Heteroannelations with Pinane-Type Chiral b-Enaminoaldehyde

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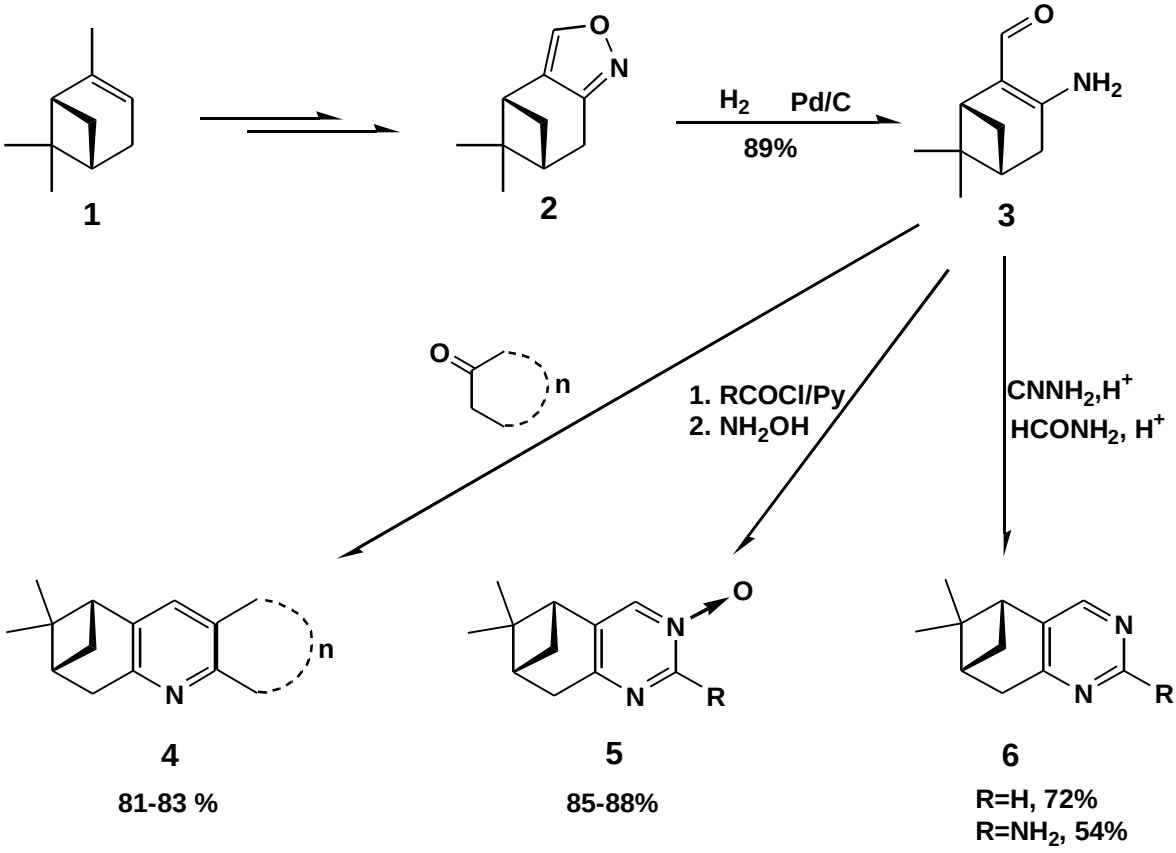
α-Pinene is among the most wide spread natural monoterpenes. Our study was planned to outwork synthetic approaches towards heterocyclic derivatives of α-pinene which are of interest from the viewpoint of biological activity. Pinane-type β-enaminoaldehyde **3** derived from the readily accessible isoxazole **2**[1] was found to be a source for series of chiral heterocycles containing pyridine and pyrimidine moieties.

Because of steric hindrance arises from bicyclic structure with *gem*-dimethylcyclobutane moiety, β-enaminoaldehyde **3** is quite stable compound towards addition reaction, and heteroannelations of **3** needs generally more rigid conditions than it has been reported for *o*-aminobenzaldehyde.[2] Acid-catalyzed reaction of **3** with cyclic ketones results in formation of pyridine-annelated products **4** in very good yields. Acylation of **3** and subsequent treatment with hydroxylamine affords the annelated pyrimidine-N-oxides **5** in excellent yields. 2-Amino- and 2-H-substituted pyrimidines **6** were also obtained in the reaction of **3** with cyanamide and formamide correspondingly.

New fused heterocyclic compounds **4-6** are prospective as potential biologically active molecules as well as chiral auxilary.



1 Chibiryaev A.M., Popov S.A., Tkachev A.V. Mendeleev Commun., 1996, 18-20

2 Caluwe P. Tetrahedron, 1980, 2359-2407