Amino Alcohols with Bicyclic Carbon Skeleton. Alternative Functionalization of Nucleophilic Reaction Centers

L. I. Kas'yan[1], E. A. Golodaeva[1], A. O. Kas'yan[2], and A. K. Isaev[1]

[1] *Dnepropetrovsk National University, per. Nauchnyi 13, Dnepropetrovsk, 49005 Ukraine*

[2] *Institut für organische Chemie, Rheinisch–Westfälische technische Hochschule, Aachen, Germany*

Received March 15, 2003

Abstract - Electron density distribution in the molecules of stereoisomeric *N*-[2-(4-nitrophenyl)-2-hydroxyethyl](bicyclo[2.2.1]hept-2-en-5-ylmethyl)amines was studied by quantum-chemical methods, and their chemical transformations were examined. According to the results of PM3 semiempirical calculations, the nitrogen atom in the amino alcohols possesses greater proton affinity, as compared to the oxygen atom. Chemoselective functionalization of the amino alcohols at the nitrogen and oxygen nucleophilic centers was effected using 4-nitrobenzoyl chloride, 4-toluenesulfonyl isocyanate, and hexamethyldisilazane in the presence of chlorotrimethylsilane. *N*,*O*-Bis-acylated amino alcohols were synthesized, one of which was subjected to oxidation with peroxyphthalic acid. The oxidation was not accompanied by heterocyclization, and it led to formation of the corresponding *exo*-epoxynorbornane derivative with the *endo*-oriented substituent at the bicyclic framework. The structure of the products was confirmed by the IR and ^{1}H NMR spectra.