Bridgehead Functionalisation of Saturated Hydrocarbons with Lead(IV) Salts

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Oxidation of a series of adamantanes, bicyclo[3.3.1]nonane, and diamantane with lead tetra-acetate in trifluoroacetic acid–dichloromethane solution in the presence of chloride ion at room temperature gives high yields of the trifluoroacetates of the bridgehead alcohols (based both on oxidant and on hydrocarbon). By subsequent hydrolysis bridgehead alcohols are obtained in >88% overall yields from adamantane and 1-alkyladamantanes; bicyclo[3.3.1]nonane gives bicyclo[3.3.1]nonan-1-ol (88%), and diamantane gives a mixture of diamantan-1-ol and diamantan-4-ol in a ratio controlled by the reaction conditions. Further equilibration of the trifluoroacetate of diamantan-1-ol gives a 1 : 1 mixture of the trifluoroacetates of diamantan-1-ols and -4-ols. The high selectivity is illustrated by very low reactivity with methylcyclohexane and 3-methylhexane, and the deactivating influence of the trifluoroacetate group protects the primary products from further oxidation. Further adamantanes with an electron-withdrawing 1-substituent show low reactivity and either give products in low yield or do not react. The trifluoroacetate group is readily displaced by reaction with acetonitrile in ' one-pot ' conversion of hydrocarbons into amides.

FUNCTIONALITY may be introduced into the adamantane nucleus by a variety of methods. Radical processes in general lead to a mixture of products of bridgehead and non-bridgehead substitution, which are difficult to separate. Ionic processes, however, lead predominantly [1] to bridgehead functionalisation. For example bromination of adamantane (1) in liquid bromine gives [2] high yields of bridgehead bromide (2). Analogous brominations have been used to functionalise bicyclo[3.3.1]nonane (3),[3] diamantane (4),[4] a series of adamantanes,[5] protoadamantane,[6] and even [5] bicyclo[2.2.2]octane (5). Adamantanes are also functionalised by oxidation with sulphuric acid, either alone [7] or with t-butyl alcohol and hydrogen halide mixtures,[8,9] and with [10] fluorosulphuric acid.

Oxidation of these polycyclic hydrocarbons by metal oxidants has received relatively little attention. Treatment of adamantane with chromium trioxide in acetic acid–acetic anhydride is reported [11] to give a bridgehead product in 52% yield, or a mixture [12] of products. Oxidation with lead tetra-acetate in acetic acid is an inefficient process because of further oxidation of initially formed materials [13] and the formation of both bridgehead and non-bridgehead functionalised products. The claim that the oxidation gives uniquely the products of bridgehead substitution is not substantiated by our work.

Lead tetra-acetate is a versatile organic oxidising agent [14] in reactions involving electrophilic additions, but its use in the oxidation of hydrocarbons is limited to processes involving thermal or photochemical radical decomposition.[15] Lead tetrakistrifluoroacetate has been introduced as a more powerful oxidant which is capable of oxidising less reactive aromatic compounds and heptane.[16] Lead tetra-acetate in trifluoroacetic acid has been used to oxidise these less reactive aromatic substrates,[17] and even tetramethylsilane,[18] and the

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synthetic utility[19,20] is shown in the oxidation of aromatic compounds. The present paper shows that lead tetra-acetate in trifluoroacetic acid containing chloride ion can be used to introduce functional groups into hydrocarbons in high yields, in a process of promising synthetic potential. Elsewhere we will discuss mechanistic aspects of this work.

RESULTS AND DISCUSSION

In preliminary experiments the reactivity of lead tetra-acetate with an excess of adamantane in trifluoroacetic acid–dichloromethane was studied. Dichloromethane was used as co-solvent to keep the hydrocarbon in solution. Adamantane (1) gave 1-adamantyl trifluoroacetate (6) in high yield (94% based on hydrocarbon consumed) as the only product. Similarly bicyclo-[3.3.1]nonane (3) and diamantane (4) give bridgehead functionalised products in high yield. However, under the same conditions methylcyclohexane and 3-methylhexane were far less reactive; no products were observed (g.l.c.) in ethereal extracts of these reaction mixtures, and little hydrocarbon was consumed. Again little reaction took place with bicyclo[2.2.2]octane (5) under conditions effective in the oxidation of adamantane; after reaction under more vigorous conditions bicyclo-[2.2.2]octan-1-ol (7) was observed as the major product but in poor yield. These preliminary results are shown in Table 1.

TABLE 1

Oxidation of an excess of hydrocarbon by lead tetra-acetate in trifluoroacetic acid–dichloromethane (1 : 1)

Hydrocarbon	Conditions [a]	% Hydrocarbon lost [b]	Product, yield (%) [c]
(1)	20 °C, 1 h [d]	90	(6), 94
(3)	20 °C, 1.75 h [d]	90	(8), 74
(4) [e]	20 °C, 35 min [d]	84	(9), 80; (10), 9 [f]
(5)	Reflux, 8 h [d]	18	(7), 45; (11), 26; (12), 24; (13), 5 [f,g]
Methylcyclohexane	20 °C, 2 h	*h*	No products observed; 25% Pb^{IV} consumed
Methylcyclohexane	20 °C, 40 h	*h*	38% Pb^{IV} consumed
3-Methylhexane	20 °C, 2 h	*h*	No products observed; 23% Pb^{IV} consumed
3-Methylhexane	20 °C, 40 h	*h*	38% Pb^{IV} consumed
None	20 °C, 2 h		8% Pb^{IV} consumed
None	20 °C, 40 h		12% Pb^{IV} consumed
(1)	20 °C, 2 h [d,i]	87	(6), 98
(1)	20 °C, 15 min [j]	70	(6), 85
(4) [e]	20 °C, 30 min [d,i]	93	(9), 80; (10), 14 [f]

[a] Hydrocarbon (2 mmol) and unpurified reactive 'lead tetra-acetate' (1 mmol) in trifluoroacetic acid (5 ml) and dichloromethane (5 ml). [b] Based on oxidant. [c] By g.l.c. analysis based on hydrocarbon consumed. [d] Time for complete loss of oxidant (starch–iodide test). [e] Hydrocarbon partly soluble. [f] Products analysed after hydrolysis. [g] Yields based on products. [h] Not recorded. [i] With added lithium chloride (0.05M). [j] With added lithium bromide (0.05M).

Several noteworthy features of these results led to the subsequent experimental work described below. With bridged hydrocarbons such as adamantane (1), bicyclo-[3.3.1]nonane (3), and diamantane (4) the oxidative functionalisation is experimentally very easy, the products are obtained in high yield, and the labile trifluoroacetate substituent permits alternative functionality to be introduced by nucleophilic displacement. Further, the reactivity of a hydrocarbon with lead tetra-acetate depended upon the batch of metal acetate used. Similar effects with lead tetra-acetate have been previously reported.[21] Lead tetra-acetate is prepared commercially by the reaction of lead oxides with acetic acid–acetic anhydride and chlorine, and may contain chloride ion impurity.[22] Our observation of the varied reactivity of different batches of the lead tetra-acetate prompted an investigation of the effect of added halide ion on the oxidation of adamantane.

Reactivity was estimated by iodimetric titration of reaction mixtures, which determined the total lead(IV) and free molecular halogen content. Typical results for adamantane depend upon halide ion. A pure sample of lead tetra-acetate reacts slowly at room temperature. Addition of potassium fluoride (0.05M) does not accelerate oxidation of the hydrocarbon, but acceleration is observed in the presence of lithium chloride (0.05M) or lithium bromide (0.05M). Addition of bromide ion caused an initial rapid reaction (77% of oxidant consumed in 5 min), but subsequent loss of oxidant was very slow (87% consumed in 6 h). These results are consistent with oxidation of bromide ion to free molecular bromine by Pb^{IV} [orange-red colour in solution and absence of precipitate of lead(IV) oxides on aqueous quenching], and further indicate that a lead(IV) complex is the oxidant of the hydrocarbon, not free bromine. Addition of chloride ion caused a rapid loss of oxidant (100% in 2 h). As observed elsewhere[21,23] chloride ion is an effective catalyst of oxidations by lead(IV), and in our study is more effective than other halide ions. The observation of these catalytic effects required that our preliminary study establishing the relative reactivity of bridged hydrocarbons with respect to acyclic or simple monocyclic hydrocarbons be confirmed by comparable results of reactions in the presence of added chloride ion.

Under standard conditions [hydrocarbon (2 mmol)

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[20] J. R. Campbell, J. P. Kalman, J. T. Pinhey, and S. Sternhell, *Tetrahedron Letters*, 1972, 1763.

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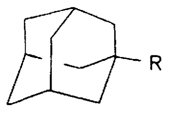
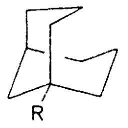
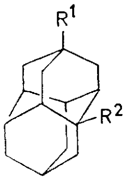
and lead tetra-acetate (1 mmol) in trifluoroacetic acid (5 ml) and dichloromethane (5 ml)] with added lithium chloride (solution 0.05M), methylcyclohexane, 3-methylhexane, and bicyclo[2.2.2]octane (5) were unreactive at room temperature ($t_{\frac{1}{2}}$ in 140, 160, and 200 min, respectively) in comparison with bicyclo[3.3.1]nonane (3) ($t_{\frac{1}{2}}$ *ca.* 4 min) and the more reactive *cis*-decalin, adamantane, and diamantane (4) ($t_{\frac{1}{2}} < 4$ min). Hence the observed rates are controlled by the relative reactivity of the hydrocarbons with a lead(IV) complex. Further results in Table 1 establish that added halide ion does not adversely effect the high yields of trifluoroacetates.



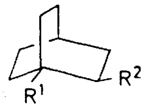
(1) R = H
(2) R = Br
(6) R = $O_2C\cdot CF_3$
(14) R = OH
(31) R = NHAc



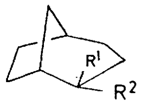
(3) R = H
(8) R = $O_2C\cdot CF_3$
(23) R = OH
(36) R = NHAc



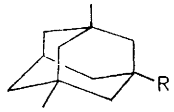
(4) $R^1 = R^2 = H$
(9) $R^1 = H, R^2 = OH$
(10) $R^1 = OH, R^2 = H$
(24) $R^1 = H, R^2 = O_2C\cdot CF_3$
(25) $R^1 = O_2C\cdot CF_3, R^2 = H$



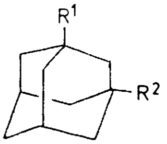
(5) $R^1 = R^2 = H$
(7) $R^1 = OH, R^2 = H$
(11) $R^1 = H, R^2 = OH$



(12) $R^1 = OH, R^2 = H$
(13) $R^1 = H, R^2 = OH$



(15) R = H
(16) R = OH
(35) R = NHAc



(17) $R^1 = Me, R^2 = H$
(18) $R^1 = Me, R^2 = OH$
(19) $R^1 = Et, R^2 = H$
(20) $R^1 = Et, R^2 = OH$
(21) $R^1 = Pr^i, R^2 = H$
(22) $R^1 = Pr^i, R^2 = OH$
(26) $R^1 = CO_2Me, R^2 = H$
(27) $R^1 = CH_2\cdot OAc, R^2 = H$
(28) $R^1 = CH_2\cdot CO_2Me, R^2 = H$
(29) $R^1 = CH_2\cdot OAc, R^2 = OH$
(30) $R^1 = CH_2\cdot CO_2Me, R^2 = OH$
(32) $R^1 = Me, R^2 = NHAc$
(33) $R^1 = Et, R^2 = NHAc$
(34) $R^1 = Pr^i, R^2 = NHAc$

Optimum conditions for synthetically useful conversion of hydrocarbons into trifluoroacetates were sought. By use of a slight excess of lead(IV) in the presence of added chloride ion, high conversions into the trifluoroacetates were obtained. Results are shown in Table 2, with yields based on isolated alcohols following hydrolysis, and purification by either sublimation or preparative t.l.c. (see Experimental section). To complete reaction with the less reactive bicyclo[3.3.1]nonane (3) a greater excess of oxidant was used. In all cases products were of satisfactory purity (>98%) and g.l.c. analysis further showed the absence of non-bridgehead alcohols with adamantane (1), bicyclo[3.3.1]nonane (3), or diamantane (4) and of diols with adamantane. With diamantane (4) small amounts (*ca.* 3%) of products of longer retention time were observed. Mass spectroscopy suggested the products were diols, but even with an excess of oxidant [2.5 mol of lead(IV) per mol of diamantane] and

TABLE 2

Preparative oxidation of hydrocarbons by lead(IV) in trifluoroacetic acid–dichloromethane

Hydrocarbon	Conditions[a]	Products, yields (%)[b]
(1)	24 h	(14), 89
(15)	24 h	(16), 91
(17)	24 h	(18), 88
(19)	24 h	(20), 88
(21)	24 h	(22), 92
(4)	4 h	(9), 80; (10), 6
(3)	24 h[c]	(23), 88

[a] Hydrocarbon (5 mmol) and lead tetra-acetate (6.25 mmol) in trifluoroacetic acid (12 ml) and dichloromethane (12 ml) with added lithium chloride (0.05M) at room temperature. [b] Products isolated as alcohols; yields based on alcohol isolated from initial amount of hydrocarbon. [c] Molar ratio of oxidant to hydrocarbon 1.34 : 1.

long reaction times the yield of these diols remained low (*ca.* 6%). It is concluded that a trifluoroacetate substituent substantially deactivates the hydrocarbon.

In the case of diamantane the products are crucially dependent upon the reaction conditions. With a hydrocarbon–oxidant ratio of 1.25 : 1 the products are, after hydrolysis, the alcohols (9) (80%) and (10) (6%), but with a ratio of 2.5 : 1 the products (9) and (10) are obtained in the ratio 99 : 1. This result is explained by a kinetic formation of the trifluoroacetate (24) in preference to (25), which is complicated by a secondary process of hydride transfer from starting material to the 1-diamantylium ion derived from (24). With an excess of oxidant the concentration of diamantane capable of participation in the secondary process is always low, and hence effective isomerisation of (24) is not observed. High oxidant concentrations therefore favour formation of (24).

However, this hydride transfer can be put to synthetic advantage. 4-Substituted diamantanes are not easy to prepare. Control experiments established that addition of catalytic amounts of diamantane to the crude products of oxidation of diamantane with lead(IV) led to slow isomerisation at room temperature. More rapid and synthetically useful equilibrium was promoted by addition of sulphuric acid (0.5M). The ratio of (9) to (10) after equilibration and hydrolysis was 1 : 1, in good agreement [24] with other equilibrations of diamantyl derivatives.

The satisfactory functionalisation of these bridged hydrocarbons by this procedure suggested two extensions: a study of substituted adamantanes, and subsequent synthetic studies based on the trifluoroacetates.

An investigation of the reactions of substituted adamantanes (other than the hydrocarbons already reported) was not rewarding. 1-Bromo- and 1-chloroadamantane only gave the trifluoroacetate (6) by solvolysis, oxidation being uncompetitive. The ester (26) was largely unreactive, giving only a low yield of (6), presumably by decarboxylation. The esters (27) and (28) give high yields of alcohols (29) and (30), respectively, based on hydrocarbon consumed, after hydrolysis, but the esters are rather unreactive and conversions are low.

A further important advantage of this method of functionalisation is the ready reaction of the intermediate trifluoroacetate to permit subsequent alternative functionality to be introduced. Thus in a ‘ one-pot ’ reaction, adamantane can be converted in 85% yield into *N*-(1-adamantyl)acetamide (31) by the reaction of the intermediate trifluoroacetate with added acetonitrile. This route is an attractive alternative to the reported [25] two-step preparation of (31) *via* 1-bromoadamantane, or the electrochemical oxidation of adamantane.[26] In view of the importance of substituted adamantanes in prophylactic treatment of viruses [27] and in other pharmacological applications,[28] we have further examined the potential of this method of functionalisation.

Reactions of a series of alkyladamantanes with lead tetra-acetate followed by direct addition of acetonitrile and sulphuric acid as catalyst transformed the intermediate trifluoroacetates into the corresponding acetamides efficiently (>80% based on isolated products). The ability to carry out acid-catalysed nucleophilic displacements of the trifluoroacetate group in the crude reaction mixture greatly extends the importance of this simple method of bridgehead functionalisation. Introduction of a considerable range of functional groups by a similar method may be envisaged.

EXPERIMENTAL

G.l.c. was carried out with a Pye series 104 instrument fitted with a flame ionisation detector, by using the following columns: (A) 2 m FFAP on Chromosorb G (A.W. D.M.C.S.), 100—200 mesh (5% w/w); (B) Perkin-Elmer TCEP capillary column (50 ft); (C) 7 m diglycerol on Chromosorb W, 60—80 mesh (6% w/w). I.r. spectra were measured for solutions in chloroform with a Unicam SP 200 spectrometer. N.m.r. spectra were measured for solutions in deuteriochloroform with a Perkin-Elmer R12 and a Varian HA-100 instrument (tetramethylsilane as internal standard). Mass spectra were measured with an A.E.I. MS12 spectrometer, linked to a Pye series 104 gas chromatograph for g.l.c.–mass spectrometry. M.p.s were determined for samples sealed in capillary tubes.

Materials.—Lead tetra-acetate moist with acetic acid (B.D.H.) was partially dried by suction on filter paper under dry nitrogen. The sample was further dried over potassium hydroxide under vacuum and stored in a desiccator (P_2O_5). Analysis for lead(IV) (iodimetric titration with standard thiosulphate) indicated a purity of 96—100% for various samples. Samples of lead tetra-acetate already inactive in oxidation of adamantane were further purified by recrystallisation from acetic acid–acetic anhydride, dried as above, and used in the study concerning the effects of added halide ions. In all analyses of reactions with lead tetra-acetate, total oxidant was determined by addition of a sample to an excess of potassium iodide solution, and back titration with standard thiosulphate solution under anaerobic conditions (Vitex indicator).

Dichloromethane (Koch–Light puriss.) was washed with equal volumes of water, aqueous 10% sodium carbonate, and water, dried ($CaCl_2$), and fractionally distilled prior to use. Trifluoroacetic acid (Fluorochem) was used without further purification. The drying agent used was magnesium sulphate. Adamantan-1- and -2-ols were supplied by Emanuel. The esters (26) and (28) were prepared by standard methods from adamantane-1-carboxylic acid and 1-adamantylacetic acid, and the acetate (27) from 1-adamantylmethanol.

Hydrocarbons. Adamantane (B.D.H.) was recrystallised (MeOH) and sublimed prior to use. Methylcyclohexane

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[24] T. Courtney, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J.C.S. Perkin I*, 1972, 2691.

[25] H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, 1959, **92**, 1629; *Angew. Chem.*, 1959, **71**, 429.

[26] V. R. Koch and L. L. Miller, *J. Amer. Chem. Soc.*, 1973, **95**, 8631.

[27] D. Parkes, *Adv. Drug. Res.*, 1974, **8**, 11.

[28] K. Gerzon, E. V. Krumkalns, and D. Kau, Abstracts, 159th Meeting of Amer. Chem. Soc., Division of Petroleum Chemistry, Houston, Texas, February, 1970, p. B80.

(B.D.H.), 3-methylhexane (Koch–Light), *cis*-decalin (Cambrian), and 1,3-dimethyladamantane (Eastman–Kodak) were used as supplied. 1-Methyladamantane was prepared by the method of Schleyer *et al.*[29] (m.p. 97—99°; lit.,[29] 103°). G.l.c. analysis [column (A)] indicated adamantane as an impurity (<2%). 1-Ethyladamantane was prepared by Wolff–Kishner reduction of 1-adamantyl methyl ketone (Aldrich) in 89% yield (b.p. 98—100° at 13 mmHg; lit.,[30] 220—222° at 744 mmHg). 1-Isopropyladamantane was prepared by the method of Grob *et al.*[30] Removal of minor olefinic and polar impurities was achieved by column chromatography on silica gel impregnated with silver nitrate (5%); 1-isopropyladamantane was eluted with light petroleum (b.p. <40°). Bicyclo[3.3.1]nonane (3) was prepared by Wolff–Kishner reduction of bicyclo[3.3.1]nonan-9-one (Emanuel), in 80% yield (m.p. 140—141°; lit.,[31] 143—145°). Bicyclo[2.2.2]octane (5) was prepared by Wolff–Kishner reduction of bicyclo[2.2.2]octan-2-one,[31] in 79% yield (m.p. 169—170; lit.,[32] 169—170°). Diamantane (4) was prepared by the method of McKervey *et al.*[24] (m.p. 244—245.5°; lit.,[24] 251°).

Oxidation Procedures.—(a) *Excess of hydrocarbon.* Adamantane (272 mg, 2 mmol) was stirred in a stoppered flask at room temperature in the dark with lead tetra-acetate (1 mmol. equiv.) in trifluoroacetic acid (containing 0.1M-halide ion where necessary) (5 ml) and dichloromethane (5 ml). The reaction was followed by monitoring the loss of oxidant by the starch–iodide test. After complete reaction, the mixture was partitioned between ether (50 ml) and aqueous sodium hydroxide [2 g in ice–water (50 ml)]. The aqueous layer was further washed with ether (50 ml), and the organic extracts were combined, washed with sodium hydrogen carbonate solution (5%; 25 ml) and water (25 ml), and dried. A previously calibrated internal standard was added to the ethereal solution and the yields were estimated by g.l.c. analysis. This procedure was used for all oxidations by Pb^{IV} with an excess of hydrocarbon. With methylcyclohexane, 3-methylhexane, and *cis*-decalin only traces (<5% based on oxidant) of products were observed in the ethereal extract, and no attempt was made to identify these. With bicyclo[2.2.2]octane (4), products were analysed after hydrolysis (see below) to alcohols, on columns (A), (B), and (C). Comparison with authentic samples established the identity of the products (11)—(13), and (7) was identified by g.l.c.–mass spectrometry [*m/e* 126 (15%, M^+), 97(49), 71(9), 70(100), 55(12), 43(11), 41(16), and 39(11); no $M - 18$ peak observed].

(b) *Study of effect of added halides.* By using the above procedure, the influence of halide ion was investigated. Adamantane was oxidised in the presence of added potassium fluoride, lithium chloride, or lithium bromide. Samples were periodically removed and total oxidant was determined iodimetrically.

(c) *Synthetic procedure.* Adamantane (0.68 g, 5 mmol) and lead tetra-acetate (2.79 g, 6.25 mmol) were stirred with trifluoroacetic acid (12 ml) containing lithium chloride (0.1M) and dichloromethane (12 ml) for 24 h in the dark. All oxidant was consumed. The mixture was worked up as above and ether evaporated off to leave crude trifluoroacetate, which was heated under reflux for 1 h with aqueous sodium hydroxide (10%; 5 ml). Extraction with chloroform (2 × 25 ml) and work up of the organic layer gave adamantan-1-ol, purified by sublimation in 89% yield. As shown in Table 2 this procedure was used satisfactorily with other bridged hydrocarbons. The method of purification and physical and spectroscopic properties for the alcohols were: 1-adamantanol (14), sublimation; 3-methyladamantan-1-ol (18), sublimation at 100 °C and 3 mmHg, and recrystallisation (pentane), m.p. 127—129° (lit.,[11] 128—129°), δ 0.85 (3 H, s), 1.20—1.73 (13 H, m), and 2.14br (2 H) *m/e* 166(33%, M^+), 151(4), 110(9), 109(100, $M - 57$), 108(12), 45(34), 43(15), 41(9), and 39(5), $\nu_{max.}$ 3 500, 3 375, 1 140, 1 040, and 910 cm^{-1}; 3-ethyladamantan-1-ol (20), sublimation, m.p. 64—65° (lit.,[11] 66—67°), δ 0.62—1.90 (16 H, m) and 2.18br (2 H), *m/e* 180 (54%, M^+), 151 (100, $M - C_2H_5$), 123 (69, $M - 57$), 107(28), 95(53), 91(51), 79(24), and 41(19), $\nu_{max.}$ 3 300, 3 150, 2 900, 1 460, 1 050, and 940 cm^{-1}; 3-isopropyladamantan-1-ol (22), sublimation at 100 °C and 2 mmHg and recrystallisation (hexane), m.p. 89.5—90° (lit.,[11] 90—91°), δ 0.84 (6 H, d), 1.28—1.76 (14 H, m), and 2.20br (2 H), *m/e* 194 (7%, M^+), 152(14), 151(100, $M - C_3H_7$), 107(10), 95(27), 93(37), 43(8), and 41(12), $\nu_{max.}$ 3 550, 3 400, 1 110, 1 080, 1 020, and 950 cm^{-1}; 3,5-dimethyladamantan-1-ol (16), sublimation at 95 °C and 2 mmHg and recrystallisation (hexane), m.p. 96—97° (lit.,[11] 96.5—97°), δ 0.86 (6 H, s), 1.00—1.70 (13 H, m), and 2.17br (1 H), *m/e* 180 (56%, M^+), 165 (19, $M - 15$), 123(100 $M - C_4H_9$), 109 (100, $M - 71$), 107(71), 91(14), 55(13), and 41(21), $\nu_{max.}$ 3 550, 3 400, 1 140, 970, and 920 cm^{-1}; bicyclo[3.3.1]nonan-1-ol (23), sublimation at 120 °C and 15 mmHg and recrystallisation (hexane), m.p. 184—184° (lit.,[3] 182—184°), δ 1.45 (s, OH) and 1.42—2.35 (15 H, m), *m/e* 140 (12%, M^+), 107(12), 98(29), 97(100), 79(31), 67(17), 55(22), 43(16), 41(32), and 39(17), $\nu_{max.}$ 3 570, 3 450, 1 160, 1 120, 1 090, 1 000, 960, and 870 cm^{-1}; diamantan-1-ol (9), preparative t.l.c. and recrystallisation (hexane), m.p. 290—292° (lit.,[24] 292—294°), δ 1.25 (1 H, s, OH) and 1.3—2.20br (19 H, m), *m/e* 204 (43%, M^+), 186 (100, $M - 18$), 130(28), 95(70), 94(60), 91(28), 79(24), and 41(25), $\nu_{max.}$ 3 600, 3 450, and 1 105 cm^{-1}; diamantan-4-ol (10), preparative t.l.c. and recrystallisation (hexane), m.p. 204—206° (lit.,[24] 206—208°), δ 1.25 (1 H, s, OH) and 1.60—2.00br (19 H, m), *m/e* 205 (15%, $M + 1$), 204 (100, M^+), 109(16), 108(12), 107(10), 96(3), 95(9), and 41(8), $\nu_{max.}$ 3 600, 3 450, 1 310, and 1 105 cm^{-1}; ester (29), column chromatography on silica gel and recrystallisation (pentane), m.p. 55—56°, δ 1.35—1.85 (10 H, m), 2.07 (3 H, s), 2.23br (2 H), and 3.78 (2 H, s); *m/e* 224 (26%, M^+), 164(38), 151 (100, $M - C_3H_5O_2$), 107(43), 95(35), 93(50), 91(25), and 43(43); $\nu_{max.}$ 3 350, 3 250, 2 850, 1 710, 1 260, 1 040, and 920 cm^{-1}; ester (30), column chromatography on silica gel and recrystallisation (pentane), m.p. 53—55°, δ 1.47—1.70 (13 H, m), 2.14 (2 H, s), 2.20br (2 H), and 3.63 (3 H, s); *m/e* 224 (73%, M^+), 167(74), 151(63), 135(41), 107(100), 95(43), 93(34), and 74(20); $\nu_{max.}$ 3 550, 3 400, 1 715, 1 250, 1 115, and 1 030 cm^{-1}.

The ester (26) was rather unreactive and gave a low yield of products. In the case of the esters (27) and (28) oxidation was incomplete but moderate yields of (29) and (30) were obtained following chromatography.

Equilibration of the Diamantyl Trifluoroacetates (24) *and* (25).—Diamantane (0.94 g) was stirred with ' active ' lead tetra-acetate (2.90 g) in trifluoroacetic acid (12 ml) and

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dichloromethane (12 ml) for 6 h at room temperature. The mixture was cooled to 0 °C and diamantane (50 mg) and sulphuric acid (98%; 0.67 ml) were added. A white precipitate separated. The mixture was stirred at 0 °C for 8 h. Subsequent hydrolysis, extraction, and chromatographic separation as described above gave diamantane (4) (54 mg), diamantan-1-ol (9) (0.46 g, 45%), diamantan-4-ol (10) (0.42 g, 41%), and unidentified diols [20 mg; *m/e* 220(M^+) and 202 ($M - 18$)].

Diamantan-1-*ol* (9).—Diamantane (0.94 g) was stirred with lead tetra-acetate (5.64 g) in trifluoroacetic acid (12 ml) containing lithium chloride (0.1M) and dichloromethane (12 ml) for 7 days. Work-up as previously described (but here giving copious precipitation of lead dioxide) gave diamantan-1-ol contaminated by materials with longer retention times (*ca.* 6%). Reaction under these conditions for 6 h gave diamantan-1-ol (9) little contaminated by either diamantan-4-ol (10) (<1%) or products of longer retention time.

Preparation of Acetamides.—Adamantane (0.68 g, 5 mmol) and 'active' lead tetra-acetate (3 g, 6.25 mmol) were stirred at room temperature for 48 h in trifluoroacetic acid (12 ml) and dichloromethane (12 ml). Acetonitrile (1.5 ml) and concentrated sulphuric acid (98%; 0.68 ml) were added to the solution. A precipitation of lead salts was observed. After further stirring for 8 h the mixture was poured into chloroform (50 ml) and water (50 ml), and the trifluoroacetic acid was neutralised by slow addition of sodium carbonate. Insoluble lead salts were filtered off and washed with chloroform (50 ml), the aqueous layer was extracted with chloroform, and the organic extracts were combined. The solution was dried ($MgSO_4$) and the solvent removed to give a white solid (1.02 g). Sublimation (150 °C and 1.5 mmHg) gave *N*-(1-adamantyl)acetamide (0.98 g, 98%), m.p. 134—141°, which after recrystallisation from cyclohexane (yield 0.84 g, 85%) had m.p. 148—149° (lit.,[33] 148—149°). The following amides were prepared by the same procedure (overall yield from hydrocarbon to purified product is indicated); *N*-(3-methyl-1-adamantyl)-acetamide (32) (79%), m.p. 107—107.5° (lit.,[34] 108—109°) (from pentane); *N*-(3-ethyl-1-adamantyl)acetamide (33) (83%), m.p. 104—105° (from hexane), *m/e* 221.177 9 (calc. for $C_{14}H_{23}NO$: 221.178 0); *N*-(3-isopropyl-1-adamantyl)-acetamide (34) (80%), m.p. 102—103° (from hexane), *m/e* 235.193 9 (calc. for $C_{15}H_{25}NO$: 235.193 6); *N*-(3,5-dimethyl-1-adamantyl)acetamide (35) (85%), m.p. 112—112.5° (lit.,[35] 110–111°) (from hexane); *N*-(bicyclo[3.3.1]-nonan-1-yl) acetamide (36) (68%), m.p. 86—87° (from hexane), *m/e* 181.146 1 (calc. for $C_{11}H_{19}NO$: 181.146 6) [a further quantity (12%) was obtained by preparative t.l.c. of the mother liquors following crystallisation].

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