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THERMOLYSIS OF *N,N,N*-TRIMETHYL-1-ADAMANTYLAMMONIUM HYDROXIDE

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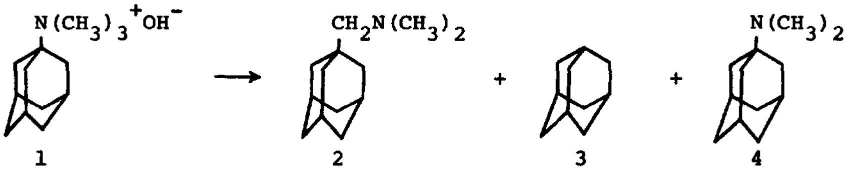
The Stevens rearrangement[1] has received appreciable attention since it was first observed. However, there are relatively few examples involving simple alkyl systems.[1,2] We have investigated this reaction with the adamantyl system in which elimination is theoretically possible as a competing process, but energetically unfavorable. The formation of adamantene *via* various types of eliminations has recently been reported.[3]

Decomposition of 1[4] at 140-175°C (1 mm) provided the Stevens rearrangement product, *N,N*-dimethyl-1-aminomethyladamantane[5] (2) (26%), adamantane (3) (10%), and the parent amine, *N,N*-dimethyl-1-aminoadamantane[4] (4) (49%). Authentic 4 was prepared by methylation of 1-aminomethyladamantane with formic acid--formaldehyde.



1 2 3 4

Our findings are significant in that the prior literature appears to contain no examples entailing migration of a secondary or tertiary group.[6,7] Both carbanion and radical character have been proposed[1] for the migrating entity in the Stevens rearrangement. Preferential rearrangement of the tertiary structure in our case is in keeping with a radical pathway. Relief of strain may also be a contributing factor.

The generation of adamantane is similar to formation of neopentane in the Stevens rearrangement of *N,N,N*-trimethylneopentylammonium iodide.[2] Parent amine (**4**) is probably formed from **1** *via* S_N2 attack by hydroxide ion. There was no evidence (glpc) of products which might arise from adamantene such as the dimer and adamantanol.

Since no bridgehead olefin was detected from pyrolysis of **1**, in contrast to the homoadamantyl[7] and certain bicyclic[8] systems, these data indicate a limit to the type of olefin which can be formed by Hofmann elimination. Since adamantene is so highly strained, its formation cannot compete favorably with rearrangement.

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6. Similar results were observed by J. L. Fry, M. G. Adlington, R. C. Badger, and S. K. McCullough, *Tetrahedron Lett.*, this issue, using *N,N,N*-trimethyladamantylammonium hydroxides. We thank Professor Fry for making available his results prior to publication.
7. For related work involving the homoadamantyl nucleus, see B. L. Adams and P. Kovacic, *J. Amer. Chem. Soc.*, in press.
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