INTRAMOLECULAR REARRANGEMENT IN THE 1,7-DIOXA-8-AZABICYCLO[4,3,0]NONANE SERIES

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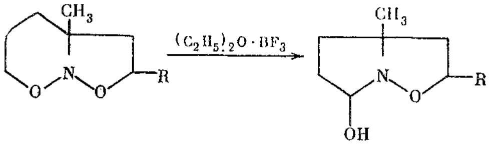
The reaction of 1,7-dioxa-8-azabicyclo[4,3,0]nonane derivatives (Ia, b) [1] with an equimolar amount of boron trifluoride etherate in absolute benzene proceeds with intramolecular rearrangement with contraction of the six-membered ring to form 6-hydroxy-1-oxa-7-azabicyclo[3, 3, 0]octane derivatives:



a R = C_6H_5
b R = $COOCH_3$

(I a,b) (II a, b)

(IIa) was obtained in 50% yield and had mp 91-96° [hexane–CCl_4 (4:1)]. Found: C 71.23; H 7.77; N 6.70%. $C_{13}H_{17}NO_2$. Calculated: C 71.23; H 7.76; N 6.39%. PMR spectrum (δ, ppm, $CDCl_3$): singlet 1.42 (CH_3), multiplet 5.04 (H_2 and H_6), diffuse peak 4.45 (OH), multiplet 1.90 (H_3, H_4, H_5).

(IIb) was obtained in 28% yield and had mp 87-90° [hexane–CCl_4 (4:1)]. Found: C 53.75; H 7.32; N 6.82%. $C_9H_5NO_4$. Calculated: C 53.73; H 7.46; N 6.97%. PMR spectrum: singlet 1.30 (CH_3), triplet 4.57 (H_2), multiplet 4.92 (H_6), singlet 3.67 (OCH_3), diffuse peak 4.06 (OH), two multiplets at 2.31 and 1.88 (H_3, H_4, H_5).

Bands at 3510 (OH) and 3200 cm^{-1} (bonded OH) are present in the IR spectra of CCl_4 solutions of (IIa) and (IIb). The intensity of the latter band decreases when the solutions are diluted, which is evidence for the presence of an intermolecular hydrogen bond.

The reaction to obtain (IIa, b) is noncatalytic, since the yields of (IIa, b) decrease symbatically when the amount of BF_3 etherate is decreased.

LITERATURE CITED

1. I. E. Chlenov, N. S. Morozova, V. I. Khudak, and V. A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2641 (1970).

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