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SHORT COMMUNICATIONS

Participation of Molecular Oxygen in Cyclization of 5-Arylmethyleneamino-4-(3,4-dimethoxyphenyl)pyrazoles

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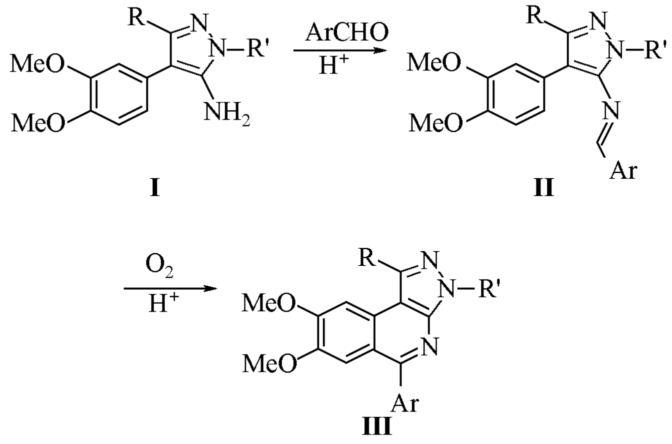
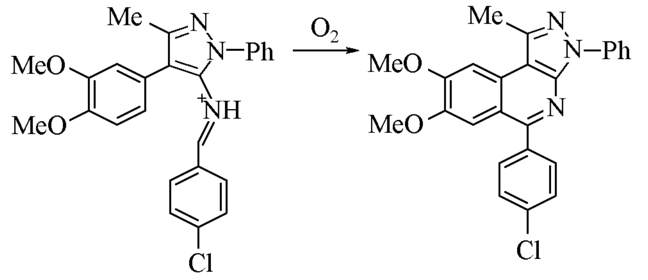
The reaction of 5-amino-4-(3,4-dimethoxyphenyl)pyrazoles (**I**) with benzaldehydes in strong organic acids gives rise to 5-aryl-3*H*-pyrazolo[3,4-*c*]isoquinolines (**III**) [1, 2]. The reaction proceeds via intermediate formation of 4-aryl-5-methyleneaminopyrazoles (**II**) isolated in considerable yields, and continues by oxidation of the N^4–C^5 bond and aromatization of pyridine ring of the polyheterocycle (Scheme 1). The presence of oxygen is a necessary condition for azomethine cyclization that has not been formerly marked in the cyclization processes along Pikte–Spengler procedure, also under the conditions we have used [3].

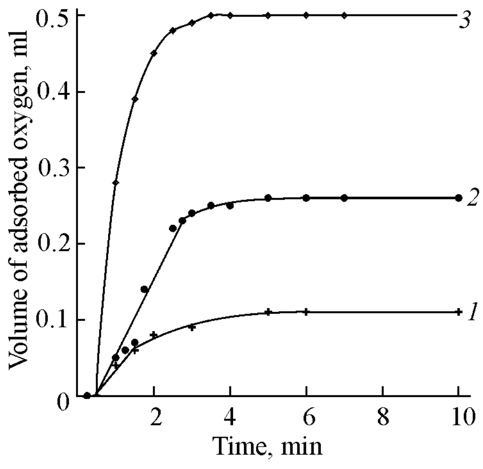
Scheme 1.



Scheme 2.



We attempted to reveal the role played by oxygen in transformation of 4-(3,4-dimethoxyphenyl)-3-methyl-1-phenyl-5-(4-chlorobenzylideneamino)pyrazole into 1-methyl-7,8-dimethoxy-3-phenyl-5-(4-chlorophenyl)-3*H*-pyrazolo[3,4-*c*]isoquinoline. The oxygen uptake in the course of the process was measured by the gas volume consumed on the device described in [4]. The reaction was studied in the temperature range 29–50°C and substrate concentrations 0.026–0.233 mol l^{-1}, partial oxygen pressure



Kinetic curves of oxygen consumption in oxidation of 4-(3,4-dimethoxyphenyl)-3-methyl-1-phenyl-5-(4-chlorobenzylideneamino)pyrazole in TFA, 29.5°C, p(æ$_2$) 760 mm Hg, concentration, mol l^{-1}: (*1*) 0.027, (*2*) 0.035, (*3*) 0.052.

was 760 mm Hg, solvent used was trifluoroacetic acid (TFA).

In the course of reaction oxygen is fast consumed. The kinetic curves are typical curves with saturation (see figure) evidencing complete consumption of the oxidizable substrate. The maximum oxygen consumption was about 0.2 mol per one mole of the substrate. The oxidation rate depended on the acidity of the solvent: thus addition to TFA (pK_a 0.23 [5]) of formic acid (pK_a 3.75) notably reduced the reaction rate.

The mechanism of this reaction is not known in detail; however it is presumable that one stage of the process consists in oxidation of 4-(3,4-dimethoxyphenyl)-3-methyl-1-phenyl-5-(4-chlorobenzylideneamino)pyrazole into 1-methyl-7,8-dimethoxy-3-phenyl-5-(4-chlorophenyl)-3*H*-pyrazolo[3,4-*c*]isoquinoline (Scheme 2).

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