DIRECT AMINATION OF 3-SAFRANONE

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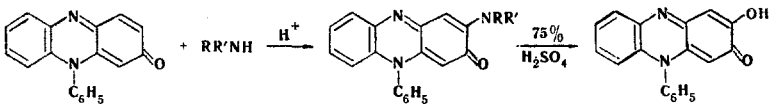
We have ascertained, that, in contrast to 3-phenoxazone and 3-phenothiazone, for which nucleophilic substitution in both the benzoid and quinoid rings is possible [1], in 3-safranone only the hydrogen atom in the 2 position is replaced by an aliphatic or aromatic amine or cycloalkylamine residue. Substitution proceeds smoothly if 3-safranone is heated for 4-6 h in alcohol, benzene, or dimethylformamide with a twofold excess of amine in the presence of its hydrochloride or catalytic amounts of concentrated hydrochloric acid and also if a large excess of the amine is used. The reaction products were isolated by chromatography on Al_2O_3 with elution with chloroform; the yields ranged from 30 to 40%.



II-IX X

The site of entry of the nucleophile was proved in the case of 2-amino-3-safranone (II). Its hydrolysis in 75% sulfuric acid gave the known 2-hydroxy-3-safranone (X). A hypsochromic shift of the long-wave absorption band (by 50-60 nm) relative to the starting 3-safranone (I) is observed in the electronic spectra of II-IX; this is also characteristic for 2-amino derivatives of 3-phenoxazone and 3-phenothiazone.

The results of elementary analysis for all of the compounds obtained were in agreement with the calculated values. The Rf values were determined on Silufol UV-254 with chloroform as the solvent.

The following compounds were obtained: 2-amino-3-safranone (II), mp 239-240°, Rf 0.41, λ_{max} 465 nm, log ε 3.43; 2-methylamino-3-safranone (III), mp 305-307°, Rf 0.33, λ_{max} 452 nm, log ε 3.48; 2-diethylamino-3-safranone (IV), mp 149-150°, Rf 0.70, λ_{max} 465 nm, log ε 3.53; 2-anilino-3-safranone (V), mp 257-258°, Rf 0.83, λ_{max} 468 nm, log ε 3.51; 2-(p-nitroanilino)-3-safranone (VI), mp 289-290°, Rf 0.84, λ_{max} 352, 465 nm, log ε 3.08, 3.38; 2-(p-methoxyanilino)-3-safranone (VII), mp 215-216°, Rf 0.82, λ_{max} 467 nm, log ε 3.52; 2-N-methylanilino-3-safranone (VIII), mp 250-251°, Rf 0.85, λ_{max} 467 nm, log ε 3.83; 2-piperazino-3-safranone (IX), mp 188-190°, Rf 0.69, λ_{max} 468 nm, log ε 3.43.

LITERATURE CITED

1. T. K. Pashkevich, G. B. Afanas'eva, K. I. Pashkevich, and I. Ya. Postovskii, Khim. Geterotsikl. Soedin., 353 (1975).

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