

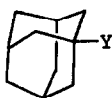
PYROLYSIS OF N,N,N-TRIMETHYLADAMANTYLAMMONIUM HYDROXIDES.  
UNUSUAL STEVENS REARRANGEMENTS

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Pyrolysis of alkyl quaternary ammonium hydroxides to effect Hofmann elimination has often been used very successfully to synthesize a variety of highly strained bridgehead olefins.<sup>1,2</sup> By way of contrast, we wish to report that we have not found any evidence to indicate that the pyrolysis of either N,N,N-trimethyl-1-adamantylammonium hydroxide, 1a, or N,N,N-trimethyl-2-adamantylammonium hydroxide, 2a, yields the long sought olefin adamantene,<sup>3</sup> 3, as a product.<sup>4</sup>



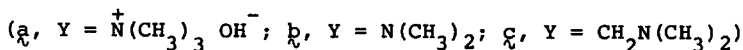
1



2



3



Instead, both 1a and 2a yield products arising from pathways involving Stevens rearrangements and direct nucleophilic displacements by base at methyl carbon.

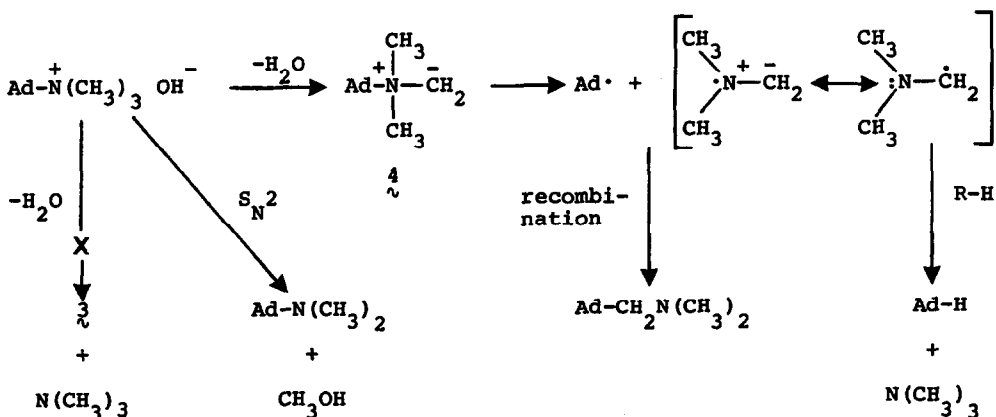
The quaternary ammonium hydroxides were prepared from their respective amines by standard procedures.<sup>2,5,6</sup> The pyrolysis apparatus consisted of two 5-ml Pyrex flasks connected by a short Pyrex tube. Pyrolyses were conducted under a pressure of <1 torr of dry nitrogen by raising a heated bath around the flask containing the dry hydroxide. Pyrolysis products were collected in the liquid nitrogen-cooled receiver.

Pyrolysis of  $1a$  at  $160^\circ$  gave, in addition to water, methanol, and trimethylamine, 64% N,N-dimethyl-1-aminoadamantane,  $1b$ , 31% N,N-dimethyl-1-aminomethyladamantane,  $1c$ , and 5% adamantane.<sup>7,8,9</sup>

Similarly, pyrolysis of  $2a$  at  $160^\circ$  gave, besides water, methanol, and trimethylamine, 91% N,N-dimethyl-2-aminoadamantane,  $2b$ , 8.6% N,N-dimethyl-2-aminomethyladamantane,  $2c$ , and 0.4% adamantane.<sup>7,8</sup>

It is not surprising that in both systems the major pyrolysis product is the parent N,N-dimethyl amine. Formation of these products by direct  $S_N2$  displacement by nucleophilic base upon methyl carbon is a well-known reaction which becomes important when Hofmann elimination either is impossible or would lead to a highly strained olefin such as  $3$ .<sup>2,4,10,11</sup>

More surprising is the formation of the Stevens rearrangement products  $1c$  and  $2c$ . Migration of simple secondary and tertiary alkyl groups has not been commonly observed to occur in quaternary ammonium ions under these conditions.<sup>14</sup> The rearrangement products may be formed by dissociation of the respective nitrogen ylide,  $4$ , into a radical pair<sup>15</sup> followed by recombination. Escape from the radical pair followed by hydrogen abstraction would lead to the observed adamantane and trimethylamine products. If such a mechanism is indeed followed, then it may reflect the relative ease of formation and lifetimes of the 1- and 2-adamantyl radicals<sup>16</sup> as well as the high energy of adamantene.



## Acknowledgements:

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## References:

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2. J. A. Chong and J. R. Wiseman, J. Amer. Chem. Soc., 94, 8627 (1972) and references cited therein.
3. (a) A. H. Alberts, J. Strating, and H. Wynberg, Tetrahedron Lett., 3047 (1973); (b) J. E. Gano and L. Eizenberg, J. Amer. Chem. Soc., 95, 972 (1973); (c) D. Lenoir, Tetrahedron Lett., 4049 (1972); (d) D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, J. Chem. Soc. Chem. Commun., 1186 (1972) and references cited therein.
4. Adams and Kovacic have recently obtained evidence for the formation of bridgehead homoadamantene, in addition to Stevens rearrangement and nucleophilic displacement products, from pyrolysis of N,N,N-trimethyl-3-homoadamantylammonium hydroxide: B. L. Adams and P. Kovacic, 166th National Meeting of the American Chemical Society, Chicago, Ill., August, 1973, Abstract ORGN-21; J. Amer. Chem. Soc., in press.
5. All new compounds gave satisfactory elemental analyses and had spectral properties consistent with their assigned structures.
6. Quaternization of 2b with methyl iodide in ethanol containing sodium carbonate proceeded without difficulty. This is somewhat surprising, since the quaternary ammonium ion which results must have a steric strain energy comparable to that found in 2-tert-butyladamantyl systems: cf. J. L. Fry, E. M. Engler, and P. v. R. Schleyer, J. Amer. Chem. Soc., 94, 4628 (1972); C. W. Woodworth, V. Buss, and P. v. R. Schleyer, Chem. Commun., 569 (1968).
7. Relative percentages. Yields based on decomposed hydroxides were essentially quantitative. Pyrolysis at higher temperatures was more rapid, but

- gave the same qualitative results. Pyrolysis products were identified by comparison of their glpc retention times and ir and nmr spectra with those of known compounds which were prepared by standard methods.
8. Formaldehyde and dimethylamine could not be detected in the pyrolysis products under conditions in which known samples of each could be detected in mixtures. Neither could 1- or 2-adamantanol or their methyl ethers be found in the pyrolysis products.
  9. Similar behavior of 1a has been noted also by B. L. Adams, J.-H. Liu, and P. Kovacic, accompanying paper.
  10. A. C. Cope and E. R. Trumbull, Org. Reactions, 11, 317 (1960).
  11. Neither 1,3-dehydroadamantane<sup>12</sup> nor 2,4-dehydroadamantane,<sup>13</sup> potentially formed by 1,3-elimination from 1a or 2a, respectively, was found in the pyrolysis product mixture (<0.2%).
  12. R. E. Pincock, J. Schmidt, W. B. Scott, and E. J. Torupka, Can. J. Chem., 50, 3958 (1972).
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  15. Less likely is an ion pair: cf. A. R. Lepley, Chem. Commun., 1460 (1969); U. Schöllkopf and U. Ludwig, Chem. Ber., 101, 2224 (1968).
  16. I. Tabushi, Y. Aoyama, S. Kojo, J. Hamuro, and Z. Yoshida, J. Amer. Chem. Soc., 94, 1177 (1972) and references cited therein.