Competitive Substitution and Fragmentation Reactions of Cation Radicals Derived from Adamantanes

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Summary 1-Alkyladamantanes undergo anodic oxidation in dry acetonitrile to give 3-alkyl-1-adamantyl acetamides and anodic fragmentation to give 1-adamantylacetamide; fragmentation is favoured by loss of a tertiary fragment but is not sensitive to temperature change.

LITTLE is known concerning the reactivity of cation radicals of saturated hydrocarbons. Anodic substitution[1] of linear alkanes and anodic fragmentation of branched alkanes[2] in dry acetonitrile have been reported. However, yields of the primary products of fragmentation have been generally low. In a series of substituted adamantanes, we now show the influence of structure upon the competing pathways of substitution and fragmentation.

The Table shows the products obtained after quenching with water, following oxidation of a solution of the adamantane in dry acetonitrile at a controlled anode potential of 2·5 V using a platinum gauze as anode and a silver wire in 0·01 M $AgNO_3$–acetonitrile as reference electrode. Typically, using $Bu^n{}_4N^+BF_4^-$ as electrolyte only 0·4 mA cm^{-2} flowed at 2·5 V as background current but the addition of an adamantane led to an initial current of 4 mA cm^{-2}. When the current had fallen to *ca.* 0·9 mA cm^{-2}, water was added and g.l.c. analysis showed high coulombic yields (>85%) and the product distribution shown in the Table. The low anode potential, and the large increase in current on addition of an adamantane show that the hydrocarbons are the electroactive species. Cyclic voltammetry establishes the irreversibility of a 2-electron wave at *ca.* 2·5 V for each hydrocarbon.

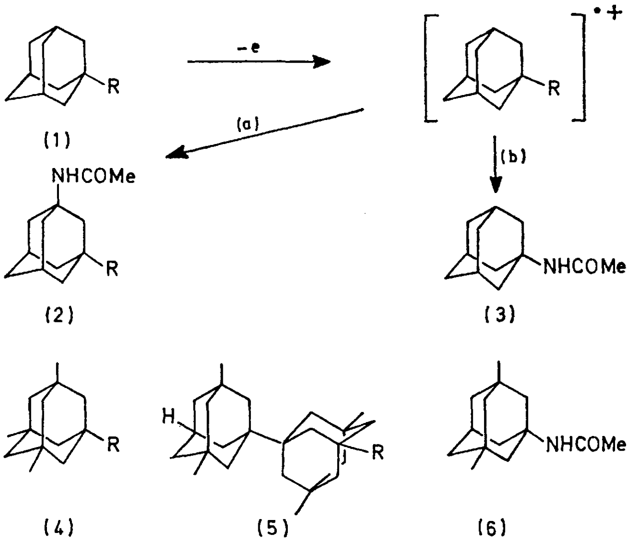
Table

Distribution of products from anodic oxidation of substituted adamantanes[a]

Compound	Product[b] and % yield Substitution	 Fragmentation
(1) R = H	(2) R = H 74	—
(1) R = Et	(2) R = Et 77	(3) 0
(1) R = Pr^i	(2) R = Pr^i 75	(3) 9[d]
(1) R = Pr^i [c]	(2) R = Pr^i 63	(3) 8[d]
(1) R = Bu^t	(2) R = Bu^t 7	(3) 62[d]
(4) R = Bu^t	—	(4) R = NHCOMe 91[d]
(5) R = H	(5) R = NHCOMe < 0·1	(6) 80

[a] Controlled potential electrolysis at 2·5 V for all compounds except (5) R = H (2·2 V). [b] Products identified by g.l.c. comparison with authentic samples. [c] Oxidation performed at − 30 °C. [d] No amide was observed derived from the second alkyl fragment; there is precedent for failure to capture cations in dry acetonitrile, J. Y. Becker, L. L. Miller, and T. M. Siegel, *J. Amer. Chem. Soc.*, 1975, **97**, 849.

Photoelectron spectroscopy indicates extensive delocalisation of the HOMO in adamantane[3] and oxidation by loss of a single electron is much more facile than for branched- or linear-alkanes. The effect of bridgehead alkyl substituents on the HOMO of an adamantane is small (first adiabatic I.P. for adamantane is 9·20 eV and for 1-t-butyladamantane is 8·96 eV) and so with a series of 1-alkyladamantanes loss of an electron from the adamantyl portion may be expected in each case. A resultant cation radical might undergo anodic substitution [pathway (a) in Scheme] or undergo fragmentation [pathway (b)]. The good coulombic and product yields reported in the Table permit an analysis of the fate of the initially formed cation radical. Fragmentation is observed as the dominant pathway when loss of a tertiary fragment from an adamantane can occur, no fragmentation is observed when a primary fragment might leave and in the case of 1-isopropyladamantane, although some fragmentation is observed, substitution is the dominant pathway. This product distribution has permitted an examination of the effect of temperature upon the competition between substitution and fragmentation. Our observation that a temperature difference of *ca.* 50° makes little difference to the product distribution from 1-isopropyladamantane contrasts with the suggestion[2] that low temperatures are necessary for successful cleavage of branched alkanes. We believe that in the case of acyclic branched alkanes, substantial side reactions complicate the analysis of the fate of the initially formed cation radical. Our study suggests that structure controls the chemistry of ion radicals of cyclic hydrocarbons and that $\Delta S^{\ddagger}$ for the anodic substitution and fragmentation reactions are not significantly different as previously suggested.



Scheme

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