HOMOLYTIC ADDITION OF 1,3-DIOXOLANE TO PYRIDINE

I. A. Borisova, V. V. Zorin,
S. S. Zlotskii, and D. L. Rakhmankulov

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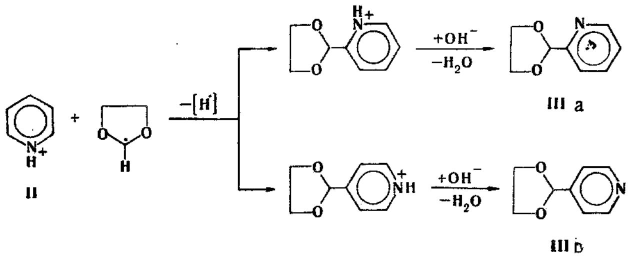
We have established that the hydroxyl radical-initiated (from the $FeSO_4 + H_2O_2$ redox system) reaction of 1,3-dioxolane (I) with protonated (by sulfuric acid) pyridine (II) in an aqueous medium gives 2-(1,3-dioxa-2-cyclopentyl)- (III) and 4-(1,3-dioxa-2-cyclopentyl)pyridine (IIIb) (IIIa,b were obtained in 51% yields based on the unchanged pyridine). For this, 0.03 mole of a saturated solution of $FeSO_4$ and 0.03 mole of a 33% solution of hydrogen peroxide in water were added in the course of 15 min at 5-10°C to a flat-bottomed glass reactor equipped with a magnetic stirrer and containing a mixture of 0.1 mole of 1,3-dioxolane, 0.03 mole of 50% sulfuric acid, and 0.02 mole of pyridine. The pH of the medium was brought up to 7.0-8.0 with a saturated solution of K_2CO_3. Compounds IIIa,b were extracted with chloroform, separated with a column filled with silica gel [in a hexane–ethyl acetate system (5:1)], and identified by chromatography from the coincidence of the retention times with those of authentically synthesized samples of IIIa,b in phases with different polarities.



The hydroxyl radicals detach a hydrogen atom from acetal I, as a result of which primarily 1,3-dioxa-2-cyclopentyl radicals are formed. The latter have nucleophilic properties and react with protonated pyridine to give IIIa,b. The primary formation of the 2-substituted isomer is observed; on the whole, this is characteristic for reactions involving the homolytic substitution of protonated heteroaromatic bases under the influence of nucleophilic carbon-centered radicals.

Compound IIIa had bp 91°C (5 mm). PMR spectrum in CCl_4 (with hexamethyldisiloxane as the internal standard): 4.2 (m, 4H, OCH_2), 4.9 [s, 1H, OCH(Ar)O], 6.9-7.2 (m, m-2H, Ar), 7.3-7.5 (m, p-1H, Ar), and 8.1-8.4 ppm (m, o-2H, Ar). Compound IIIb had bp 98°C (5 mm). PMR spectrum: 3.8 (m, 4H, OCH_2), 5.2 [s, 1H, OCH(Ar)O], 6.9-7.2 (m, m-2H, Ar), and 8.1-8.4 ppm (m, o-2H, Ar).

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