

# Anodic Chemistry of Adamantyl Compounds. Some Scissible Carbon, Halogen, Hydrogen, and Oxygen Substituents

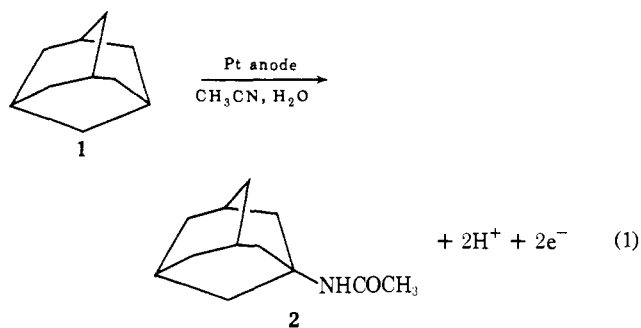
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**Abstract:** The anodic oxidation of adamantane was performed potentiostatically at platinum in acetonitrile. Passage of two electrons/molecule of current produced *N*-(1-adamantyl)acetonitrilium ions as the major product. Aqueous work-up produced 1-adamantylacetamide in yields of 65–90% based on the initial amount of adamantane. Quenching the anolyte with methanol led to the corresponding imino ether. A process involving direct oxidation of adamantane is proposed. A series of 1-substituted adamantanes was also oxidized on a preparative scale. Bromide, acetyl, and hydroxymethyl were cleaved anodically, and 1-adamantylacetamide resulted. Chlorine, fluorine, carbomethoxy, methyl, cyano, and acetoxymethyl were not cleaved, and high yields of 3-substituted 1-acetamidoadamantanes were produced. These results are rationalized in terms of the HOMO of the reactant and the stability of the fragments which would be possible by cleaving the substituent. Analogies with mass spectrometry are drawn.

Knowledge of the anodic chemistry of aliphatic molecules is extremely sparse. Carboxylate salts constitute the only class of compounds which has been extensively investigated in terms of variations in reactant structure and oxidation conditions. Many other classes of aliphatic compounds can, however, be directly oxidized at a platinum electrode in a suitable nonaqueous solvent and it appears that unique and possibly useful reactions might ensue.<sup>2</sup>

It has been found that even certain alkanes can be oxidized at sufficiently high electrode potentials.<sup>3</sup> Adamantane (1) can, for example, be converted to 1-adamantylacetamide (2) by oxidation in acetonitrile solvent<sup>4</sup> (eq 1). This indicates that, even if the func-



tional groups on an aliphatic molecule do not readily oxidize at the anode, the substrate may still be oxidizable. Indeed, if positionally selective monoacetamidation like the above could be generally achieved, it would certainly be useful in synthesis. This study was designed to probe the anodic reactivity of a variety of functional groups. 1-Adamantane derivatives (3) were chosen for study because the observed anodic chemistry of adamantane was simple, the desired reactants were readily available, and because adamantane oxidizes at a low potential relative to many other aliphatic hydrocarbons. Our purpose was to gain an initial impression as to whether the functional group would be reactive or

if the chemistry would be confined to the hydrocarbon portion of the molecule.

Many of the classes of compounds represented in this study by adamantyl compounds had not been previously oxidized. The others had received such limited attention that no firm prediction could be made about their anodic reactions. Although the compounds studied are all tertiary derivatives and adamantane chemistry could be unique, this study has satisfied our goal and provided some evocative indications of new and general reactions.

## Results

Preparative electrolyses were performed potentiostatically in a three-compartment cell at room temperature. The anodic, cathodic, and reference electrode solutions were separated by glass frits which allowed enough diffusion for conductivity but prevented gross mixing of these three solutions. This simplifies the chemistry and prevents variations in the reference electrode potential. The anode was a platinum sheet, the reference electrode system Ag–0.1 *N* AgNO<sub>3</sub> in acetonitrile. Acetonitrile–lithium perchlorate was used in both anode and cathode compartments. This electrolyte is not dry even though the solvent was routinely distilled from phosphorus pentoxide before use and the lithium perchlorate was “anhydrous.” The anode and cathode compartments were crudely purged with nitrogen in most experiments. This did not affect the anodic process. It did, however, make the cathode mixture cleaner. The background current with this system was <0.3 mA/cm<sup>2</sup> at 2.5 V and usually about 0.1 mA/cm<sup>2</sup> at 2.3 V. Initial currents with added adamantane were 50–100 times the background. During the run the current dropped with time and was discontinued when the background level was reached. The reaction time for adamantane oxidation was about 2 hr. Coulometry was accomplished with an electronic counter. The coulometric data reported are uncorrected for background current, but if the coulometry was corrected assuming that the current due to background oxidation was that which was determined without added substrate, the *n* values were lowered by less than 0.1. Oxidations with substituted adaman-

(1) Fellow of the Alfred P. Sloan Foundation.

(2) A. J. Fry, “Synthetic Organic Electrochemistry,” Harper and Row, New York, N. Y., 1972, Chapter 8.

(3) M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1969).

(4) L. L. Miller and V. R. Koch, *ibid.*, 693 (1973).

tanes behaved similarly. With the exception of three 1-substituted adamantanes, only minor electrode filming was observed.

In most experiments, however, the anode potential was pulsed to about 0 V for 1 sec every 10 sec. This did result in higher currents and more rapid oxidations. With several compounds, including adamantane, it was found that pulsing was detrimental to the yield. Thus the yield of **2** from **1** using the above pulsing sequence was 75%. Without pulsing the reaction time was 3 hr and the yield rose to 90%.

The products reported in Table I were isolated after

**Table I.** Oxidation Products of 1-Adamantyl-X (**3**)

Substituent	Anode potential, <sup>a</sup> V	<i>n</i> <sup>b</sup>	Product (% yield) <sup>c</sup>
H	2.35	2.1	<b>2</b> (90) <sup>d</sup>
Br	2.35	3.2	<b>2</b> (89)
Cl	2.50	2.1	<b>4</b> , X = Cl (91)
F	2.50	2.4	<b>4</b> , X = F (65)
CH <sub>3</sub>	2.35	2.3	<b>4</b> , X = CH <sub>3</sub> (91)
CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub>	2.45	2.2	<b>4</b> , X = CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub> (52)
CH <sub>2</sub> OH	2.35	2.2	<b>2</b> (37) <sup>e</sup>
COCH <sub>3</sub>	2.35	2.8	<b>2</b> (44)
CO <sub>2</sub> CH <sub>3</sub>	2.45	2.1	<b>4</b> , X = CO <sub>2</sub> CH <sub>3</sub> (64)
CN	2.50	2.2	<b>4</b> , X = CN (41)
OH	2.35	1.2	<b>2</b> (41) <sup>f</sup>
OCH <sub>3</sub>	2.15	1.0	<b>2</b> (58) <sup>f</sup>

<sup>a</sup> Measured with respect to Ag-0.1 N AgNO<sub>3</sub> in acetonitrile.

<sup>b</sup> Number of electrons transferred per molecule of added substrate.

<sup>c</sup> Yields based on isolated products compared to added reactant.

<sup>d</sup> This yield obtained without pulsing. <sup>e</sup> 1-Adamantylcarbonyl acetate was isolated in 20% yield. <sup>f</sup> This product was probably generated in a nonelectrochemical reaction.

column chromatography on silica gel. They were identified by standard spectroscopic and glc techniques and by comparison with published data. Product **2** from adamantane could be isolated by concentrating the anolyte, followed by extraction with ether and water. CAUTION: Do not concentrate the anolyte to dryness as it contains perchloric acid! Evaporation of the ether gave relatively pure **2**, mp 140–143°.

1-Chloro-, 1-cyano-, 1-fluoro-, 1-acetoxymethyl-, and 1-carbomethoxy-3-acetamidoadamantanes (**4**) have not, to our knowledge, been previously reported. In addition to proper elemental analyses, the mass, ir, and nmr spectra were sufficient to establish the structures with confidence. Of particular importance is distinguishing between isomers. Thus, the acetamide group could be attached at position 2, 3, 4, or 6. Position 3 is expected from the work with adamantane, and the nmr spectra confirm this assignment. If the amide group was attached at a secondary position, the CH-NHCOCH<sub>3</sub> resonance should be readily identified at low field ( $\delta \sim 4$ ).<sup>5</sup> If the original substituent (X) had rearranged to a secondary carbon, this would also give a low-field resonance.

Cyclic voltammograms were recorded for each compound. The  $E_p/2$  values are in Table II. Adamantane gave two anodic peaks. The anodic peak positions were dependent on sweep rate and there was no evidence of a reversible cathodic peak even at sweep rates of 100 V/sec. The peak heights were compared with

(5) F. W. van Deursen and J. Bakker, *Tetrahedron*, **27**, 4593 (1971).

**Table II.** Voltammetric Data on 1-Adamantyl-X (**3**)

Substituent	$E_p/2$ , <sup>a</sup> V	Substituent	$E_p/2$ , <sup>a</sup> V
H	2.36	COCH <sub>3</sub>	1.96
Br	2.54	CO <sub>2</sub> Me	2.56
Cl	2.64	CN	2.68
F	2.64	OH	2.12
CH <sub>3</sub>	2.40	OMe	2.05
CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub>	2.36	NHCOCH <sub>3</sub>	1.90
CH <sub>2</sub> OH	2.15		

<sup>a</sup> Sweep rate 0.1 V/sec, 10<sup>-2</sup> M substrate, 10<sup>-1</sup> M (*n*-Bu)<sub>4</sub>NBF<sub>4</sub>-CH<sub>3</sub>CN, 10<sup>-1</sup> M Ag<sup>+</sup>-Ag reference.

those for a known one-electron oxidation under the same conditions and  $n = 2$  was indicated. The variation of peak current for the first peak with sweep rate was studied and a linear relationship between  $i_p$  and  $\nu^{1/2}$  was found over the range of sweep rates 0.05 to 0.5 V/sec. At a 0.1 V/sec and 10<sup>-2</sup> M adamantane, the first anodic peak occurs at 2.51 V and the second at 3.10 V. Sweeping in the cathodic direction, two broad peaks occurred between 0.0 and -1.0 V. The second anodic scan was similar to the first and gave no anodic peak at 2.2 V, corresponding to the oxidation of **2**. Even sweeping the narrow region 2.0–2.6 V gave no evidence for formation of **2** even though it was isolated in preparative experiments. Similar voltammetric data were noted for other substituted adamantanes.

## Discussion

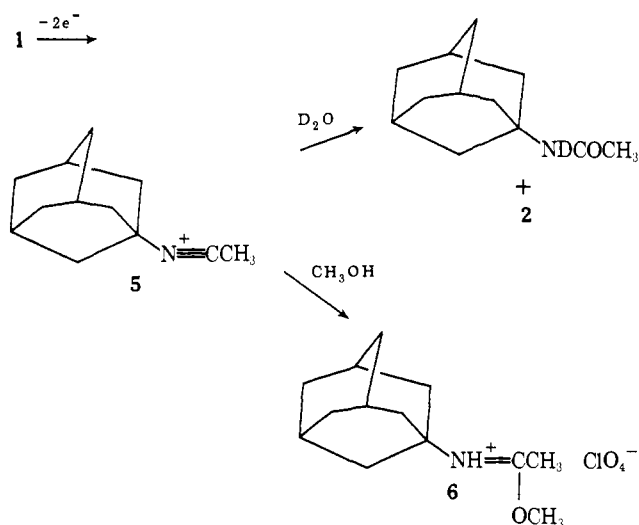
The oxidation products for a variety of substituted adamantanes (**3**) have been characterized. Two general reaction types are observed: substitution of acetamide for hydrogen and substitution of acetamide for the functional group. These reactions have some synthetic interest as a route to pharmacologically useful substituted 1-adamantylamines.<sup>6</sup> Most importantly, this study begins to reveal the anodic reactivity (or lack of it) of a variety of aliphatic compounds. The following discussion correlates the results, suggests mechanistic explanations, and explores the analogy between mass spectrometry and anodic reactions.

**Adamantane.** The results demonstrate that the acetamidation of adamantane is very clean and positionally selective. Although a wide variety of reaction conditions were not explored, the effect of changing the supporting electrolyte was investigated and tetraethylammonium and tetramethylammonium fluoroborate gave the same product in 80 and 65% yield, respectively. With fluoroborate electrolytes, anodic filming was observed and the pulsing sequence described previously was employed. Thus, the yields obtained with fluoroborate are comparable to those achieved with perchlorate when the applied potential was pulsed to 0 V. Perchlorate electrolytes are disadvantageous because of safety. Lithium perchlorate is, however, more easily removed because of its greater water solubility, and higher currents are passed with this electrolyte. The highest yield achieved was 90% using lithium perchlorate.

The isolation of high yields of product **2** is only possible because a nonoxidizable precursor **5** is actually the stable product in the anolyte and amide, **2**, only results upon aqueous work-up. Cyclic voltam-

(6) W. L. Davies, *et al.*, *Science*, **144**, 862 (1964); P. E. Aldrich, *et al.*, *J. Med. Chem.*, **14**, 535 (1971).

metry does not show the presence of **2** from adamantane oxidation in a normal analytical experiment or even when a solution of **1** undergoing preparative oxidation at a large platinum electrode is assayed with a separate platinum button electrode. Since synthetic mixtures of **1** and **2** give waves for each compound, it is quite clear that **2** is not present in the anolyte. The acetonitrilium ion, **5**, is the most logical species which can produce amide upon work-up. Its presence was verified by quenching the reaction after electrolysis with deuterium oxide and with methanol. The deuterium oxide quench followed by normal work-up gave 50% incorporation of deuterium. The methanol quench followed by chloroform extraction before neutralization gave a 70% yield of the imino ether perchlorate, **6**.



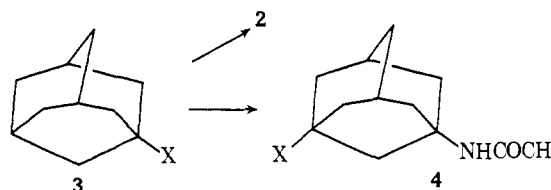
Product **6** was characterized and was converted to the neutral imino ether. Of particular importance in the structure proof were comparisons of ir and nmr data with literature values for similar imino ethers.<sup>7</sup>

The pathway to acetonitrilium ion is not well defined, but there is clear voltammetric evidence for direct oxidation of adamantane. The process can be performed at potentials well below background using several electrolytes, and the dependency of  $i_p$  on sweep rate is consistent with a diffusion-controlled process. Furthermore, it is found that neither 2,3-dimethylbutane nor 2,4,4-trimethylpentane are attacked when a mixture of adamantane and these electroinactive hydrocarbons are oxidized. This argues against an indirect substitution reaction which would involve reactive tertiary hydrogens.<sup>8</sup>

This acetamidation reaction could be of synthetic interest for more complex substrates. For this purpose the oxidation of adamantane was performed in a beaker with a 38 cm<sup>2</sup> platinum gauze anode. The anode potential was controlled at 2.15 V. The initial current was 500 mA, background current was 150 mA, and in 20 min a 60% yield of **2** was obtained upon work-up. It therefore appears feasible to carry out this reaction in an undivided cell to readily provide gram amounts of this product. This could be useful for the simple high yield preparation of 3-substituted 1-adamantylamines which are known to be pharmaco-

logically active.<sup>6</sup> Use of methanol in the work-up gives an added dimension since reduction of the imino ethers would produce *N*-alkyladamantylamines.<sup>7</sup>

**Adamantyl Halides.** 1-Adamantyl fluoride, chloride, and bromide were investigated.<sup>4</sup> Oxidation of the iodide seemed unnecessary in light of previous knowledge<sup>9</sup> and the results obtained. It was found that the chloride and fluoride oxidized at potentials somewhat higher than adamantane and that substitution of nitrogen for hydrogen at the 3 position was observed. The coulometry was close to two electrons per molecule, as would be expected from a process analogous to eq 1. Glc gave no evidence for the formation of 1-adamantylacetamide. 1-Adamantyl bromide, however, produced



**2** in high yield, demonstrating that bromide competes favorably with hydrogen as a leaving group. Coulometry gave  $n = 3.2$  and cyclic voltammetry showed the Br<sub>2</sub>, Br<sub>3</sub><sup>-</sup>, and Br<sup>-</sup> couples. The exact nature of the bromine species present has not, however, been elucidated.

In each of these three adamantyl halide reactions, initial electron transfer involves an orbital primarily located on the adamantyl moiety, not the halogen. We have attempted to determine an approximate potential for removing an electron from the nonbonding bromine orbital by running the cyclic voltammograms of *tert*-butyl bromide and *n*-propyl bromide.<sup>10</sup> These compounds did not give a peak before background in dry acetonitrile-tetramethylammonium fluoroborate or lithium perchlorate, which showed their  $E_p > 3$  V vs. Ag-AgNO<sub>3</sub>. This makes it abundantly clear that at  $E < 2.5$  V, electrons will not be lost from the chloride, fluoride, or bromide of alkyl halides. This is in agreement with predictions based on ionization potentials.<sup>11</sup> The photoelectron spectrum of 1-adamantyl bromide also indicates that gas phase ionization involves an orbital largely localized in the adamantane moiety.<sup>12</sup>

There is one previous report of anodic oxidation of an alkyl bromide.<sup>13</sup> *n*-Propyl bromide in acetonitrile was oxidized at an unknown anode potential, and cleavage of the bromine in a reaction similar to that found here was proposed. In this experiment, however, the only products identified were cyclopropane and propene in about 1% yield by glc. This reaction must be performed at potentials well into background due to the high oxidation potential of *n*-propyl bromide.

An earlier study demonstrated that iodine was anodically cleaved from a variety of simple alkyl iodides under the conditions used in this study.<sup>9</sup> Thus, the weaker C-I and C-Br bonds are cleaved while C-Cl and C-F are not.

It is of interest to compare these results with the unimolecular fragmentation of adamantyl halides ob-

(7) S. Julia and R. J. Ryan, *C. R. Acad. Sci.*, **274**, 1207 (1972).

(8) Oxidation of adamantane in methanol does not give any change in the adamantane: T. Shono and A. Ikeda, *J. Amer. Chem. Soc.*, **94**, 7892 (1972).

(9) L. L. Miller and A. K. Hoffmann, *ibid.*, **89**, 593 (1967).

(10) Experiments performed by B. Watkins.

(11) L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37**, 916 (1972).

(12) G. Mateescu and S. Worley, *Tetrahedron Lett.*, 5285 (1972).

(13) T. Keating and P. S. Skell, *J. Org. Chem.*, **34**, 1479 (1968).

served by mass spectrometry.<sup>14</sup> Since both reaction types could involve cation radical fragmentation, a direct correlation could result. It is found that 1-adamantyl bromide and chloride both fragment to give adamantyl cation ( $m/e$  135) as the base peak.<sup>14</sup> 1-Adamantyl fluoride, however, does not lose fluorine; the base peak is  $m/e$  97 at both 25 and 70 eV. These data demonstrate that as the carbon-halogen bond strength increases, it becomes more difficult to cleave this bond. The same phenomenon partially accounts for the anodic reactions. The relatively weak carbon-bromine or carbon-iodine bonds are cleaved, but adamantyl chloride and fluoride lose a proton.

**Carbon-Substituted Adamantanes.** Only a few compounds in which a carbon atom is attached to the 1 position were studied, but some intriguing results were obtained. A previous study had demonstrated that 1-adamantylcarboxylate (**3**,  $X = \text{CO}_2^-$ ) underwent the expected anodic decarboxylation reaction.<sup>15</sup> We have found that  $\text{CH}_2\text{OH}$  and  $\text{COCH}_3$  are also cleaved. Contrastingly,  $\text{CH}_3$ ,  $\text{CH}_2\text{OCOCH}_3$ ,  $\text{CO}_2\text{CH}_3$ , and  $\text{CN}$  are not cleaved. All this chemistry can be rationalized from a consideration of the HOMO of **3** and the stability of the fragments formed by cleavage of the carbon-substituent bond. For clarity, however, the following discussion is divided into the chemistry of methylene derivatives  $\text{CH}_2\text{OH}$ ,  $\text{CH}_3$ , and  $\text{CH}_2\text{OCOCH}_3$  and carbonyl derivatives of  $\text{COCH}_3$  and  $\text{CO}_2\text{CH}_3$ .

Within the methylene class only  $\text{CH}_2\text{OH}$  is cleaved.<sup>16</sup> In all these compounds the  $E_p/2$  values and IP data<sup>11</sup> indicate that the HOMO is an adamantane orbital. The rate of scission of the substituent,  $X$ , will be much more sensitive to the nature of  $X$  than will the rate of proton loss. Substituents which can be cleaved to form relatively stable fragments will produce product **2**; the others will lose a proton to give **4**. Thus,  $\text{CH}_2\text{OH}$  can leave as  $\cdot\text{CH}_2\text{OH}$ ,  $+\text{CH}_2\text{OH}$ , or as formaldehyde and a proton. All these fragments should be more stable than  $\cdot\text{CH}_3$  and  $\cdot\text{CH}_2\text{OAc}$  ( $\cdot = \cdot$  or  $+$ ), and this adequately rationalizes the discontinuity in the chemistry. The stabilities of  $\cdot\text{CH}_2\text{X}$  species can be estimated from the  $\sigma$  values for  $X$ . The  $\sigma_{\text{para}}$  values are  $\sigma_{\text{H}} = 0$ ,  $\sigma_{\text{OH}} = -0.37$ , and  $\sigma_{\text{OAc}} = +0.31$ .<sup>17,18</sup> The value for hydroxy indicates that it would stabilize a radical or cation much better than acetate or hydrogen. The cleavage of  $\text{CH}_2\text{OH}$  has been found previously for aromatic compounds of the type  $\text{PhCH(R)CH}_2\text{OH}$ .<sup>19,20</sup> In these oxidations initial electron transfer involves the aromatic  $\pi$  system. Fragmentation produces a benzylic cation and  $\cdot\text{CH}_2\text{OH}$ . Future studies will probe the hypothesis that  $\text{CH}_2\text{OH}$  will be cleaved anodically

(14) Z. Dolejšek, S. Hala, V. Hanus, and S. Landa, *Collect. Czech. Chem. Commun.*, **31**, 435 (1966).

(15) F. N. Stepanov, V. F. Baktan, and S. S. Guts, *Sin. Prir. Soedin., Ikh Analogov Fragmentov*, **1965**, 95 (1965); *Chem. Abstr.*, **65**, 6276 (1966).

(16) In the oxidation of **3**,  $X = \text{CH}_2\text{OH}$ , a 20% yield of **3**,  $X = \text{CH}_2\text{OCOCH}_3$ , is found. This appears to arise from an indirect reaction catalyzed by electrogenerated acid. Attack of the reactant alcohol on protonated acetonitrile produces an imino ether **3**,  $X = \text{CH}_2\text{OC}(\text{NH})\text{CH}_3$ . Upon work-up this imino ether will lead to the observed ester **3**,  $X = \text{CH}_2\text{OCOCH}_3$ .

(17)  $\sigma_{\text{para}}$  values<sup>18</sup> were used because the substituent can interact by resonance.  $\sigma_{\text{para}}^+$  could be more appropriate and would emphasize the difference since  $\sigma_{\text{OH}}^+ = -0.92$ .

(18) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 173.

(19) Unpublished work of V. R. Koch.

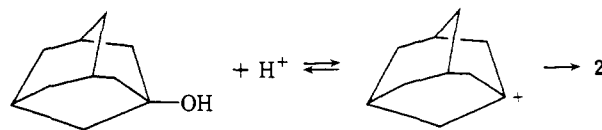
(20) Private communication from T. Shono.

from  $\text{RCH}_2\text{OH}$  whenever a relatively stable, *e.g.*, tertiary or  $\pi$ -delocalized,  $\text{R}^+$  is formed.

Comparison with mass spectral data leads to a situation similar to that encountered with the halide derivatives. Both 1-methyl- and 1-hydroxymethyladamantane cleave the substituent in the mass spectrometer.<sup>14</sup> Since proton abstraction by a base is not possible under these conditions, cleavage is much more probable regardless of the leaving group.

The difference in chemistry between the carbonyl derivatives, 1-acetyl- and 1-carbomethoxyadamantane, is not well interpreted in terms of differences in leaving group abilities. The acetyl and methoxyformyl cations or radicals should be of similar stability and leave with similar rates. The key to interpreting the difference in reactivity comes from the widely different  $E_p/2$  values (Table II). Although the carbomethoxy derivative has an  $E_p/2$  similar to that of adamantane, the acetyl compound oxidizes at an abnormally low potential. This suggests that the HOMO for the latter is an oxygen nonbonding orbital instead of an adamantane orbital. In agreement with this interpretation we find that a variety of large ketones oxidize in the range 2.0–2.4 V. Esters, on the other hand, have  $E_p/2$  values greater than 2.9 V. The photoelectron spectra of **3** ( $X = \text{COCH}_3$ ,  $\text{CO}_2\text{CH}_3$ ) and **1** were recorded and substantiated this hypothesis.<sup>21</sup> The ester has a lowest ionization potential (9.38 eV) nearly equal to that of adamantane (9.28 eV) and the fine structure of this band is very similar in both cases. The ketone, however, has a new band at 8.88 eV and an analysis of the fine structure indicates that this band is due to ionization of the carbonyl oxygen. The pes data indicate that initial electron transfer from ester should involve the adamantyl moiety and, indeed, the resulting chemistry is confined to this part of the molecule. In contrast, the ketone should initially give up an electron from the nonbonding carbonyl oxygen and an  $\alpha$ -cleavage with analogy in ketone mass spectrometry results. This reaction may be general for ketones in which the carbonium ion fragment, *e.g.*, adamantyl, is relatively stable. Previous studies have demonstrated that benzyl ketones anodically fragment in this way.<sup>22</sup> We are currently exploring aliphatic ketones. Initial results with *tert*-butyl methyl ketone indicate the anodic formation of *tert*-butylacetamide.

**Oxygen-Substituted Adamantanes.** 1-Methoxyadamantane and 1-adamantanol were oxidized under the usual conditions and produced **2**. This result was somewhat surprising in light of the high carbon-oxygen bond strength and the corresponding instability of  $\cdot\text{OCH}_3$ ,  $\cdot\text{OH}$  species ( $\cdot = +, \cdot$ ). Previous studies in this laboratory have, however, shown that alcohols can be chemically converted to amides by electrogenerated acid.<sup>23</sup> Unbuffered acid is formed in most electrooxidations in nonaqueous media and can catalyze Ritter reactions of the kind shown for adamantanol.



(21) L. L. Miller, V. R. Koch, T. Koenig, and M. Tuttle, *J. Amer. Chem. Soc.*, **95**, 5075 (1973).

(22) L. L. Miller, V. R. Koch, M. E. Larscheid, and J. F. Wolf, *Tetrahedron Lett.*, 1389 (1971).

This possibility was tested by carrying out a partial oxidation of adamantanol and then monitoring the concentrations of alcohol and **2** by glc. It was found that the conversion was taking place in the absence of electrolysis. A similar result was found for methoxyadamantane. Therefore, postulation of an electrochemical route for conversion of these compounds to **2** is unnecessary.

In order to investigate the electrochemistry, a solution buffered with potassium carbonate was employed. Although this compound is poorly soluble in the anolyte, previous studies have shown that it does quench acid-catalyzed Ritter reactions in anodic systems, producing alcohol products instead of amides.<sup>23</sup> The oxidation of 1-methoxyadamantane in the presence of carbonate gave 1-adamantanol (9%), 1-methoxyadamantane (4%), and adamantylacetamide (7%). The remainder of the starting material was unaccounted for and, therefore, no useful comments on the electrochemistry of these compounds can be made. Carbonate quenches the acid, but even the observed products could result from acid-catalyzed processes near the anode surface where the acid concentration is very high and the buffering may be ineffective.

**Summary.** The results demonstrate that adamantane and its derivatives can be anodically oxidized using controlled potentials to yield acetamides in good yield. The reaction should be valuable for producing substituted adamantylamines by hydrolysis of the acetamide and *N*-alkyl-*N*-adamantylamines by reduction of the imino ether. The results suggest that adamantane is not unique and that the substitution for hydrogen reaction might be applied to a variety of aliphatic compounds. Although adamantane has a relatively low oxidation potential, many alkyl groups are oxidized in the accessible potential region, below background oxidation. The adamantyl cation is not of unusual stability<sup>24</sup> but does lead only to substitution so that reactions involving cations which can eliminate may give lower acetamide yields.

Chemical oxidations of adamantane generally produce 2-adamantanone.<sup>24</sup> Adamantane can, however, be aminated at the 1 position using trichloramine<sup>25</sup> or by a hydride transfer reaction involving acetonitrile, sulfuric acid and *tert*-butyl alcohol.<sup>26</sup>

The cleavage reactions of 1-acetyl-, 1-bromo-, and 1-hydroxymethyladamantane are of great interest. Each of these reactions mimics a mass spectral result and they indicate the feasibility of preparative scale mass spectrometry. Cleavage of acetyl and hydroxymethyl could have useful synthetic ramifications and the generality of these reactions will be explored. It has already been established that the benzyl analogs behave similarly. In general, cleavage only appears favorable if a stable cation or radical can be formed from both fragments of a molecule. The final products indicate that both fragments are converted to cations.

## Experimental Section

**General.** Starting materials and products were analyzed by ir on

(23) E. A. Mayeda and L. L. Miller, *Tetrahedron*, **28**, 3375 (1972).

(24) R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(25) P. Kovacic and P. D. Roskos, *J. Amer. Chem. Soc.*, **91**, 6457 (1969).

(26) W. Haaf, *Angew. Chem.*, **73**, 144 (1961); T. Sasaki, S. Eguchi, and T. Toru, *Bull. Chem. Soc. Jap.*, **41**, 236 (1968).

a Perkin-Elmer 457 grating spectrometer. Nmr spectra were taken on Varian A60-A or T-60 instruments and chemical shifts are reported in  $\delta$  units. Mass spectra were recorded with an AEI Model MS-12 spectrometer. Glc analyses were performed on a Bendix 2300 gas chromatograph equipped with thermal conductivity detectors. Either a 10 ft  $\times$  0.25 in., 8% SE-30 on Chromosorb W column, or an 8 ft  $\times$  0.25 in., 10% Apiezon-L on Chromosorb W column was used. Melting points were measured in sealed capillary tubes by a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc.

**Materials.** Adamantane, 1-bromoadamantane, 1-adamantanol, and 1-acetyladamantane were commercial samples (Aldrich) and were used without further purification. 1-Carbomethoxyadamantane and 1-adamantylmethanol were supplied by Professor G. J. Gleicher.

1-Chloroadamantane was obtained from the reaction of 1-adamantanol and thionyl chloride according to the procedure of Stetter and coworkers,<sup>27</sup> mp after sublimation 159–160° (lit.<sup>27</sup> mp 162–164°).

1-Fluoroadamantane was prepared by refluxing 1-bromoadamantane with anhydrous silver fluoride in cyclohexane according to the procedure of Fort and Schleyer.<sup>28</sup> A 5% impurity identified as 1-adamantanol was removed by chromatographing the reaction mixture on a silica gel column with Skelly Solve. The 1-fluoroadamantane eluted ahead of 1-adamantanol and was then sublimed, mp 257–259° (lit.<sup>29</sup> mp 260°).

1-Cyanoadamantane was obtained by the reaction of 1-bromoadamantane and cuprous cyanide in pyridine,<sup>29</sup> mp after sublimation 193–194° (lit.<sup>29</sup> mp 193–194°).

1-Methoxyadamantane was prepared by refluxing 1-bromoadamantane and silver oxide in anhydrous methanol.<sup>29</sup> The nmr and ir spectra were identical to those reported in the literature.<sup>29,30</sup>

1-Methyladamantane was prepared by reacting 1-bromoadamantane with methylmagnesium iodide in a high pressure aerosol bottle.<sup>31</sup> A 10% impurity identified as 1-iodoadamantane was removed as follows. The reaction mixture was taken up in ether, shaken with 10% aqueous silver nitrate, filtered, and concentrated. The concentrate was chromatographed on a silica gel column with Skelly Solve. 1-Methyladamantane eluted prior to the impurities, mp after sublimation 102–103° (lit.<sup>31</sup> mp 101–103°).

1-Adamantylcarbonyl acetate was obtained by refluxing 250 mg (1.50 mmol) of 1-adamantylmethanol with 2 ml (28 mmol) of freshly distilled acetyl chloride for 15 min. The reaction mixture was cooled, poured into 10 ml of ice water, and extracted with ether. The organic layer was shaken once with 50 ml of a 5% sodium bicarbonate solution and once with 50 ml of water. After drying over anhydrous magnesium sulfate, the ether was evaporated, leaving 250 mg of a clear, colorless oil (80%) which was pure by glc and gave an nmr spectrum identical to that previously reported.<sup>28</sup>

All of the 1-substituted adamantanes had purities in excess of 99% by glc.

**Preparative Electrolyses of Adamantane.** The electrochemical cell, frits, and electrode parameters were as described previously.<sup>32</sup> A Model 61RS or 70HV1/90 Wenking potentiostat was employed for controlled potential electrolysis. A square wave pulse to 0 V from a Model 126 Exact VCF sweep generator was generally used. It was determined that pulsing to 0 V for 1 sec every 10 sec allowed high currents to be maintained. Without pulsing the reaction time was increased by about 50% but the yield of **2** was higher. Coulometry was performed with an Acromag Model 212-LX-1 current integrator.

The acetonitrile (Eastman) was twice distilled from phosphorus pentoxide and stored under nitrogen and over Fisher 4A molecular sieves. Anhydrous lithium perchlorate (G. F. Smith Chemical Co.), tetramethylammonium tetrafluoroborate (Aldrich), or tetraethylammonium tetrafluoroborate (Southwestern) was used as the electrolytes (0.1 M) without purification. Dry nitrogen was con-

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tinuously bubbled through the anode and cathode compartments. The cell was thermostated at room temperature during the electrolysis. Rapid stirring of the anolyte was achieved with a magnetic stirrer and Teflon stir bar.

When an oxidation was completed, the reaction mixture was worked up as follows. The clear, colorless anolyte was reduced to about 25 ml on a roto-vap [CAUTION: Do not strip too dryness; contains perchloric acid!], taken up in ether, shaken with 5% sodium bicarbonate solution, washed with water, and dried over anhydrous magnesium sulfate. After evaporation of the ether, a white solid identified as *N*-(1-adamantyl)acetamide (**2**) was isolated as the sole product in yields ranging from 65 to 90% based upon the amount of added adamantane. The melting point and ir and nmr spectra were identical to those reported in the literature.<sup>27,28</sup> It was found that the yield of amide could be raised by ~5% by the addition of 1–2 ml of glacial acetic acid<sup>28</sup> to the anolyte before oxidation. No adamantyl acetate was found under these conditions.

A similar work-up of the catholyte yielded from 2 to 10 mg of the acetamide due to product migration through the frit separating the two compartments. In any case this amount was never of sufficient quantity to markedly affect the yield or material balance.

**Oxidation of Adamantane in a Beaker.** Adamantane (220 mg, 1.62 mmol) was oxidized at 2.15 V in a 100-ml, tall form beaker fitted with three concentric electrodes. The outer electrode was a 120 cm<sup>2</sup> cylindrical cathode, the middle a 38 cm<sup>2</sup> cylindrical platinum gauze anode, and the inner reference a 5 mm o.d. glass tube fitted with a fine frit and silver wire. Background current at 2.15 V was 150 mA and the initial current was 500 mA. The cell was thermostated in an ice bath while 3.2 mF/equiv was passed to effect a 60% conversion to **2**.

**Anolyte Quenching with D<sub>2</sub>O and Methanol.** Adamantane (146 mg, 1.06 mmol) was oxidized to completion at 2.45 V. Prior to work-up 2 ml of D<sub>2</sub>O was added to the anolyte. Nmr integration of the acetamide product (**2**) showed a 50% incorporation of deuterium for the amido proton.

Adamantane (218 mg, 1.60 mmol) was oxidized to completion at 2.45 V. Prior to work-up, 5 ml of absolute methanol was added to the anolyte. After concentration on a roto-vap the acidic anolyte was poured into 200 ml of water and extracted three times with 100-ml portions of ether to remove any **2**. The anolyte was next extracted with 3 × 100 ml portions of chloroform which, after drying over anhydrous magnesium sulfate and solvent strip, yielded 344 mg (70%) of a white solid identified as the perchlorate salt of 1-adamantyliminomethoxyethane (**6**): mp 216–217° (dec); ir (Nujol) 3226, 3145, 3086, 1653, 1558, 1332, 1266, 1124, 1053, 625 cm<sup>-1</sup>; nmr (DMSO-*d*<sub>6</sub>) δ 4.24 (s, 3 H), 2.51 (s), 2.08 (br), 1.72 (br).

*Anal.* Calcd for C<sub>13</sub>H<sub>21</sub>NO<sub>3</sub>Cl: C, 50.81; H, 7.17; N, 4.56; Cl, 11.40. Found: C, 50.91; H, 7.27; N, 4.66; Cl, 11.11.

The adamantyl imino ether perchlorate was taken up in 10% aqueous sodium bicarbonate solution and extracted with 2 × 100 ml of HCCl<sub>3</sub>. After washing the organic layer once with water, drying, and stripping the solvent, a clear, colorless oil identified as 1-adamantyliminomethoxyethane remained (**3**, X = N=C(OCH<sub>2</sub>)CH<sub>3</sub>); ir (HCCl<sub>3</sub>) 2924, 2865, 1692, 1451, 1439, 1372, 1272, 1220, 1064, 893, 806 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 3.51 (s, 3 H), 2.00 (s), 1.86 (br), 1.72 (br); mass spectrum *m/e* 207.

**Oxidation of Adamantane in the Presence of Hydride Donors.** Adamantane (202 mg, 1.48 mmol) was oxidized to completion at 2.35 V in the presence of 198 mg (2.30 mmol) of 2,3-dimethylbutane. Upon work-up, 65% of **2** was isolated as the sole amide product.

In the presence of 256 mg (2.24 mmol) of 2,2,4-trimethylpentane, 225 mg (1.64 mmol) of adamantane was oxidized to completion at 2.35 V. Upon work-up, 60% of **2** was isolated as the sole amide product.

Neither 2,3-dimethylbutane nor 2,2,4-trimethylpentane contributed to the background current at 2.35 V.

**Preparative Electrolyses of 1-Substituted Adamantanes.** The method of oxidation, work-up, and product isolation was identical to that described for adamantane. Lithium perchlorate was used exclusively as the base electrolyte. Yields are based upon the amount of added substrate. Except where noted, the anolytes remained clear and colorless throughout the electrolyses.

**1-Acetyladamantane.** This ketone (**3**, X = COCH<sub>3</sub>) (218 mg, 1.22 mmol) was oxidized at 2.35 V for 3 hr. The initial current was 110 mA but rapidly dropped due to anodic filming. By scraping the clear, colorless globules off the platinum anode and pulsing

slightly, cathodic high currents were restored. After work-up, 103 mg of a white solid identified by nmr and glc as **2** (44%) remained as the sole product.

**Oxidation of 1-Adamantylmethanol.** 1-Adamantylmethanol (**3**, X = CH<sub>2</sub>OH) (230 mg, 1.37 mmol) was oxidized at 2.35 V for 2.5 hr. The initial current was 135 mA, which rapidly decayed due to anodic filming. A thin colorless film was scraped off the electrode several times during the oxidation to restore high currents. After work-up, 164 mg of a yellowish slush was obtained which was composed of a trace of starting material and two products by glc. Silica gel chromatography of the reaction mixture afforded 90 mg of **2** (37%) and 56 mg of 1-adamantylcarbinyl acetate (20%).

**Oxidation of 1-Bromoadamantane.** 1-Bromoadamantane (440 mg, 2.05 mmol) was oxidized at 2.35 V for 2.5 hr. The initial current was 100 mA and increased to 130 mA over the next 20 min before slowly dropping into background. The current increase was accompanied by the development of a bright yellow color in the anolyte which remained throughout the oxidation. After work-up, 392 mg of a yellow oil was recovered, of which the major product was identified as **2** (89%). The remainder of the reaction mixture was composed of several uncharacterized colorless oils which eluted prior to 1-bromoadamantane on an SE-30 glc column.

**Oxidation of 1-Methoxyadamantane.** 1-Methoxyadamantane (150 mg, 0.91 mmol) was oxidized at 2.15 V for 1 hr. The initial current was 240 mA. After work-up, 104 mg of a white solid identified as **2** (58%) was recovered as the sole product. Only 0.99 mF/equiv of electricity was required to effect complete consumption of starting material. 1-Methoxyadamantane was then oxidized (2.15 V) for only 10 min. The anolyte was halved; portion I was immediately worked up and portion II was allowed to stir at room temperature for 4 hr prior to work-up. Glc of the product mixtures confirmed the instability of 1-methoxyadamantane in the anolyte. Portion I contained 49% 1-methoxyadamantane and 51% 1-adamantyl acetamide. Portion II contained 14% 1-methoxyadamantane and 86% 1-adamantylacetamide.

**Oxidation of 1-Adamantanol.** 1-Adamantanol (312 mg, 2.05 mmol) was oxidized at 2.35 V for 2 hr. The initial current was 240 mA. After work-up, 162 mg of a white solid identified as **2** (41%) was isolated as the sole product.

To test the possibility of acid catalysis, a partial oxidation of 1-adamantanol was performed. The portion immediately worked up was composed of 80% 1-adamantanol and 20% 1-adamantylacetamide. The portion allowed to stir for 4 hr prior to work-up was composed of 10% 1-adamantanol and 90% 1-adamantylacetamide.

**Oxidation of 1-Methyladamantane.** 1-Methyladamantane (165 mg, 1.10 mmol) was oxidized at 2.35 V for 2 hr. The initial current was 90 mA. After work-up 210 mg of a white solid identified as 1-methyl-3-acetamidoadamantane (91%) (**4**, X = CH<sub>3</sub>) was obtained as the sole product. The material was sublimed at 95–100° (10<sup>-3</sup> Torr): mp 104–106° (lit.<sup>34</sup> mp 108–109°); ir (CHCl<sub>3</sub>) 3440, 3320, 2920, 2860, 1650, 1500, 1450, 1360, 1120, 910 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 5.78 (br, 1 H), 1.90 (s, 3 H), 1.61 (br), 1.45 (br), 0.82 (s, 3 H).

*Anal.* Calcd for C<sub>13</sub>H<sub>21</sub>NO: C, 75.36; H, 10.14; N, 6.76. Found: C, 75.00; H, 10.32; N, 6.64.

**Oxidation of 1-Cyanoadamantane.** This compound (307 mg, 1.90 mmol) was oxidized at 2.50 V for 4.5 hr. The initial current was 70 mA. After work-up, 168 mg of a white solid was recovered which contained a trace of starting material, the remainder being 1-cyano-3-acetamidoadamantane (41%) (**4**, X = CN). The acetamide was purified on a silica gel column and sublimed at 100–110° (10<sup>-3</sup> Torr): mp 105–108°; ir (CHCl<sub>3</sub>) 3440, 3320, 3000, 2920, 2860, 2240, 1660, 1500, 1450, 1360, 1290, 1120 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 5.55 (br, 1 H), 2.38 (s), 2.20 (br), 2.08 (s), 1.95 (s, 3 H), 1.71 (br).

*Anal.* Calcd for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>O: C, 71.56; H, 8.26; N, 12.84. Found: C, 71.12; H, 8.39; N, 12.49.

**Oxidation of 1-Carbomethoxyadamantane.** 1-Carbomethoxyadamantane (442 mg, 2.28 mmol) was oxidized at 2.45 V for 4 hr. The initial current was 180 mA. A thin, whitish film coated the amide after several minutes of oxidation. Removing the film by scraping the anode with a spatula did not, however, affect the current. After work-up, 390 mg of a slightly yellow oil which later solidified was isolated. The material was chromatographed on a silica gel column. A small amount of starting material eluted prior to a white solid which was identified as 1-carbomethoxy-3-

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acetamidoadamantane (64%) (**4**, X = CO<sub>2</sub>CH<sub>3</sub>). After sublimation at 100–115° (10<sup>-3</sup> Torr): mp 115–118°; ir (CHCl<sub>3</sub>) 3440, 3320, 3000, 2920, 2860, 1725, 1660, 1500, 1460, 1430, 1300, 1170, 900 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 5.45 (br, 1 H), 3.66 (s, 3 H), 2.18 (s), 2.00 (br), 1.90 (s, 3 H), 1.80 (br), 1.61 (br).

*Anal.* Calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>3</sub>: C, 66.93; H, 8.37; N, 5.58. Found: C, 66.75; H, 8.62; N, 5.31.

**Oxidation of 1-Adamantylcarbonyl Acetate.** This compound (178 mg, 0.86 mmol) was oxidized at 2.45 V for 2 hr. The initial current was 80 mA. After work-up, 117 mg of a slightly yellow oil was recovered. Glc revealed a trace of starting material, the remainder being 1-acetoxymethyl-3-acetamidoadamantane (52%) (**4**, X = CH<sub>2</sub>O<sub>2</sub>CCH<sub>3</sub>). The reaction mixture was chromatographed on a silica gel column; the acetamide eluted as a clear, colorless oil which later solidified. After sublimation at 90–100° (10<sup>-3</sup> Torr): mp 83–85°; ir (CHCl<sub>3</sub>) 3440, 3320, 2920, 2860, 1725, 1705, 1500, 1450, 1360, 1240, 1030 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 5.40 (br, 1 H), 3.78 (s, 2 H), 2.09 (s, 3 H), 2.00 (s), 1.90 (s, 3 H), 1.70 (br), 1.50 (br).

*Anal.* Calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>3</sub>: C, 67.92; H, 8.68; N, 5.28. Found: C, 67.59; H, 8.81; N, 5.05.

**Oxidation of 1-Chloroadamantane.** 1-Chloroadamantane (245 mg, 1.44 mmol) was oxidized at 2.50 V for 2 hr. The initial current was 145 mA. After work-up, 300 mg of a slightly yellow oil which later solidified was recovered. The material was identified as 1-chloro-3-acetamidoadamantane (92%) (**4**, X = Cl). One recrystallization from cyclohexane afforded white plates, mp 118–121°. Sublimation at 100° (10<sup>-3</sup> Torr): mp 124–126°; ir (CHCl<sub>3</sub>) 3440, 3320, 2920, 2860, 1665, 1500, 1450, 1360, 1350, 1290, 1125, 830, 630 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 6.10 (br, 1 H), 2.41 (s), 2.07 (br), 1.91 (s, 3 H), 1.64 (br).

*Anal.* Calcd for C<sub>12</sub>H<sub>18</sub>NOCl: C, 63.30; H, 7.91; N, 6.15; Cl, 15.60. Found: C, 63.38; H, 8.05; N, 5.91; Cl, 15.90.

**Oxidation of 1-Fluoroadamantane.** 1-Fluoroadamantane (324 mg, 2.10 mmol) was oxidized at 2.50 V for 3 hr. The initial current was 70 mA. After work-up, 323 mg of a white slush was recovered. The material was chromatographed on a silica gel column and 289 mg of a white solid identified as 1-fluoro-3-acetamidoadamantane (65%) (**4**, X = F) was isolated. After sublimation at 90–110° (10<sup>-3</sup> Torr): mp 134–138°, positive Beilstein test; ir (CHCl<sub>3</sub>) 3440, 3320, 3000, 2920, 2860, 1650, 1500, 1470, 1360, 1342, 1330, 1295, 1235, 910 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 5.48 (br, 1 H), 2.24 (s), 2.15 (s), 2.02 (s), 1.91 (s, 3 H), 1.70 (br).

*Anal.* Calcd for C<sub>12</sub>H<sub>18</sub>NOF: C, 68.25; H, 8.53; N, 6.64. Found: C, 68.76; H, 8.84; N, 6.32.

**Cyclic Voltammetry.** Cyclic voltammograms were taken with a PAR Model 170 Electrochemistry System. An enclosed two-compartment cell equipped with a nitrogen bubbler was used. The reference, 0.1 M AgNO<sub>3</sub>-Ag, was separated from the working and counter electrodes by a Luggin capillary and a three-way Teflon stopcock. The working electrode was a 1-cm platinum wire about which was wound a helically shaped platinum counter electrode. A 0.1 M (*n*-Bu)<sub>4</sub>NBF<sub>4</sub>-CH<sub>3</sub>CN solution was employed for all voltammograms. The tetrabutylammonium tetrafluoroborate electrolyte was prepared by mixing hot concentrated aqueous solutions of potassium tetrafluoroborate (Alfa Inorganics) and tetrabutylammonium bromide (Eastman). On cooling, white crystals of tetrabutylammonium tetrafluoroborate appeared. The electrolyte was filtered, recrystallized three times from water, and dried in a vacuum oven for 3 days at 100°.

Cyclic voltammograms were run at 10<sup>-2</sup> M substrate concentrations at 0.05, 0.1, 0.2, and 0.5 V/sec. *E*<sub>p/2</sub> values are quoted for rates of 0.1 V/sec. No reverse cathodic peak from cation radical reduction was observed for any of the adamantyl compounds even at the fastest sweep rates except where noted.

Initial currents were determined to be proportional to adamantane concentrations. When the peak current (*i*<sub>p</sub>) less background was plotted against adamantane concentrations varying from 2 to 11 mM, a straight line which passed through zero resulted.

Coulometric data from preparative electrolyses of adamantane indicated that two electrons/molecule were passed. A comparison of *i*<sub>p</sub> for 10<sup>-3</sup> M ferrocene (which is known to undergo a reversible one-electron oxidation) with *i*<sub>p</sub> for 10<sup>-3</sup> M adamantane supports an overall two-electron process. The ratio *i*<sub>p Ad-H</sub>/*i*<sub>p ferrocene</sub> was 1.95.

Cyclic voltammograms of 1-bromoadamantane revealed, after one cycle in the anodic direction, two new oxidation waves at +0.38 and +0.65 V and two reduction waves at +0.44 and -0.10 V. Addition of tetraethylammonium bromide enhanced the two oxidation waves. Presumably these waves are due to Br<sup>-</sup>, Br<sub>3</sub><sup>-</sup> and Br<sub>2</sub><sup>-</sup>, Br<sub>2</sub> couples. A yellow color was observed to develop after several sweeps.

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