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** Работа выполнена при поддержке гранта РФФИ 18-016-00190.*

УДК 547.866.5

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PSEUDOPERICYCLIC DEAROMATIVE 1,6-CYCLIZATION OF 1-(2-PYRIDYL)-2-AZABUTA-1,3 DIENES: SYNTHESIS AND RING-CHAIN VALENCE EQUILIBRIA OF 4*H*-PYRIDO[1,2-*a*]PYRAZINES*

Keywords: nitrogen heterocycles, fused-ring systems, rhodium, 2*H*-azirines, electrocyclic reactions.

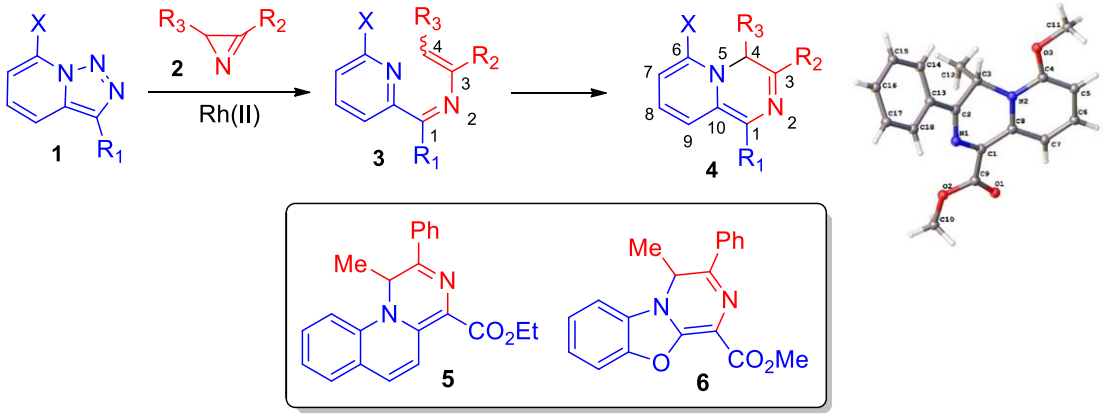
The 1,6-electrocyclization of diazahexa-1,3,5-trienes is a promising and atom-economic method for the synthesis of heterocyclic compounds, such as dihydropyrimidine/pyrimidine, dihydropyrazine/pyrazine and pyridazine [1–4]. Of particular interest are the 1,6-electrocyclizations of diazatrienes in which the C=N-termini is a part of an aromatic system, for example pyridine. Such cyclizations should proceed with dearomatization of the C=N bond containing substituent and formation of non-aromatic fused heterocycles.

In this work, we studied 1,6-electrocyclizations of 1-(2-pyridyl)-2-azabuta-1,3-dienes **3** as representatives of 1,4-diazahexatrienes with the C=N bond incorporated in aromatic pyridine system. 2-Azadienes **3** for the study were synthesized by the Rh(II)-catalyzed reaction of triazolopyridines **1** with 2*H*-azirines **2**.

It was found that these 1,6-electrocyclizations can afford stable 4*H*-pyrido[1,2-*a*]pyrazines **4** despite the fact that the reaction proceeds with irreversible dearomatization of the pyridine aromatic system.

Azadienes **3** containing an electron-withdrawing substituent at the C1 and a hydrogen, alkyl or aryl group at the C4 were able to undergo such 1,6-

electrocyclization. The 4-alkyl-substituted pyridopyrazines **4** turned out to be stable at room temperature, they were isolated and characterized by NMR spectroscopy.



Pyridopyrazines **4** with a phenyl group at the C4 were in a valence equilibrium with the corresponding 2-azadienes **3** even at room temperature. In contrast, 2-azadienes **3** containing a phenyl substituent or an ester group at the C1 and C4 positions did not cyclize to pyridopyrazines **4**. The 1,6-cyclization was also expanded to the synthesis of tricyclic compounds: 1*H*-pyrazino[1,2-*a*]quinolone derivative **5** and 4*H*-benzo[4,5]oxazolo[3,2-*a*]pyrazine derivative **6**.

The presence of the highly-conjugated 8-amino-1-azaoctatetraene moiety in the pyridopyrazine structure determines the relative stability of the pyridopyrazines **4** and makes them colored from yellow to violet. As follows from the experimental results and DFT calculations, a relative thermodynamic stability of 4*H*-pyrido[1,2-*a*]pyrazines **4** in comparison with 1-(2-pyridyl)-2-azabuta-1,3-dienes **3** significantly increases in the absence of a substituent at the C6. According to the calculation results, the 1,6-electrocyclization under consideration is a pseudopericyclic reaction proceeding through a significantly flattened transition state.

The results obtained are of great importance because they expand the scope of the 1,6-electrocyclization in organic synthesis.

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** This work was done under support of the RSF (grant 19-73-10090) using resources of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies, Computing Centre of the Research Park of St. Petersburg State University.*