UNEXPECTED SPIROCYCLIZATION OF 3-BENZOYL-3-(2-PYRIDYLAMINO)-1,3-DIHYDROBENZO[c]FURAN-1-ONE

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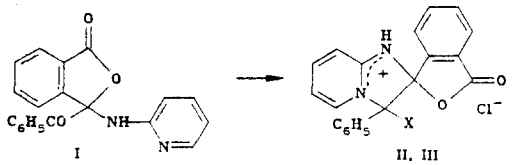
From the reaction of 3-benzoyl-3-chloro-1,3-dihydrobenzo[c]furan-1-one [1] with an equimolar mixture of 2-aminopyridine and triethylamine in dioxane at 100°C, we obtained 3-benzoyl-3-(2-pyridylamino)-1,3-dihydrobenzo[c]furan-1-one [1]. In its IR spectrum, bands of the phthalide and benzoyl C=O group are observed (see [2]). We have shown that during the preparation of a hydrochloride of compound I, the oxygen atom of the benzoyl group is protonated with the simultaneous intramolecular alkylation of the pyridine nitrogen atom, and the colorless 1,2'3,3'-tetrahydro-3'-hydroxy-3-oxo-3'-phenylspiro[benzo[c]furan-1,2'-1H-imidazo[1,2-a]pyridinium] chloride (II) is formed. The C=O band of the benzoyl is absent in its IR spectrum, and the phthalide C=O band is shifted to the high frequencies, as we have previously observed in [3] in the spectra of 5,3'-spirophthalidofuranid-2-ones. The action of thionyl chloride on compound I results in a vigorous exothermal reaction, and the colorless 3-chloro derivative III is formed. The action of water at room temperature causes the hydrolysis III → II.



I

II, III

II X=OH; III X=Cl

Compound I. mp 163...164°C (from EtOH), yield 69%. IR spectrum in Nujol: 3375 (N–H), 3075, 2915, 1753 (phthalide C=O), 1685 (benzoyl C=O), 1613, 1583, 1508 cm^{-1}; in dioxane: 1780, 1695, 1607, 1584 (sh.), 1508 cm^{-1}. After standing in dioxane solution for 96 h, a new band appears in the IR spectrum at 1644 cm^{-1} (the intensity of the remaining bands practically does not change), which can be explained by the appearance of a pyridoneimine tautomer.

Compound II. mp 260°C (dec., from anhydrous EtOH). IR spectrum in Nujol: 2920 (OH, broad band), 1792 (phthalide C=O), 1643 and 1526 (skeletal vibrations of pyridinium ring [4, p. 579]), 1575 cm^{-1}.

Compound III. mp 200°C (turns yellow)...220°C (dec). IR spectrum in Nujol: 3012, 2506, 1792 (phthalide C=O), 1655, 1552 cm^{-1} (skeletal vibrations of the pyridinium ring [4, p. 579]).

The data on the elemental analysis of the synthesized compounds correspond to the calculated values.

LITERATURE CITED

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