NEW SYNTHESIS OF 3-NITRO-5-HYDROXYBENZOFURANS

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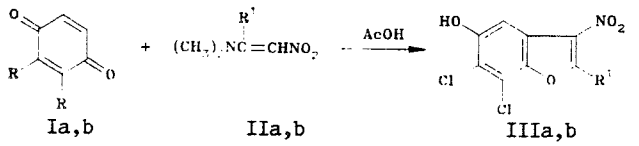
Information on the synthesis of 3-nitro-5-hydroxybenzofurans does not go beyond results on the direct nitration of 2-arylbenzofurans [1, 2] and the preparation of 3-nitrobenzofurans having electron donor substituents (SR, NHR) in position 2 [3]. We have discovered a new method of synthesis of the hitherto unknown 3-nitro-5-hydroxybenzofurans IIIa-d, which have either no substituent, or a methyl group, in position 2. The method is based on the condensation of p-benzoquinones Ia,b with nitroenamines IIa,b under the conditions of the Nenitzescu reaction in acetic acid at 20°C (in the case of compounds IIIa,c, in the presence of p-toluenesulfonic acid).



Ia,b IIa,b IIIa,b

III a R=R¹=H; b R=H, R¹=CH₃; c R=Cl, R¹=H; d R=Cl, R¹=CH₃

The initial nitroenamines are readily prepared by the reaction of amidoacetals with nitromethane [4]. The yields of benzofurans IIIa-d amounted to 68, 62, 44, and 20% respectively. The structure of compounds IIIa-d was demonstrated by mass spectrometry and PMR data. In the PMR spectra, in DMSO-D_6, of the compounds prepared, signals were observed for the proton of OH at 9-11 ppm, of the benzene ring at 6.9-7.6 ppm, 2-H (for IIIa,c) at 9.26 and 9.43 ppm respectively, and of the 2-CH_3 group (for IIIb,d) at 2.88 ppm. Elemental analyses were in agreement with calculations.

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