A NEW SYNTHESIS FOR 1-AZAADAMANTANE FROM 1-BORAADAMANTANE

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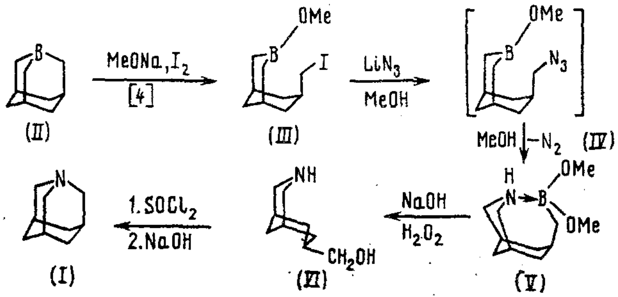
UDC 542.91:547.518:547.1′127

One of the methods for the synthesis of secondary amines is the reaction of organoboranes with organic azides [1]. An intramolecular variant of this reaction [2] was used to develop a convenient method for the preparation of 1-azaadamantane (I) from 1-boraadamantane (II); (II) has been obtained previously only with considerable difficulty.

Heating of 3-methoxy-7α-iodomethyl-3-borabicyclo[3.3.1]nonane (III), prepared from (II) [4], with lithium azide in methanol at reflux for 15 h gave internal complex 7α-dimethoxyborylmethyl-3-azabicyclo[3.3.1]nonane (V) (δ^{11}B 6.7 ppm). The oxidation of (V) without isolation gave 7α-hydroxymethyl-3-azabicyclo[3.3.1]nonane (VI). Heating (VI) with $SOCl_2$ in benzene at 80°C for 0.5 h and subsequent alkaline treatment led to 1-azaadamantane (I) in 85% yield relative to (VI), mp 258-260°C (sublimes) [5].



The key step in this approach is the conversion of azide (VI) to (V) by means of migration of a group from boron to nitrogen with the loss of a nitrogen molecule (intramolecular anionotropic rearrangement).

Alcohol (VI) was obtained in 50% yield relative to (III), mp 56-57°C. PMR spectrum in $CDCl_3$ (δ, ppm): 2.65 (CH_2N), 3.43 (CH_2O). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 25.5 ($C^{1,5}$), 27.6 (C^9), 29.2 ($C^{6,8}$), 31.5 (C^7), 52.6 (CH_2N), 67.5 (CH_2O).

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