1,2,3,4-tetrahydroquinoline (IIIa) was obtained according to the literature data ([3]), m.p. 171–172°. 3.5 g of (IIIa) was mixed with 0.5 g of potassium bisulfate and heated to 160–180° in a sulfuric-acid bath until the evolution of bubbles ceased.

The melt was dissolved in alcohol, filtered, and left to crystallize. White crystals, m.p. 132–133° (from alcohol). Yield of (IVa): 2.3 g, or 70% of theory.

$C_{18}H_{17}ON$. Found, %: C 81.94; H 6.45; N 5.45
Calculated, %: C 82.09; H 6.51; N 5.33

Molecular weight by Rast: 278; calculated: 263.

Similar results were also obtained with the α-isomer ([3]).

2. **Hydrogenation of 1-benzoyl-2,6-dimethyl-1,2-dihydroquinoline** (IVa) was carried out in ethyl alcohol over reduced platinum oxide. Crystals with m.p. 103–104° were obtained; they melted without depression with authentic 1-benzoyl-2,6-dimethyl-1,2,3,4-tetrahydroquinoline.

3. **Hydrolysis of 1-benzoyl-2,6-dimethyl-1,2,3,4-tetrahydroquinoline** (IVa). A 7.5 g portion of substance (IVa) was heated for 4 hours with 300 ml of a 10% aqueous-alcoholic solution of sodium hydroxide. The alcohol was distilled off, and the residue was steam-distilled. The presumed 2,6-dimethylquinoline separated in the distillate as an oil and was extracted with ether. The picrate, m.p. 185–186°, melted without depression with authentic 2,6-dimethylquinoline picrate. The yield of the quinoline base was 30% of theory. The residue in the flask for steam distillation was mixed with conc. hydrochloric acid. After extraction with ether and purification, the white crystals melted with benzoic acid without depression at 119–120°.

4. **Thermal decomposition of 1-benzoyl-2,6-dimethyl-1,2,3,4-tetrahydroquinoline** (IVa). A 10 g portion of substance (IVa) was heated to boiling and boiled for 15 min, after which the oil-like mixture was fractionated in vacuo. Two fractions were obtained. The first distilled up to 158°/12 mm and was fairly pure 2,6-dimethylquinoline, which was proved by the preceding method. Yield 42%. The second fraction distilled above 158° and rapidly crystallized. Crystals with m.p. 103–104° melted without depression with authentic 1-benzoyl-2,6-dimethyl-1,2,3,4-tetrahydroquinoline. Yield 28%.

5. **1-Benzoyl-2,6,8-trimethyl-1,2-dihydroquinoline** (IVb). The benzoyl derivative of the β-isomer of 2,6,8-trimethyl-4-hydroxy-1,2,3,4-tetrahydroquinoline ([2]) (IIIb), with m.p. 149–150°, under conditions analogous to those in item 1, gave crystals with m.p. 108–109° (from alcohol).

Found, %: C 82.29; H 7.07; N 5.01
$C_{19}H_{19}ON$. Calculated, %: C 82.28; H 6.90; N 5.05

Molecular weight by Rast: 275; calculated: 277.

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Note: Figure translations are in progress. See original paper for figures.