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4-Oxahomoadamantane from Intramolecular, Nucleophilic Participation by Hydroxyl under Hofmann Elimination Conditions[1,2]

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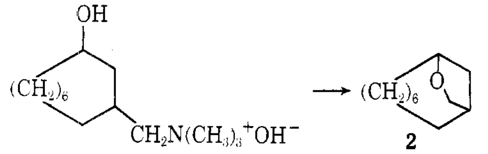
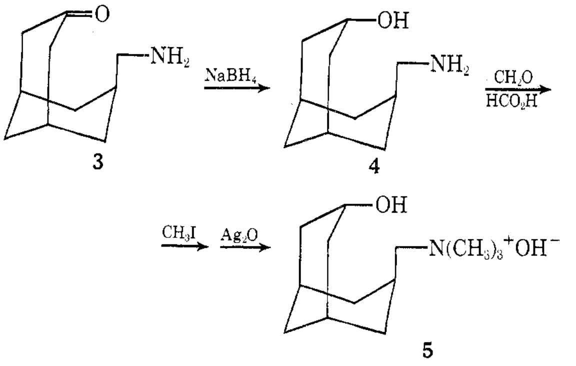
We are prompted by a recent report[3] to communicate our results on intramolecular, nucleophilic displacement under Hofmann elimination conditions. Hirsch and coworkers obtained[3] 2 (five-membered ring formation, 33% yield) by decomposition of the quaternary hydroxide 1 (eq 1) along with lesser quantities of other products.



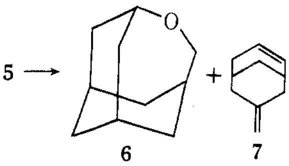
1 2 (1)

We investigated **5**, which was synthesized from *endo*-7-aminomethylbicyclo[3.3.1]nonan-3-one (**3**)[4,5] according to eq 2. Thermolysis of crude **5** produced 4-oxahomoadamantane[6,7] (**6**, seven-membered ring formation, 19% overall yield from **3**) and minor amounts of 7-methylenebicyclo[3.3.1]non-2-ene[5] (**7**, 2% overall yield from **3**) (eq 3).



3 4 5 (2)

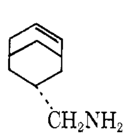
Since nucleophilic displacement of tertiary amines is known[8] to compete with straightforward elimination, this type of intramolecular alkylation process involving the alkoxide form of **5** appears reasonable.



6 7 (3)

A number of analogous examples are recorded in the prior literature.[8] The six-membered ether, thebenone, was generated from tetrahydrothebainonemethine by a similar process involving the phenolic hydroxyl. In addition, β-amino alcohol precursors gave rise to epoxides from participation by the neighboring hydroxyl group. Formation of *trans*-β-methylstyrene oxide from the quaternary hydroxide derived from ephedrine serves to illustrate. In the previous work,[3,8] cyclization involved formation of three-, five-, and six-membered rings.

Diolefin **7** most likely is formed by dehydration of **4** in the presence of formic acid, followed by exhaustive methylation and Hofmann elimination. Compound **4** is known to undergo partial dehydration to the corresponding amino alkene **8**[7] on exposure to 20% formic acid (1 day at reflux).[2,9]



8

Experimental Section

Compound **3** (9.3 g, 0.055 mol) was reduced in ethanol with sodium borohydride to the corresponding endo alcohol **4**.[10] After addition of water, the product was extracted with chloroform. Evaporation of the dried solution provided the desired material, which was subjected to the Hofmann elimination procedure.[5] The intermediates were not purified. A white, solid product, 4-oxahomoadamantane (**6**, 1.32 g, 17% overall yield from **3**) sublimed into the condenser during reaction. Identification was effected by comparison with spectral data for the authentic material.[6,11] The distillate from pyrolysis was extracted with ether. The organic layer was washed with dilute hydrochloric acid, then with water, dried, and freed of solvent. GLC analysis of the liquid product (0.3 g) revealed the presence of **6** (40%) and **7** (60%, 2% overall yield from **3**).

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Registry No.—**3**, 34650-78-7; **4**, 21933-00-6; **5**, 54517-88-3; **6**, 21898-86-2; **7**, 37439-70-6.

References and Notes

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