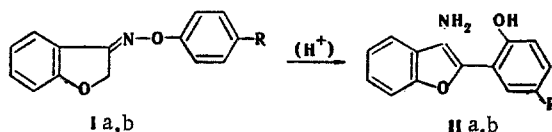


The rearrangement (effected by heating in alcohol solutions of hydrogen chloride) of aryl ethers of 2,3-dihydrobenzofuran-3-one oxime (Ia,b), which are formed by the reaction of O-arylhydroxylamines with the indicated ketone (Ib can also be obtained from the ketone oxime and 4-chloronitrobenzene), leads to the previously unknown 2-(2'-hydroxyaryl)-3-amino benzofurans (IIa,b) in ~60% yields; IIa had mp 104-105°C (from aqueous alcohol), and IIb had mp 201-203°C (from acetic acid; vacuum dried at 85°C).



I, II a R=H; b R=NO<sub>2</sub>

Amines IIa,b are quite stable compounds, the acid hydrolysis of the amino group in which is hindered, evidently because of the pronounced shift of the tautomeric equilibrium of the ketimine-enamine system to favor the enamine form. Compounds IIa,b have amphoteric properties. The UV spectra of IIa,b (and of the hydrochloride of IIa) are characterized by an intense ( $\log \epsilon$  4.27-4.32) long-wave absorption maximum at 320 nm (the spectrum of IIb also contains additional absorption at 300-310 nm, which corresponds to the 4-nitrophenol fragment); this constitutes evidence for significant conjugation in the molecule [the intensity of the long-wave maximum at 327 in the spectrum of 2,3-dihydrobenzofuran-3-one, which models ketimino form II, is considerably lower ( $\log \epsilon$  3.68)]. The IR spectrum of IIa (CHCl<sub>3</sub>, c 0.1-0.01 M) contains bands at 3360 and 3300 cm<sup>-1</sup> corresponding to  $\nu_{\text{NH}_2}$  vibrations and a band at 1628 cm<sup>-1</sup> ( $\delta_{\text{NH}_2}$ ), which, like the preceding bands, vanishes when the compound is deuterated, as well as broad bands at 2300-2900 cm<sup>-1</sup> due to an intramolecular hydrogen bond. The singlet signal of 2-C of the furan ring, which should correspond to the ketimine form, is not observed in the PMR spectra of IIa,b; the signal of the proton attached to 2-C is also absent in the spectrum (in d<sub>6</sub>-DMSO) of the N-acetyl derivative of IIa (mp 221-222°C), but broad singlets corresponding to NHCO and phenolic hydroxyl protons appear at 9.5 and 10.2 ppm. In addition to the amide I band (1685 cm<sup>-1</sup>), an amide II band (1525 cm<sup>-1</sup>), which vanishes after deuteration, is characteristic for the IR spectrum of the N-acetyl derivative (in d<sub>6</sub>-DMSO). Consequently, the addition of an acetyl group to the nitrogen atom of IIa is not sufficient to shift the equilibrium to favor the ketimine form. Good results of analysis for C, H, and N were obtained for all of the compounds; the molecular weights were determined by mass spectrometry.