Anodic Oxidation of Substituted Adamantanes

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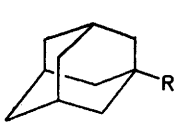
Photoelectron spectra and voltammetric data are reported for a series of 1-alkyladamantanes. Anodic oxidation of the series in either trifluoroacetic acid or acetonitrile gives charge-delocalised cation radicals. Whereas adamantane, 1-ethyladamantane, and 1-isopropyladamantane gave products by proton loss from the cation radical, other more highly substituted derivatives, *e.g.* 1-t-butyladamantane, give products preferentially by fragmentation of a carbon–carbon bond. Competition between deprotonation and fragmentation is controlled by the stability of the leaving carbocation; only if a tertiary group leaves is fragmentation dominant.

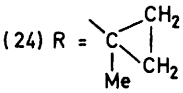
In contrast to the electrochemical oxidation of saturated hydrocarbons in aqueous solution, which is of little preparative value, similar oxidations in non-aqueous solvents with tetra-alkylammonium tetrafluoroborates as electrolytes are of considerable interest. In acetonitrile, aliphatic hydrocarbons give [1] *N*-alkylacetamides in current and organic yields of 35—40%. Alicyclic hydrocarbons having lower ionisation potentials may be oxidised in the lower potential range imposed by the use of a perchlorate salt as electrolyte. Adamantane gives [2] *N*-(1-adamantyl)acetamide in 65—90% yield. Trifluoroacetic acid [1] has also been used as solvent for anodic oxidation of saturated hydrocarbons. Thus n-octane [1] gives isomeric trifluoroacetates in 75% current yield. Studies are also reported in fluorosulphuric acid.[3]

From electroanalytical studies [1] it has been deduced that in acetonitrile or in trifluoroacetic acid, the hydrocarbon gives up an electron at the anode to give a cation radical. Electrochemical generation is the simplest unambiguous preparation of such cation radicals, yet few systematic studies of possible competitive processes from the ion radical have been reported. Miller *et al.*[2] examined the adamantanes (1)—(5) and found that compounds (3)—(5) gave 3-substituted adamantylacetamides but that compounds (1) and (2) preferentially underwent fragmentation to give adamantylacetamide. Miller *et al.*[4] have also investigated the oxidation of branched aliphatic hydrocarbons and of t-butylcyclohexane. Oxidation of t-butylcyclohexane in acetonitrile at −45 °C gave the highest product yields (63% of t-butylacetamide and 47% of cyclohexylacetamide). However, in studies with branched alkanes low yields (<5%) were obtained at room temperature. With acyclic hydrocarbons it appears that inefficient trapping of carbocation intermediates as nitrilium ions leads to low yields of products, and so the conclusions concerning competitive deprotonation or fragmentation of the ion radicals are based on inadequate product balances.

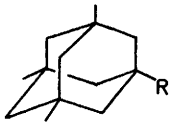
As a result of our interest in the possible oxidation by metal salts of saturated hydrocarbons [5] *via* cation radical intermediates, we sought to examine a system whereby saturated hydrocarbons would give cation radicals capable of competitive deprotonation and fragmentation. We required substrates giving high yields of primary products to permit satisfactory mechanistic conclusions. We describe in this paper the results of such studies with substituted adamantanes, which give stable cationic intermediates,[2] as expected by the requirement of Bredt's rule. In the following paper [5] we compare the electrochemical study with oxidations using metal salts. Some preliminary results [6] have been published.



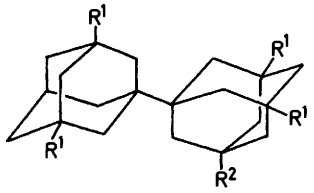
(1) R = CH_2·OH
(2) R = COMe
(3) R = Me
(4) R = CO_2Me
(5) R = CH_2·OAc
(6) R = Et
(7) R = Pr^i
(8) R = Bu^t
(20) R = O_2C·CF_3
(23) R = CMe:CH_2



(24) R =



(9) R = Bu^t
(17) R = NHAc
(22) R = O_2C·CF_3
(33) R = OH



(10) R^1 = R^2 = H
(11) R^1 = Me, R^2 = H
(19) R^1 = Me, R^2 = NHAc
(34) R^1 = Me, R^2 = OH

RESULTS

In order to optimise the conditions for preparative electrolysis, preliminary voltammetric studies in acetonitrile or in trifluoroacetic acid at a platinum electrode, and complementary analyses of photoelectron spectra of the adamantanes were made. Results are shown in Table 1. A typical voltammogram of adamantane is shown in Figure 1, and a typical photoelectron spectrum of an adamantane in Figure 2. Although in more favourable cases [7] addition of alumina to acetonitrile to scavenge nucleophilic species permits observation of the reduction

[1] D. B. Clark, M. Fleischmann, and D. Pletcher, *J.C.S. Perkin II*, 1973, 1578
[2] V. R. Koch and L. L. Miller, *J. Amer. Chem. Soc.*, 1973, **95**, 8631.
[3] J. P. Coleman and D. Pletcher, *Tetrahedron Letters*, 1974, 147.
[4] T. M. Siegel, J. Y. Becker, and L. L. Miller, *J.C.S. Chem. Comm.*, 1974, 341.
[5] S. R. Jones and J. M. Mellor, *J.C.S. Perkin II*, 1976, following paper.
[6] G. J. Edwards, S. R. Jones, and J. M. Mellor, *J.C.S. Chem. Comm.*, 1975, 816.
[7] V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.

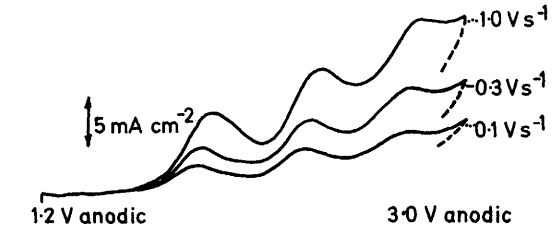
of the cation radical on the reverse sweep in cyclic voltammetry, in our study no such evidence of cathodic waves was observed. Thus, reduction was not observed in

TABLE 1

Voltammetric data and photoelectron spectra of adamantanes and other saturated hydrocarbons in acetonitrile

Compound	$E_{p/2}$/V [a]	E_p/V [b]	Adiabatic I_p/eV
Adamantane	2.37	3.00	9.20
1-Ethyladamantane (6)	2.40	3.00	9.06
1-Isopropyladamantane (7)	2.37	2.98	8.98
1-t-Butyladamantane (8)	2.33	2.97	8.96
1,3-Dimethyladamantane	2.40	3.00	9.15
1,3,5-Trimethyl-7-t-butyladamantane (9)	2.37	3.02	8.90
1,1′-Biadamantane (10)	[c]	[c]	8.53
3,3′,5,5′-Tetramethyl-1,1′-biadamantane (11)	2.05 [d]	3.00 [d]	8.50
Diamantane (12)	2.14 [d]	2.70 [e]	8.59
Bicyclo[3.3.1]nonane	2.58	3.28	9.35
Methylcyclohexane	2.85		
cis–trans-Decalin	2.57	3.20	*ca.* 9.35
N-(1-Adamantyl)acetamide	2.00		

[a] Sweep rate 0.1 V s^{-1}; [substrate] = 10mM; electrolyte $Bu^n_4NBF_4$; reference 10^{-2}M-$AgNO_3$/Ag. [b] Peak potential for second wave; sweep rate 0.3 V s^{-1} (see A. Bewick, G. J. Edwards, S. R. Jones, and J. M. Mellor, *Tetrahedron Letters*, 1976, 631). [c] Insoluble in MeCN. [d] Result obtained by using saturated solution, owing to limited solubility. [e] Third peak observed at 3.07 V.



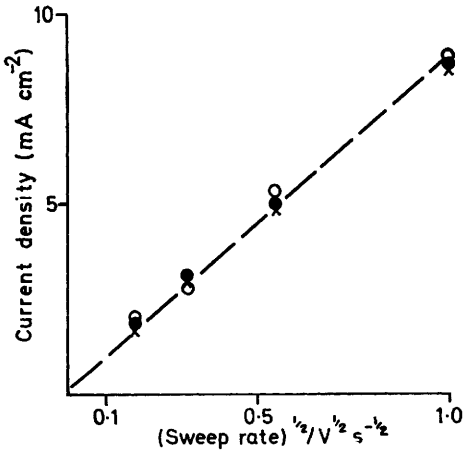


FIGURE 1 Voltammetry of 0.010M-adamantane and 0.10M-tetrabutylammonium tetrafluoroborate in trifluoroacetic acid; reference electrode silver wire; area of working electrode 0.16 cm^2; (×) first wave; (○) second wave; (●) third wave

dichloromethane at −78 °C or in trifluoroacetic acid, indicating the short lifetime of the cation radicals obtained from these hydrocarbons.

Previous studies [2] have shown that the first wave in the cyclic voltammogram of adamantane represents a two-electron process. Comparison of the peak heights for other hydrocarbons with that of adamantane indicates in each case a two-electron wave. Further, a linear relationship was observed between the current for the peak potential (i_p) and the square root of the sweep rate ($v^{\frac{1}{2}}$), indicating an overall diffusion control.

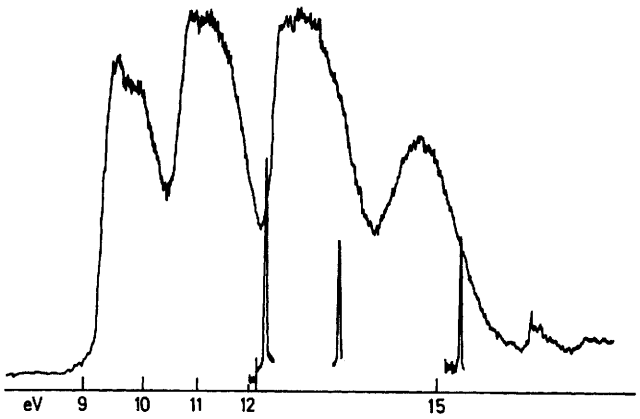


FIGURE 2 Photoelectron spectrum of 1,3-dimethyladamantane

Preparative electrolyses were conducted in dry acetonitrile at a platinum electrode at an anode potential of *ca.* 2.5 V with respect to a Ag/0.01M-$AgNO_3$ electrode. Results are shown in Table 2. Products after work-up were characterised by spectroscopic methods and by comparison with authentic samples.

TABLE 2

Anodic oxidation of 1-substituted adamantanes in acetonitrile

		Products and yields [b]	
Compound	*n* Value [a]	Fragmentation	Substitution
Adamantane	2.08		(13) 74%
1-Ethyladamantane (6)	1.85	(13) 0%	(14) 77%
1-Isopropyladamantane (7)	2.19	(13) 9%	(15) 75%
1-t-Butyladamantane (8)	2.50	(13) 62%	(16) 7%
1,3,5-Trimethyl-7-t-butyladamantane (9)	2.67	(17) 91%	
3,3′,5,5′-Tetramethyl-1,1′-biadamantane [c] (11)	1.92	(18) 80%	(19) <0.1%
1-Isopropyladamantane [d] (7)	1.90	(13) 8%	(15) 63%

[a] ±10%; *n* = number of electrons transferred per molecule of substrate consumed, after correction for background. [b] Yields based on starting material consumed. [c] Oxidation at 2.2 V; all other hydrocarbons at 2.5 V with respect to Ag/0.01M-$AgNO_3$ in acetonitrile. [d] Oxidation at −30 °C; all other oxidations at *ca.* 20 °C.

Further preparative studies were conducted in trifluoroacetic acid after preliminary electroanalytical data (Table 3) indicated a similar anodic behaviour to that observed in acetonitrile. Preparative results are shown in Table 3.

DISCUSSION

Our use of substituted adamantanes to search for evidence of cation radical intermediates was founded on the hypothesis that a cation radical derived from a 1-substituted adamantane would be delocalised and therefore offer the possibility of competitive deprotonation or fragmentation of a carbon–carbon bond.

TABLE 3

Voltammetric data and results of anodic oxidation of adamantanes in trifluoroacetic acid

Compound	$E_{p/2}$/V [a]	n Value [b]	Anode potential (V)	Products and yields [c] from controlled potential electrolysis
Adamantane	1.75	1.90	1.8	(20) 82%
1-t-Butyladamantane (8)	1.40	1.19	1.6	Adamantane 21%; (20) 26%; (21) 36%
1,3,5-Trimethyl-7-t-butyladamantane (9)	1.50	1.91	1.7	(22) 90%

[a] Sweep rate 0.1 V s^{-1}; [substrate] = 10 mM; electrolyte $Bu^n_4NBF_4$; reference Ag wire. [b] ±4%; n = number of electrons transferred per molecule of substrate reacted; background contribution negligible. [c] Yields based on starting material consumed.

Earlier photoelectron studies [8] with adamantane, and our own results (Table 1), clearly indicate that, both in the parent hydrocarbon and in simple alkyladamantanes, the particularly low ionisation potentials for saturated hydrocarbons must be explained by substantial interactions between σ_{CC} orbitals. Consequently, the favourable geometry of adamantanes permits electron removal from a delocalised HOMO giving a delocalised ion radical. The mass spectra of polysubstituted adamantanes offer some support for this view. For example, 1,3,5-trimethyl-7-t-butyladamantane shows peaks at 219 (M − 15) and 177 (M − 57).

A prerequisite of our search for cation radical intermediates in metal salt oxidations was the ability unambiguously to generate ion radicals, which could give products characteristic of such an intermediate, but products inaccessible by other pathways.

In solution the most sure method of formation of cation radicals is electrochemical oxidation. Anodic oxidations of adamantane and some functionalised adamantanes [2] have already been reported. These studies suggest that adamantane is oxidised in acetonitrile at *ca.* 2.5 V by an ECE process requiring a short-lived adamantane cation radical as intermediate. The results of cyclic voltammetry shown in Table 1 and other electroanalytical data indicate a similar process for the substituted adamantanes. Similarly, results obtained in trifluoroacetic acid (Table 3) indicate an analogous process. In both solvents deprotonation or a further chemical process at the stage of the cation radical is suggested, and there is no evidence to support an EEC pathway requiring an incipient dication of adamantane.

Product studies with monosubstituted adamantanes* (6)—(8) confirm the analysis of competitive fragmentation and deprotonation at the stage of the cation radical. The balance between the two processes is largely determined by the nature of the fragmenting group. In acetonitrile, 1-t-butyladamantane (8) gives mainly fragmentation (62%) with a little reaction at a carbon–hydrogen bond (7%). In contrast, 1-ethyladamantane (6) undergoes no fragmentation and 1-isopropyladamantane (7) only slight fragmentation (9%). These results are explained by the relative stability of the fragmenting species. A primary group is far too unstable to be lost, a secondary group is lost with great difficulty, but a tertiary group is sufficiently stable to permit fragmentation in preference to deprotonation. The fragmentation pathway is particularly important in t-butyladamantanes (8) and (9) where the leaving group is a t-butyl cation and in the biadamantane (11) where the leaving group is the adamantyl cation.

In trifluoroacetic acid similar results are obtained for (8) and (9). Fragmentation is dominant. With 1-t-butyladamantane (8) the observation of predominant fragmentation is complicated by secondary processes. These processes are signalled by the anomalously low n value for t-butyladamantane in comparison with other substrates, and by observation of adamantane as a product. Hydride transfer processes, well known with adamantyl or t-butyl cations [9] in acidic media, are indicated. The lack of substituted adamantanes in the oxidation of 1,3,5-trimethyl-7-t-butyladamantane and the normal n value indicate the lack of secondary reactions for this substrate.

In oxidations in acetonitrile, both alkyl fragments were not always isolated as products. From the biadamantane (11), where both alkyl fragments correspond to stable cations incapable of elimination, a good product balance (80%) was observed. By comparison with authentic samples of isopropylacetamide and t-butylacetamide, these amides were shown not to be obtained by anodic oxidation of (7) and (8) in dry acetonitrile. This result appears to have a close analogy, as follows. In anodic oxidation of t-butyl ketones using dry acetonitrile [10] the yield of t-butylacetamide was very low, but in moist acetonitrile high yields of t-butylacetamide were obtained. We attribute these observations to a reversible equilibrium between the nitrilium ion and the alkyl cation. In moist acetonitrile the nitrilium ion is trapped and therefore amide is formed. In dry acetonitrile equilibration leads to loss of the cation by elimination. Olefinic products would be easily further oxidised or possibly polymerised under the reaction conditions.

* Recent results establish that anodic oxidation of cyclopentane in fluorosulphuric acid proceeds unambiguously by an ECE process (S. Pitti, M. Herlem, and J. Jordan, *Tetrahedron Letters*, 1976, 3221).

[8] W. Schmidt, *Tetrahedron*, 1973, **29**, 2129.

[9] M. A. McKervey, *Chem. Soc. Rev.*, 1974, **3**, 479; W. Haaf, *Chem. Ber.*, 1963, **96**, 3359.

[10] J. Y. Becker, L. L. Miller, and T. M. Siegel, *J. Amer. Chem. Soc.*, 1975, **97**, 849; J. Y. Becker, L. R. Byrd, L. L. Miller, and Y. H. So, *ibid.*, p. 853.

It has been suggested previously[4] on the basis of studies with acyclic alkanes that low temperatures particularly favour a fragmentation pathway with respect to deprotonation of an anodically generated cation radical. Side reactions of the type described above particularly complicate the analysis with acyclic hydrocarbons. Our study with isopropyladamantane (7), which shows that a difference of *ca.* 50 °C makes little difference to the product distribution, contrasts with the earlier study. The adamantyl system permits much higher product balances than found with acyclic systems, and we consider that structure controls the chemistry of ion radicals of cyclic hydrocarbons. There is no evidence, as previously suggested,[4] that $\Delta S^{\ddagger}$ values for the anodic substitution and fragmentation reactions are substantially different.

EXPERIMENTAL

General experimental details were as reported in a previous paper.[11] High resolution mass spectra were recorded at the Physico-chemical Measurements Unit, Harwell.

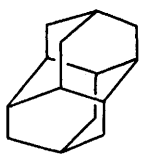
Materials.—Trifluoroacetic acid (Fluorochem) was distilled before use. Acetonitrile was purified by the following modification of the method of O'Donnell *et al.*[12] Acetonitrile (2 l) was heated under reflux for 3 h with benzoyl chloride (30 ml), and distilled (2 ft Vigreux column) on to water (30 ml). The distillate (1 800 ml) was heated under reflux for 12 h with anhydrous sodium carbonate (60 g) distilled, and then heated under reflux for 16 h with sodium carbonate (30 g) and potassium permanganate (45 g). Distillation from the permanganate was carried out, and phosphorus pentaoxide was added to the distillate until a white powder remained undissolved. Acetonitrile was distilled from the phosphorus pentaoxide onto an excess of calcium hydride, and the suspension was heated under reflux for 18 h. Distillation (6 ft fractionating column packed with glass helices; rejection of the first 150 ml) gave pure acetonitrile, which was transparent above 190 nm and showed no peaks on cyclic voltammetry in the range 1.5—3.5 V *versus* Ag/Ag^{+} 0.01M electrode. For all experiments acetonitrile was previously passed through a column of alumina[13] (Brockmann Grade I) previously activated by heating under vacuum at 120 °C for 24 h.

Tetra-n-butylammonium tetrafluoroborate was prepared by the method of Fleischmann.[1]

Photoelectron Spectra.—Vacuum u.v. photoelectron spectra were recorded with a Perkin-Elmer PS 18 spectrometer, calibrated by using the xenon line (12.13 eV) and the argon line (15.76 eV). Adiabatic ionisation potentials were recorded.

Cyclic Voltammetry.—An undivided cell was washed with distilled water and acetone, and dried under vacuum at 110 °C for 2 h before use. A solution of the hydrocarbon (*ca.* 10mM) in acetonitrile containing 0.1M-$Bu^{n}_{4}NBF_{4}$ was used and voltammograms were recorded over the range 1.5—3.5 V against a silver electrode in 10^{-2}M-silver nitrate. For sweep speeds less than 1 V s^{-1} a Bryan's Series 26000 A4 XY recorder was used. For faster sweep speeds a Tektronic 5030 dual beam oscilloscope was employed. The working electrode was a 1 cm platinum wire of area 0.16 cm^2, and the secondary electrode was a cylindrical platinum gauze.

In trifluoroacetic acid cyclic voltammograms were obtained by using 0.4M-$Bu^{n}_{4}NBF_{4}$ over the range 1.0—3.0 V against a silver wire electrode in trifluoroacetic acid solution



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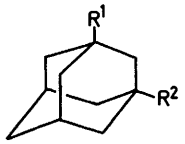
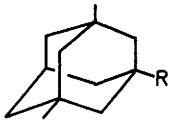
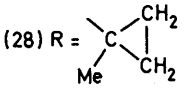
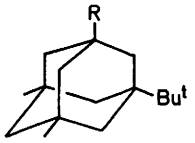


(13) R^1 = H, R^2 = NHAc
(14) R^1 = Et, R^2 = NHAc
(15) R^1 = Pr^i, R^2 = NHAc
(16) R^1 = Bu^t, R^2 = NHAc
(21) R^1 = Bu^t, R^2 = $O_2C{\cdot}CF_3$
(32) R^1 = Bu^t, R^2 = OH

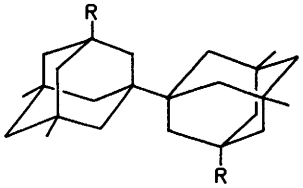


(18) R = NHAc
(25) R = Bu^t
(26) R = C(OH)Me_2
(27) R = CMe : CH_2





(29) R = Br



(30) R = Me
(31) R = Br
(35) R = OH
(36) R = NHAc

containing background electrolyte on a solution 10mM in substrate.

Preparative Electrolysis in Acetonitrile.—All electrochemical experiments were carried out with either a Chemical Electronics Potentiostat TR 70/7A or a valve potentiostat and a waveform generator RB 1. The anode was platinum gauze (1 cm^2), the secondary electrode platinum sheet (4 cm^2), and the reference electrode a silver wire dipping into a 10^{-2}M-solution of silver nitrate in acetonitrile containing the background electrolyte. In a divided cell both anolyte and catholyte were 0.1M-solutions of $Bu^{n}_{4}NBF_{4}$ in acetonitrile. The potential was pulsed to 0.0 V for one second in every ten. In all cases the background current was measured at the working potential before addition of the hydrocarbon. Typically the anolyte (15 ml) was flushed with dry nitrogen and then stirred gently with a Teflon magnetic follower. The background varied between 0.1 and 0.4 mA. Added adamantane (30 mg) caused an increase in current to *ca.* 4 mA. Electrolysis was continued until the current had dropped to

[11] S. R. Jones and J. M. Mellor, *J.C.S. Perkin I*, in the press.
[12] J. F. O'Donnell, J. T. Ayres, and G. K. Mann, *Analyt. Chem.*, 1965, **37**, 1161.
[13] T. Osa and T. Kuwana, *J. Electroanalyt. Chem.*, 1969, **22**, 389.

ca. 0.6—0.8 mA or until 2 Faradays of electricity per mole of hydrocarbon had been passed. In all cases the anolyte remained colourless and the catholyte turned yellow. Water (0.2 ml) was added to the anolyte and catholyte and samples were injected directly for g.l.c. analysis. The amount of material in the catholyte due to migration through the sinter (Type 4) was usually less than 5%, and was neglected.

The yields of products and of residual hydrocarbon were measured by using internal standards. Packing in the injector end of the column was replaced after every 20 injections. Products were identified by g.l.c. comparison with authentic compounds on 5% OV-1 on Chromosorb G AW DMCS (100—120 mesh). No products other than those shown in Table 2 were observed. Assignments were confirmed by g.l.c.–mass spectrometry.

Preparative Electrolysis in Trifluoroacetic Acid.—Electrolysis in trifluoroacetic acid was conducted as in acetonitrile. The potential was pulsed to 0.4 V anodic for one second in every thirty. After electrolysis the anolyte was quenched by pouring into ether (50 ml) and sodium hydroxide [5 g in ice–water (150 ml)]. After extraction, products were identified by g.l.c. comparison with authentic compounds on 5% OV-1 and 5% FFAP on Chromosorb G AW DMCS (100—120 mesh). Results are shown in Table 3.

Preparation of Hydrocarbons.—Methylcyclohexane (B.D.H.), decalin (*cis–trans*-mixture; Cambrian) and 1,3-dimethyladamantane (Eastman Kodak) were used as supplied. Preparation and purification of the following hydrocarbons have been described previously: adamantane, 1-ethyladamantane, 1-isopropyladamantane, bicyclo[3.3.1]-nonane, and diamantane.[11]

1-t-Butyladamantane (8) was prepared from 1-isopropenyladamantane (23). Isopropenyladamantane [14] (2.16 g) and di-iodomethane were added to a zinc–copper couple [15] (1.68 g), which had been heated under reflux in ether (13 ml) with a crystal of iodine for 5 min. The resultant mixture was heated under reflux for 20 h, the solution filtered, and the precipitate washed with more ether. The combined ethereal solutions were washed with saturated ammonium chloride, then sodium disulphite solution, and finally water. Removal of solvent from the ethereal solution gave a crude product, which was purified by chromatography on silica gel (100 g) impregnated with 5% (w/w) silver nitrate. Elution with pentane gave 1-(1-adamantyl)-1-methylcyclopropane (24) (1.83 g, 79%). Sublimation gave crystals, m.p. 61—62°. Hydrogenation of this product as described previously at 50 °C (Adams catalyst in acetic acid) gave 1-t-butyladamantane (8), m.p. 110—111° (from methanol) (lit.,[14] 112—113°).

1,3,5-Trimethyladamantane was prepared from 1,3-dimethyladamantane by bromination to give 1-bromo-3,5-dimethyladamantane, followed by coupling of the bromo-compound with methylmagnesium iodide.[16] The product, b.p. 88—90° at 18 mmHg (lit.,[16] 82° at 13 mmHg) had 1,3-dimethyladamantane as an impurity (1%).

1,3-*Dimethyl*-5-*t*-*butyladamantane* (25).—1,3-Dimethyladamantane was converted by a standard procedure [17] to 3,5-dimethyladamantane-1-carboxylic acid, m.p. 94—96° (lit.,[18] 106—108°). The acid (12.6 g) in ethanol (100 ml) was saturated with dry hydrogen chloride and heated under reflux for 24 h. Removal of solvent and extraction afforded a crude oil (14.0 g). Distillation gave ethyl 3,5-dimethyladamantane-1-carboxylate (11.5 g, 80%), b.p. 108—110° at 1.3 mmHg. The ester (9.24 g) in ether (30 ml) was added slowly to methylmagnesium iodide [from magnesium (2.6 g) and methyl iodide (15.1 g)] in ether (35 ml). The mixture was heated under reflux for 3 h, then cooled, and saturated aqueous ammonium chloride was added at 0 °C. Extraction into ether and work-up afforded an oil (8.72 g), which was purified by distillation (b.p. 104—106° at 1.3 mmHg).

This alcohol (26) (8.7 g) was heated under reflux in acetic anhydride for 24 h, then the mixture was cooled and poured into ice–water (200 g) and pentane (100 ml). The pentane extract was washed with sodium hydrogen carbonate solution and water and dried. Removal of the solvent gave an oil, which was distilled to give pure 2-(3,5-dimethyl-1-adamantyl)propene (27) (6.44 g, 80%), b.p. 67—68° at 0.35 mmHg.

Cyclopropane formation as described above and chromatography gave 1-(3,5-dimethyl-1-adamantyl)-1-methylcyclopropane (28) as an oil. Hydrogenation as described above then gave 1,3-dimethyl-5-t-butyladamantane (25), δ 0.81 (15 H, s), 1.00—1.50 (12 H, m), and 2.05br (1 H); $\nu_{max.}$ 2 900, 1 460, and 1 375 cm^{-1}; *m/e* 220 (M^+).

1,3,5-*Trimethyl*-7-*t*-*butyladamantane* (9).—1,3-Dimethyl-5-t-butyladamantane (4 g) was added to bromine (15 ml) over 1 h and the solution heated under reflux for 4 h, cooled, and poured into carbon tetrachloride (100 ml) and ice–water (100 ml). Solid sodium disulphite was added until the red colouration in the organic layer was absent. The aqueous layer was further extracted with carbon tetrachloride (100 ml). The combined organic layers were washed with water, dried, and evaporated to give a white solid, which was sublimed (100 °C and 0.3 mmHg) to give 1-bromo-3,5-dimethyl-7-t-butyladamantane (29) (4.96 g, 90%; g.l.c. showed >97% purity), m.p. 90—91°.

The bromide (29) (3.08 g) was heated for 3 h at 100 °C in a sealed tube with methylmagnesium bromide [from methyl iodide (5.68 g) and magnesium (0.98 g)] in ether (8 ml). The cooled solution was poured into ether (50 ml) and the excess of Grignard reagent destroyed by slow addition of dilute hydrochloric acid (5%) at 0 °C. Work-up gave a white solid (2.4 g), which was sublimed (70 °C and 0.65 mmHg), and then recrystallised from methanol to give 1,3,5-*trimethyl*-7-*t*-*butyladamantane* (9), m.p. 72—72.5°; $\nu_{max.}$ ($CHCl_3$) 2 900, 1 470, 1 380, 1 360, and 1 015 cm^{-1}; δ 0.81 (18 H, s), 1.00 (6 H, s), and 1.10 (6 H, s); *m/e* 234 (0.1%, M^+), 219 (0.3, M − 15), 178 (14), 177 (100, M − 57), and 121 (63) (Found: M^+, 234.233 7. $C_{17}H_{30}$ requires M, 234.234 8).

3,3′,5,5′-*Tetramethyl*-1,1′-*biadamantane* (11).—1-Bromo-3,5-dimethyladamantane was prepared by the method [19] of Gerzon. The bromide (5.52 g) was heated under reflux in ether with magnesium (0.28 g) for 48 h with stirring. Silver bromide (100 mg) was added and the mixture heated under reflux for a further 1 h. Water was added at 0 °C, and work-up gave an oily solid. G.l.c. indicated the mixture contained 1,3-dimethyladamantane, the starting bromide, and the dimer. Recrystallisation from ethanol

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gave white needles of 3,3′,5,5′-tetramethyl-1,1′-biadamantane (11) (2.81 g, 75%), which sublimed (140° and 0.5 mmHg) to give crystals, m.p. 152°, $\nu_{max.}$ ($CHCl_3$) 2 950, 1 470, 1 365, and 1 345 cm^{-1}; δ 0.79 (12 H, s), 1.00—1.46 (24 H, m), and 2.01br (2 H); *m/e* 326 (17%, M^+), 164 (20), and 163 (100).

3,3′,5,5′,7,7′-*Hexamethyl*-1,1′-*biadamantane* (30).—3,3′,5,5′-Tetramethyl-1,1′-biadamantane (11) (2.04 g) was heated under reflux with bromine (20 ml) for 4 h. The cooled solution was poured into chloroform (150 ml) and washed with ice–water (100 ml). Solid sodium disulphite was added until no colour remained. The chloroform extract on work-up afforded a crude product (3 g), which was recrystallised from cyclohexane to give 3,3-dibromo-5,5′,7,7′-tetramethyl-1,1′-biadamantane (31) as an off-white solid (2.5 g), m.p. >350°, $\nu_{max.}$ ($CHCl_3$) 2 900, 1 470, 1 350, and 1 335 cm^{-1}; δ 0.88 (12 H, s), 1.18 (12 H, m), and 1.97 (12 H, m); *m/e* 405 (17%, M − Br), 403 (17, M − Br), 213 (8), 211 (8), 121 (31), 119 (97), and 117 (100).

The dibromide (31) (2.54 g) was heated with methylmagnesium bromide (40 mmol) in ether for 61 h at 100 °C in a sealed tube. Work-up as described above afforded a white solid (1.95 g), which was recrystallised from benzene to give pure 3,3′,5,5′,7,7′-hexamethyl-1,1′-biadamantane (30) (1.67 g), m.p. 301—302°, $\nu_{max.}$ ($CHCl_3$) 2 900, 1 465, 1 365, and 1 350 cm^{-1}; δ 0.80 (18 H, s), 0.99 (12 H, s), and 1.10 (12 H, s); *m/e* 354 (12%, M^+), 178 (14), and 177 (100).

Preparation of Trifluoroacetates and Alcohols.—Authentic samples of trifluoroacetates were prepared by reactions of hydrocarbons with lead tetra-acetate in trifluoroacetic acid, as described in detail elsewhere.[11] Hydrolysis of the trifluoroacetates by an established procedure [11] gave the corresponding alcohols. The yields, methods of purification, and properties for the alcohols were as follows: 3-t-butyladamantan-1-ol (32) (86%), chromatography on silica gel and recrystallisation, m.p. 131—132° (hexane), δ 0.84 (9 H, s), 1.40—1.75 (13 H, m), and 2.30br (2 H), *m/e* 208 (2%, M^+), 152 (16), 151 (100, $M - C_4H_9$), 135 (14), and 107 (11), $\nu_{max.}$ 3 550, 3 450, 1 115, and 1 095 cm^{-1}; 3,5,7-trimethyladamantan-1-ol (33) (90%), sublimation, m.p. 118—119° (lit.,[20] 122—123°), δ 0.88 (9 H, s), 1.05 (6 H, s), and 1.31 (7 H, s), *m/e* 194 (22%, M^+), 179 (20, M − 15), 124 (9), 123 (100), 122 (6), 121 (45), 55 (9), and 41 (11), $\nu_{max.}$ 3 550, 3 420, 1 170, 1 105, and 1 000 cm^{-1}; 3′,5,5′,7-*tetramethyl*-1,1′-*biadamantan*-3-*ol* (34) (68%), preparative t.l.c., m.p. 173—174° hexane), δ 0.79 (6 H, s), 0.89 (6 H, s), 1.00—1.63 (25 H, m), and 2.05br (1 H), *m/e* 342 (13%, M^+), 179 (25), 163 (100), 162 (90), 123 (29), 121 (30), 120 (15), and 107 (35), $\nu_{max.}$ 3 600, 3 450, 1 190, and 1 105 (Found: C, 83.9; H, 11.2. $C_{24}H_{38}O$ requires C, 84.1; H, 11.2%); 5,5′,7,7′-*tetramethyl*-1,1′-*biadamantane*-3,3′-*diol* (35) (11%), preparative t.l.c., m.p. 258—260° (from ethyl acetate), δ 0.88 (12 H, s) and 1.00—1.50 (26 H, m), *m/e* 358 (8%, M^+), 179 (22), 163 (23), 162 (100), 123 (35), 121 (40), 120 (11), 107 (13), and 43 (24), $\nu_{max.}$ (Nujol) 3 250 and 1 060 cm^{-1} (Found: C, 80.25; H, 10.4. $C_{24}H_{38}O_2$ requires C, 80.4; H, 10.7%).

Preparation of Acetamides.—Authentic samples of acetamides were prepared by reactions of the appropriate hydrocarbons with lead tetra-acetate in trifluoroacetic acid, followed by sulphuric acid-catalysed displacement of the trifluoroacetate group by acetonitrile. Full details [11] of the procedure have been described. The yields, methods of purification, and properties for the amides were as follows: N-(3-*t-butyl*-1-*adamantyl*)*acetamide* (16) (83%), m.p. 153—154° (from hexane), δ 0.82 (9 H, s), 1.45—1.97 (12 H, m), 1.90 (3 H, s), 2.10br (2 H, s), and 5.15br (1 H), *m/e* 249 (12%, M^+), 193 (26), 192 (100), 150 (59), 136 (22), 94 (23), 58 (22), 57 (19), and 41 (17), $\nu_{max.}$ (Nujol) 3 200, 3 050, 1 640, 1 570, and 1 300 cm^{-1} (Found: M^+, 249.209 9. $C_{16}H_{27}NO$ requires M, 249.209 3); *N*-(3,5,7-trimethyl-1-adamantyl)acetamide (17) (83%), m.p. 193—194.5° (lit.,[21] 194—196°) (from hexane–ethyl acetate), δ 0.85 (9 H, s), 1.10 (6 H, s), 1.59 (6 H, s), 1.90 (3 H, s), and 5.25br (1 H), *m/e* 135 (57%, M^+) 177 (13), 164 (100), 122 (17), 121 (34), 120 (32), 107 (12), and 41 (12), $\nu_{max.}$ (Nujol) 3 300, 3 050, 1 640, and 1 560 cm^{-1} (Found: M^+, 235.194 0. Calc. for $C_{15}H_{25}NO$: M, 235.193 6); N-(3′,5,5′,7-*tetramethyl*-1,1′-*biadamantanyl*)*acetamide* (19) (70%), preparative t.l.c. and recrystallisation from ethyl acetate–hexane (1 : 1), m.p. 224—225°, δ 0.77 (6 H, s), 0.83 (6 H, s), 0.93—1.70 (24 H, m), 1.87 (3 H, s), and 2.04br (1 H), *m/e* 383 (32%, M^+), 221 (21), 220 (100), 164 (46), 163 (100), 121 (22), 107 (149), and 43 (15), $\nu_{max.}$ (Nujol) 3 250, 1 650, and 1 540 cm^{-1} (Found: M^+, 383.318 3. $C_{26}H_{41}NO$ requires M, 383.318 8); NN′-(5,5′,7,7′-*tetramethyl*-1,1′-*biadamantane*-3,3′-*diyl*)*diacetamide* (36) (16%), preparative t.l.c. and recrystallisation from ethyl acetate, m.p. 345—350° (decomp.), δ 0.86 (12 H, s), 1.0—1.24 (12 H, m), 1.5—1.72 (12 H, m), 1.89 (6 H, s), 5.15br (1 H), *m/e* 441 (15), 440 (46, M^+), 221 (17), 220 (100), 219 (14), 164 (35), 121 (18), and 44 (28), $\nu_{max.}$ (Nujol) 3 430, 3 050, 1 640, and 1 560 cm^{-1} (Found: M^+, 440.341 4. $C_{28}H_{44}N_2O_2$ requires M, 440.340 3). The preparations of *N*-(3-ethyl-1-adamantyl)acetamide (14), *N*-(3-isopropyl-1-adamantyl)acetamide (15), and *N*-(3,5-dimethyl-1-adamantyl)acetamide (18) have been described.[11]

We thank the S.R.C. for financial support.

[6/1279 *Received*, 1*st July*, 1976]

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