Hydride Transfer Reactions of Substituted Adamantyl Cations [1]

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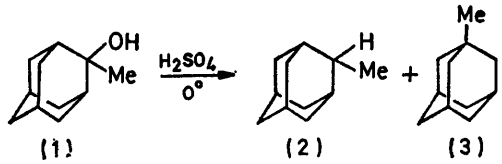
In 98% sulphuric acid at 0°, 2-methyladamantan-2-ol gives mainly 2-methyladamantane and an equilibrium mixture of 2-methyladamantan-1-ol and *syn*- and *anti*-4-methyladamantan-1-ol; at 50° the major products are 1-methyladamantane and 3-methyladamantan-1-ol; and at higher temperatures the only volatile products are 5-methyladamantan-2-one and 1-methyladamantan-2-one. The structures of the new alcohols were confirmed by comparison with the products obtained by bromination of 2-methyladamantane and hydrolysis of the mixture of bridgehead monobromides produced. 2,2-Dichloro- and 2,2-dibromo-adamantane rearrange in the presence of the appropriate aluminium halide to give 1,4- and 1,3-disubstituted products. The bromination of 2-methyladamantane and these rearrangements, which involve hydride transfer reactions, are discussed in terms of the relative stabilities of intermediate cations and of the appropriate products.

ALTHOUGH the 1-adamantyl cation exhibits neither degenerate skeletal rearrangement nor tertiary–secondary interconversion in antimony pentafluoride-based superacids over a wide range of temperatures,[2] this is certainly not the situation in some other acidic media. Geluk

[1] Portions of this work have been described in preliminary form: (*a*) M. A. McKervey, *Amer. Chem. Soc., Div. Petrol. Chem. Prep.*, 1970, **15**, B37; (*b*) M. A. McKervey, J. R. Alford, J. F. McGarrity, and E. J. F. Rea, *Tetrahedron Letters*, 1968, 5165; (*c*) M. A. McKervey, D. Grant, and H. Hamill, *ibid.*, 1970, 1975. The isomerisation of 2-methyladamantan-2-ol in 96% sulphuric acid has also been reported by H. W. Geluk and J. L. M. A. Schlatmann, *Rec. Trav. chim.*, 1969, **88**, 13; see also J. A. Bone and M. C. Whiting, *Chem. Comm.*, 1970, 115.

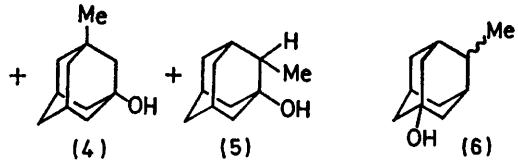
[2] (*a*) P. von R. Schleyer, R. C. Fort, jun., W. E. Watts, M. B. Comisarow, and G. A. Olah, *J. Amer. Chem. Soc.*, 1964, **86**, 4195; (*b*) D. M. Brouwer and H. Hogeveen, *Rec. Trav. chim.*, 1970, **89**, 211; (*c*) P. Vogel, M. Saunders, W. Thielecke, and P. von R. Schleyer, *Tetrahedron Letters*, 1971, 1429.

and Schlatmann [3] found that the isomeric adamantanols in 96% sulphuric acid at 28° are rapidly converted into an equilibrium mixture containing about 2% of the secondary isomer; the process is of considerable synthetic utility since with longer times at higher temperatures adamantanone is produced in good yield. More recently, the aluminium bromide-catalysed degenerate rearrangement of the adamantane skeleton has also been demonstrated.[4]



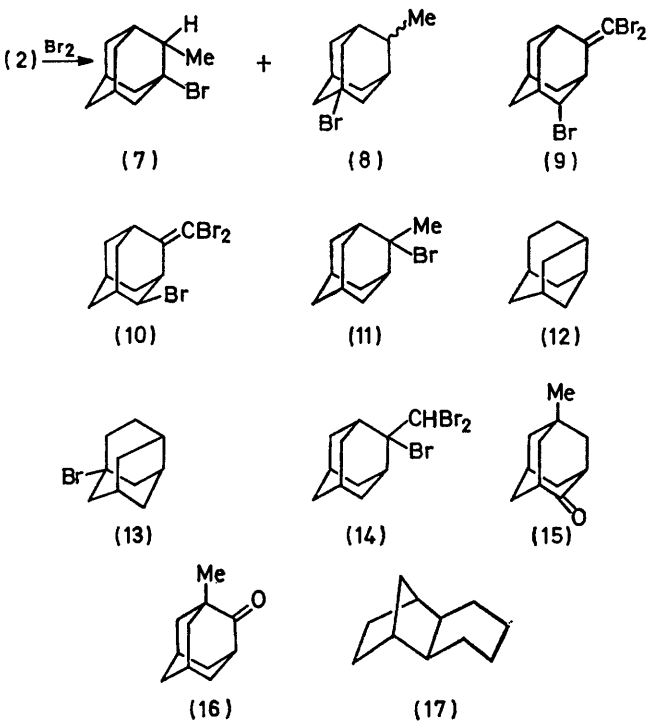
Whitlock and Siefken [5] found that the 2-methyl-2-adamantyl cation, generated in antimony pentafluoride–sulphur dioxide at low temperatures by ionisation of 2-methyladamantan-2-ol (1), displays a resistance towards rearrangement which is consistent with the suggestion based on relative solvolytic reactivities [6] that this cation is by far the most stable of all the possible methyladamantyl cations. In contrast to this result are those of the experiments to be described in this paper, which reveal that although the 2-methyl-2-adamantyl cation is undoubtedly produced from the alcohol (1) in sulphuric acid also, its behaviour in this medium is different from that observed in antimony pentafluoride–sulphur dioxide. In 98% sulphuric acid, 2-methyladamantan-2-ol undergoes a complex series of disproportionation, oxidation, and rearrangement reactions (involving both methyl and oxygen functions) the extent of which can be effectively controlled by varying the reaction duration and temperature. Seemingly similar rearrangements, catalysed by aluminium halides, occur with 2,2-dichloro- and 2,2-dibromoadamantane.

After 5 min in 98% sulphuric acid at 0° the alcohol (1) had given a product mixture which was shown by g.l.c. to contain 2-methyladamantane (2) (7%), 1-methyladamantane (3) (<1%), starting material (9%), 3-methyladamantan-1-ol (4) (2%), and three new alcohols, 2-methyladamantan-1-ol (5) (20%) and *syn*- and *anti*-4-methyladamantan-1-ol (6) (61%). Equilibration experiments subsequently revealed that the presence of a small amount of starting material in the product was only partly due to incomplete reaction; the alcohol (1) is actually present in trace amounts at equilibrium at 0° with isomers (5) and (6). The tertiary nature of the new alcohols, which were isolated in 69% yield and separated by chromatography over alumina, was indicated by their resistance to oxidation by chromic acid in acetone and by the presence in their n.m.r. spectra [$(CD_3)_2SO$] of singlets for the hydroxy-protons. The n.m.r. spectrum of isomer (5) exhibited a doublet at τ 9·01 for the methyl group, whereas in the spectrum of isomer (6) this group gave rise to two overlapping doublets at τ 8·97 and 8·99 (ratio *ca.* 1 : 1), indicating that the *syn*- and *anti*-isomers were present in about equal amounts. G.l.c. analysis of the corresponding trifluoroacetates confirmed this isomer ratio. One of the isomers, of undetermined stereochemistry, was isolated after further careful chromatography of the



mixture over alumina. The structures assigned to alcohols (5) and (6) were confirmed by synthesis.

Exposure of 2-methyladamantane (2) to boiling bromine for 4·5 h furnished a mixture of monobromides



(7) and (8), together with 21% of the epimeric tribromides (9) and (10) whose structures and mechanism of formation have been discussed elsewhere.[7] The monobromides were not isolated as such but were hydrolysed directly in aqueous dioxan. Chromatography of the product gave the individual alcohols (5) (42%) and (6) (22%) (*syn–anti* ratio *ca.* 1 : 1).

[3] H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, 1968, **24**, 5361.
[4] Z. Majerski, S. H. Liggero, P. von R. Schleyer, and A. P. Wolf, *Chem. Comm.*, 1970, 1596.
[5] H. W. Whitlock, jun., and M. W. Siefken, *J. Amer. Chem. Soc.*, 1968, **90**, 4929.
[6] J. L. Fry, J. M. Harris, R. C. Bingham, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 2540.
[7] J. R. Alford, D. Grant, and M. A. McKervey, *J. Chem. Soc.* (*C*), 1971, 880.

Two notable features of the reaction of 2-methyladamantane with bromine are the complete absence of 2-bromo-2-methyladamantane (11) from the product and the preponderance of reaction at the C-1 bridgehead position rather than at the less hindered C-5 bridgehead position. Although the functionalisation of diamondoid hydrocarbons with molecular bromine is a widely employed synthetic reaction, relatively little is known on the experimental side concerning the mechanism, beyond the conclusion reached several years ago by Stetter and his co-workers [8] that an ionic rather than a free-radical process is involved, which is to say that, regardless of how it is actually produced in bromine solution, the tertiary adamantyl cation is apparently the reactive intermediate. Recently an attempt has been made to show that conformational analysis calculations, developed earlier to predict solvolytic reactivities of bridgehead halides and arenesulphonates, can be applied successfully to the prediction of bridgehead reactivity in bromination.[9] For example, calculations which evaluate the change in strain energy in going from the ground state of protoadamantane (12) to the transition state (approximated by the appropriate cation) indicate that of the four bridgehead positions the most reactive in cationic reactions should be position 6. This has been confirmed: bromination of protoadamantane gives >95% of the 6-bromo-derivative (13).[9]

However, in applying these ideas to the bromination of 2-methyladamantane one should expect to find as the major product 2-bromo-2-methyladamantane (11); here there is an obvious discrepancy because, notwithstanding the overriding stability of the 2-methyl-2-adamantyl cation, the bromide (11) was not isolated. However, the explanation for this is simply that the 2-methyl-2-adamantyl cation is indeed generated in the reaction, but its bromination product is unstable in hot bromine. We prepared the bromide (11) from the alcohol and hydrogen bromide and noted that it is highly reactive in hot bromine, giving during 4·5 h at 60° a mixture of tribromides (9) and (10) in a ratio which was almost identical with that observed when these compounds were obtained directly from 2-methyladamantane. On the other hand, the bromides (7) and (8) were stable in hot bromine; consequently, we can equate the amount of bromination at the 2-position of 2-methyladamantane with the amount of tribromides (9) and (10) produced in the reaction.

The bromide (11) was not stable in bromine solution even at −5°; nor were the tribromides (9) and (10) formed at this temperature. Instead we isolated a new tribromide which was identified as 2-bromo-2-dibromomethyladamantane (14) from analytical and spectral data; clearly the tribromide (14) is an intermediate in the production of the tribromides (9) and (10) at the higher temperature.

[8] H. Setter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.

[9] A. Karim, M. A. McKervey, E. Engler, and P. von R. Schleyer, *Tetrahedron Letters*, 1971, 3987.

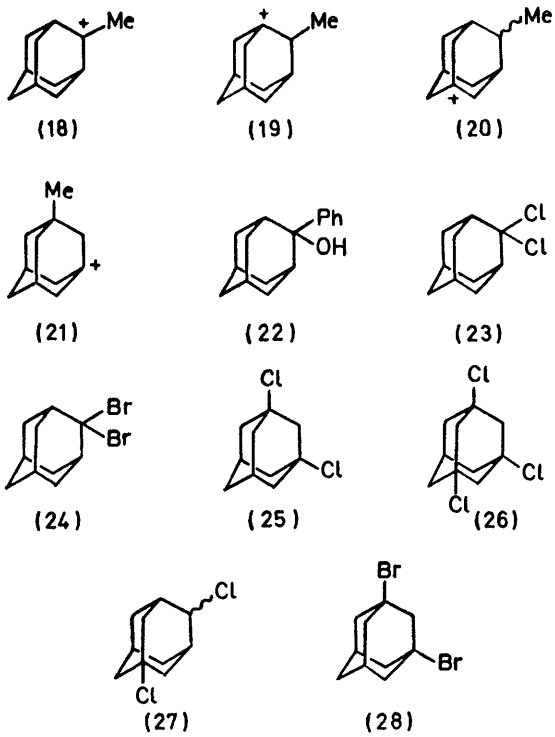
The extent of bromination at the 2-position of 2-methyladamantane *vs.* that at the bridgehead positions suggests that, of the various appropriate cations in question, the 2-methyl-2-adamantyl cation is actually the least easily formed in bromine; or else that in determining relative reactivity in bromination cation stability is not an important factor. This ratio is misleading, however, because the bridgehead positions are in any case statistically favoured, there being four of these but only one tertiary 2-position. The preponderance of bromination at the C-1 bridgehead position rather than at the less hindered C-5 bridgehead position still requires a satisfactory explanation. On steric arguments alone the former should be the less favoured of the two. This is in fact the situation with regard to the relative thermodynamic stabilities of the products; equilibration studies in which the bromides (7) and (11) were individually treated with aluminium bromide in dibromomethane at 0° showed that the equilibrium ratio of isomers (7) and (8) was *ca.* 1 : 3 in favour of the latter. Consequently, we are left with the idea that the 1-position of 2-methyladamantane is favoured in bromination because the 2-methyl-1-adamantyl cation is more stable than the 4-methyl-1-adamantyl cation. A similar situation has been observed in the Koch–Haaf carboxylation of 2-methyladamantan-2-ol.[10,11]

The fact that the mixture of alcohols obtained from 2-methyladamantan-2-ol in sulphuric acid at 0° consisted mainly of the 1,4-isomer (6) suggested that this rearrangement, like that of the corresponding bromide, had reached, or was close, to equilibrium; this was confirmed when the alcohols (5) and (6) were treated individually with sulphuric acid for 5 min at 0°. The equilibrium mixture contained, in addition to some 2-methyladamantane, the alcohols (1) (2·5%), (4) (1·5%), (5) (25·0%), and (6) (70·0%). Thus the 1,4-isomers are thermodynamically favoured at 0°. However, the appearance of small amounts of the 1,3-isomer (4) at 0° indicated that the system should be prone to more extensive isomerisation at higher temperatures; in fact when 2-methyladamantan-2-ol was exposed to 98% sulphuric acid for 5 min at 50° the 1,3-isomer (4) became the major product (36%); other products included 1- and 2-methyladamantane (ratio 10 : 1), three compounds tentatively identified as dimeric ethers (total 38%), and 5-methyladamantan-2-one (15) (3%). Ultimately, when either alcohol (1) or (4) was treated with 98% sulphuric acid for 5 h at 65° the major volatile products were the ketone (15) and 1-methyladamantan-2-one (16) in the ratio 10 : 1; the higher yield (*ca.* 15%) was obtained from isomer (4). The structures of the ketones (15) and (16) were deduced from the spectral data (see Experimental section). Interestingly, these two ketones were also produced, albeit in low yield,

[10] P. von R. Schleyer, L. K. M. Lam, D. J. Raber, J. L. Fry, M. A. McKervey, J. R. Alford, B. D. Cuddy, V. G. Keizer, H. W. Geluk, and J. L. M. A. Schlatmann, *J. Amer. Chem. Soc.*, 1970, **92**, 5246.

[11] J. R. Alford, B. D. Cuddy, D. Grant, and M. A. McKervey, following paper.

when *exo*-2,3-tetramethylenenorbornane (17) was exposed to 98% sulphuric acid at 65° for 7 h. The 1,2-ketone (16) is now much more accessible through oxidative rearrangement of 4-methylprotoadamantan-4-ol.[12]



Thus, in contrast with the results in antimony pentafluoride–sulphur dioxide, 2-methyladamantan-2-ol undergoes extensive rearrangement in concentrated sulphuric acid. The much greater stability of the 2-methyl-2-adamantyl cation (18) than of the isomeric cations (19)—(21) is apparently the controlling factor in the superacid medium, whereas in sulphuric acid the relative stabilities of the corresponding alcohols determine the product composition.[13] This is not the case with 2-phenyladamantan-2-ol (22), which could be recovered unchanged after 1 h in 98% sulphuric acid at 0°. Of the various methyladamantanols, the 2,2-isomer (1) is the least stable since the methyl and oxygen functions are each axially located with respect to one cyclohexane ring of the adamantane nucleus. In the 1,3-isomer (4), on the other hand, both substituents occupy equatorially disposed bridgehead positions; accordingly, at the higher temperature when the conditions are such as to permit both methyl and hydride shifts the 1,3-isomer predominates. At 0°, where the methyl shift is scarcely observed, equilibrium is effectively established between those isomers with the hydroxy-substituent at a bridgehead position, the 1,4-isomers being thermodynamically more stable than the 1,2-isomer. This is also the situation with the corresponding bromides. The ketones (15) and (16) are the products of oxidation and/or disproportionation of the corresponding secondary alcohols which, though they were not isolated, exist in equilibrium with the 1,3-alcohol (4) in sulphuric acid.[3]

The apparent 1,2-methyl shift in the cations (18)—(21) is now known from labelling studies to be a skeletal reorganisation during which the methyl group remains attached to the same nuclear carbon atom.[14,15] In the following paper we describe dilution experiments which establish that the apparent 1,2-hydride transfer reactions by which cations (18)—(20) are interconverted are in fact intermolecular in character.[11]

Similar kinds of rearrangements, catalysed by Lewis acids, were also observed with 2,2-dichloro- and 2,2-dibromo-adamantane [(23) and (24)]. These dihalides were prepared from adamantanone and the appropriate PX_5–PX_3 mixture.[16] When a solution of the dichloride (23) in carbon tetrachloride containing aluminium chloride was stirred at room temperature for 3 days a product was obtained consisting of 1,3-dichloroadamantane (25) (70%) and a compound (20%) which on the basis of its g.l.c. retention time was presumed to be 1,3,5-trichloroadamantane (26). The formation of the trichloride was not unexpected since Stetter *et al.*[17] have reported that treatment of adamantane with aluminium chloride in carbon tetrachloride results in appreciable amounts of trichlorination. In an attempt to detect intermediates in the rearrangement of the dichloride (23), the reaction was monitored by g.l.c. After 30 min, the solution contained starting material (20%) and two new isomers (70%), which were isolated and identified as *syn*- and *anti*-1,4-dichloroadamantane (27).[18] By changing the solvent to nitromethane complete rearrangement of the 2,2-dichloride could be achieved within 24 h at room temperature; the crude product consisted of the 1,4-isomers (27) (85%) and a third compound (15%), which was not identified but which was shown not to be 1,2-dichloroadamantane.

2,2-Dibromoadamantane (24) rearranged much more rapidly than did the dichloride; after 1 h in carbon disulphide containing aluminium bromide the product contained 1,3-dibromoadamantane (28) (75%). Although we do not have direct evidence to support our claim that these dihalide rearrangements involve intermolecular hydride transfer, we believe that the similarity to the behaviour of 2-methyladamantan-2-ol in sulphuric acid and the arguments presented in the

[12] B. D. Cuddy, D. Grant, and M. A. McKervey, *J. Chem. Soc.* (*C*), 1971, 3173; D. Lenoir, R. Glaser, P. Mison, and P. von R. Schleyer, *J. Org. Chem.*, 1971, **36**, 1821.

[13] For a discussion of the relative stabilities of tertiary hydroxy- and chloro-diamantanes see D. E. Johnston, M. A. McKervey, and J. J. Rooney, *Chem. Comm.*, 1972, 28; M. A. McKervey, D. E. Johnston, and J. J. Rooney, *Tetrahedron Letters*, 1972, 1547.

[14] Z. Majerski, P. von R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 5731.

[15] For a recent discussion of skeletal reorganisation in adamantanes see R. C. Bingham and P. von R. Schleyer, *Fortschr. Chem. Forsch.*, 1971, **18**, 1.

[16] R. L. Bixler and C. Niemann, *J. Org. Chem.*, 1958, **23**, 742.

[17] H. Stetter, M. Krause, and W. D. Last, *Chem. Ber.*, 1969, **102**, 3357.

[18] H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, 1968, **24**, 5369.

following paper are sufficient to establish the correctness of this aspect of the mechanism.

EXPERIMENTAL

M.p.s were determined for samples sealed in capillary tubes. Unless otherwise stated i.r. spectral data refer to dispersions in potassium bromide discs. ^{1}H N.m.r. spectra were measured at 100 MHz with tetramethylsilane as internal standard. Mass spectrometric data were obtained with an A.E.I. MS902 spectrometer with an ionising beam energy of 70 eV. G.l.c. refers to analysis on one of the following columns: (A) 2 m Versamid 930 on Chromosorb W (3% w/w); (B) 2 m Silicone Nitrile XF-1150 on Chromosorb W (5% w/w); (C) 2 m Silicone Gum Rubber on Chromosorb W (5% w/w); (D) 20 m capillary column coated with Apiezon L. Light petroleum had b.p. 40—60°. The drying agent employed was magnesium sulphate. 2-Methyladamantan-2-ol [19] (1) was obtained from the reaction of adamantanone with methylmagnesium bromide. 2-Methyladamantane was prepared as previously described.[7,19]

1-*Methyladamantane* (3).—A mixture of finely powdered aluminium chloride (0·5 g) and *exo*-2,3-tetramethylene-norbornane (17) (2·0 g) was placed in a sublimation apparatus and stirred overnight. The mixture was then heated and the hydrocarbon collected on a cold finger. Resublimation gave the product (1·6 g, 80%), m.p. 92—93° (lit.,[20] 95·0—97·8°).

3-*Methyladamantan*-1-*ol* (4).—A solution of 1-bromo-3-methyladamantane [21] (7·0 g) in water (100 ml) and dioxan (35 ml) containing potassium carbonate (10·0 g) was heated under reflux for 5 h. The cooled solution was extracted with dichloromethane (3 × 50 ml) and the extract was washed with water, then dried. Evaporation left an oil which soon crystallised. Recrystallisation from light petroleum gave the alcohol (4·7 g, 92%), m.p. 128—129° (lit.,[22] 128·8—129·2°), τ (CCl_4) 7·88br (2H, s, C-5 and C-7 protons), 8·33 (1H, s, OH), 8·44—8·60 (12H, m), and 9·17 (3H, s, Me).

2-*Methyladamantan*-1-*ol* (5) *and* syn- *and* anti-4-*Methyladamantan*-1-*ol* (6).—A solution of 2-methyladamantane (9·9 g) in bromine (35 ml) was heated under reflux (after the initial reaction had subsided) for 4·5 h, then cooled. Water (100 ml) and carbon tetrachloride (100 ml) were added and the organic layer and carbon tetrachloride extracts (2 × 100 ml) of the aqueous layer were shaken with aqueous sodium disulphite, washed with water, and dried. Evaporation gave an oil which was used directly.

A solution of the crude product in 40% aqueous dioxan (400 ml) containing potassium carbonate (10 g) was heated under reflux for 24 h. The cooled solution was diluted with water (1 l) and extracted with ether (4 × 100 ml). The extract was washed with water, dried, and evaporated to give an oil (15·6 g). The crude product was divided into two fractions by chromatography on alumina (500 g). Fraction (i), eluted with light petroleum, was a mixture of tribromides (9) and (10) (5·5 g, 21%), isomer ratio [g.l.c. on column (A) at 210°] 3 : 1. Fraction (ii), eluted with ether, was a mixture of alcohols (5) and (6) (8·6 g, 78%), isomer ratio [g.l.c. on column (A) at 130°] *ca.* 2 : 1.

The alcohol mixture [fraction (ii)] was subjected to a second chromatography on alumina (2 kg). Elution with light petroleum–ether (2 : 1) gave, after further purification by sublimation, 2-*methyladamantan*-1-*ol* (5) (4·6 g, 42%), m.p. 206—208° (Found: C, 79·35; H, 10·95. $C_{11}H_{18}O$ requires C, 79·45; H, 10·9%), $\nu_{max.}$ 3320 cm^{-1}, τ (CCl_4) 7·75—8·75 (15H, m, skeletal H and OH) and 9·01 (3H, d, Me). Further elution, with light petroleum–ether (1 : 1), gave, after further purification by sublimation, *syn*- and *anti*-4-methyladamantan-1-ol (6) (2·4 g, 22%), m.p. 163—168° (Found: C, 79·2; H, 10·9. Calc. for $C_{11}H_{18}O$: C, 79·45; H, 10·9%), $\nu_{max.}$ 3400 cm^{-1}, τ (CCl_4) 7·75—8·85 (15H, m, skeletal H and OH) and 8·97(d) (3H, *syn*- and *anti*-Me). G.l.c. analysis of the trifluoroacetates of alcohols (6) on column (D) at 125° gave the isomer ratio as *ca.* 1 : 1. Alcohols (6) were rechromatographed on alumina. Elution with light petroleum–ether (1 : 1) gave one of the isomers, m.p. 185—186°, of >98% purity as revealed by g.l.c. analysis of the trifluoroacetate on column (D). Further elution gave the other isomer, *ca.* 80% isomeric purity.

Isomerisation of 2-*Methyladamantan*-2-*ol in* 98% *Sulphuric Acid at* 0°.—The alcohol (4·0 g) was added in one portion to 98% sulphuric acid (80 ml) at 0°. The mixture was stirred rapidly for 5 min and then was poured on ice. The solution was extracted with ether (4 × 100 ml) and the extract was washed with saturated aqueous sodium hydrogen carbonate and water, then dried. Evaporation at atmospheric pressure through a fractionating column gave a product shown by g.l.c. analysis on column (A) at 140° to contain 2-methyladamantane (2) (7%), 1-methyladamantane (3) (<1%), starting material (9%), 3-methyladamantan-1-ol (4) (2%), 2-methyladamantan-1-ol (5) (20%), and 4-methyladamantan-1-ol (6) (61%). The entire product was placed on a column of alumina. Elution with light petroleum gave mainly 2-methyladamantane. Further elution, with light petroleum–ether (3 : 7), gave starting material (0·18 g). Elution with light petroleum–ether (4 : 6) gave 2-methyladamantan-1-ol (0·87 g, 22%), identified by comparison (g.l.c., i.r. spectrum, and m.p.) with a sample prepared from 2-methyladamantane as already described. Further elution gave 4-methyladamantan-1-ol (1·89 g, 47%), shown to be a 1 : 1 mixture of the *syn*- and *anti*-isomers by g.l.c. analysis of the trifluoroacetates on column (D) at 125°.

Equilibration of Alcohols (5) *and* (6) *in* 98% *Sulphuric Acid at* 0°.—Each alcohol (50 mg) was added to 98% sulphuric acid (3 ml) at 0°. The solution was stirred rapidly for 5 min and then was poured on ice. The solution was then processed as in the preceding experiment and the crude product was analysed by g.l.c. on column (A) at 140°, the assignments being made by co-injection of authentic samples. Each alcohol gave a product composed of a small amount of 2-methyladamantane and the alcohols (1) (2·5%), (4) (1·5%), (5) (24%), and (6) (73%).

Oxidation of 3-*Methyladamantan*-1-*ol* (4) *in* 98% *Sulphuric Acid*.—A stirred solution of the alcohol (11·6 g) in 98% sulphuric acid (84 ml) was heated at 65—75° for 6 h. From time to time 1-methyladamantane, which had sublimed from the solution, was scraped back into the flask. The cooled solution was poured on ice and the resulting mixture was steam distilled. The distillate was extracted with ether (4 × 50 ml) and the extract was washed with water and dried. Careful evaporation at atmospheric pressure

[19] P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 182.
[20] H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.
[21] K. Grezon, E. V. Krumkalns, R. L. Brindle, F. J. Marshall, and M. A. Root, *J. Medicin. Chem.*, 1963, **6**, 763.
[22] S. Landa, J. Vais, and J. Burkhard, *Z. Chem.*, 1967, **7**, 233.

through a fractionating column gave a white solid (1·7 g, 15%). The product was placed on a column of alumina (200 g). Elution with light petroleum–ether (24 : 1) gave 1-methyladamantan-2-one (16) (0·06 g, 0·5%), m.p. 98—100° (after sublimation). The dinitrophenylhydrazone had m.p. 228·5—230·0°. This ketone was identical (m.p., i.r. spectrum, and g.l.c.) with the ketone obtained by oxidising 4-methylprotoadamantan-4-ol (17) [12] with chromic acid in acetone. Further elution of the column gave, after several sublimations, *5-methyladamantan-2-one* (15) (1·3 g, 12%), m.p. 126—127° (Found: C, 80·65; H, 9·85. $C_{11}H_{16}O$ requires C, 80·45; H, 9·8%), $\nu_{max.}$ 1720 cm^{-1}, τ (CCl_4) 7·59 (2H, m, C-1 and C-3 protons), 7·80—8·40 (11H, m), and 9·12 (3H, s, Me). The *dinitrophenylhydrazone* had m.p. 179—180° (from methanol) (Found: C, 59·15; H, 5·8; N, 16·3. $C_{17}H_{20}N_4O_4$ requires C, 59·3; H, 5·85; N, 16·25%), *m/e* 344 (100%, M^+), 162 (33), and 93 (25).

Isomerisation of 2-Methyladamantan-2-ol in 98% Sulphuric Acid at 50°.—The alcohol (4·0 g) was added in one portion to 98% sulphuric acid (30 ml) at 50° and the solution was stirred rapidly for 5 min. It was then processed as for the 0° isomerisation experiment. G.l.c. analysis of the product at 140° on column (A) showed the presence of 1- and 2-methyladamantane in the ratio 10 : 1, 3-methyladamantan-1-ol (4) (major product), and a trace of 5-methyladamantan-2-one. The mixture was placed on a column of alumina. Elution with light petroleum gave a fraction g.l.c. analysis of which at 200° on column (A) showed three components in addition to 1- and 2-methyladamantane. The mass spectrum of this fraction suggested that the unknowns were probably dimeric ethers. Further elution, with light petroleum–ether (4 : 1), gave the ketone (15) (*ca.* 3%), and elution with light petroleum–ether (1 : 4) gave the 1,3-alcohol (4) (36%).

When 2-methyladamantan-2-ol (1) was treated with 98% sulphuric acid at *ca.* 65° for up to 6 h the major volatile products were the ketones (15) and (16) in *ca.* 10% yield.

2-Bromo-2-methyladamantane (11).—A solution of 2-methyladamantan-2-ol (3·0 g) in 48% hydrobromic acid (100 ml) was heated under reflux for 24 h. From time to time the sublimate in the condenser was washed out with dichloromethane. The organic solution was washed with water, dried, and evaporated, to yield the *bromide* (3·58 g, 87%), m.p. 132—135° (after sublimation) (Found: C, 57·7; H, 7·7; Br, 34·7. $C_{11}H_{17}Br$ requires C, 57·65; H, 7·4; Br, 34·9%), τ ($CDCl_3$) 7·32br (1H, s), 7·53br (1H, s), 7·66—8·50 (12H, m), and 7·91 (3H, s, Me).

1-Bromo-2-methyladamantane (7).—2-Methyladamantan-1-ol (0·19 g) in benzene (10 ml) at 0° was treated dropwise with thionyl bromide until the first permanent red colour appeared. The solution was allowed to come to room temperature and more benzene (50 ml) was added. The solution was passed down a column of alumina. Evaporation gave the *bromide* (0·14 g, 53%), m.p. 98—99° (after sublimation) (Found: C, 57·55; H, 7·45; Br, 35·15. $C_{11}H_{17}Br$ requires C, 57·65; H, 7·4; Br, 34·95%), τ (CCl_4) 7·50—8·50 (14H, m) and 8·74 (3H, s, Me).

Isomerisation of 2-Bromo-2-methyladamantane in Dibromomethane.—A solution of the bromide (0·1 g) in dibromomethane (11 ml) containing aluminium bromide (0·2 g) was stirred at 0° for 2·5 min, then poured on ice. The organic layer and dichloromethane extracts (2 × 5 ml) of the aqueous layer were combined, washed with water, and dried. As we were unable to measure accurately the isomer concentration in the product the entire mixture was subjected to complete hydrolysis for 2 h in boiling 1 : 1 dimethylformamide–0·67N-hydrochloric acid (10 ml). The cooled solution was poured into water and extracted with dichloromethane (3 × 10 ml). The extract was washed with water, dried, and concentrated. G.l.c. analysis of the crude product on column (A) at 140° showed that it was composed of 4-methyladamantan-1-ol (66·4%), 2-methyladamantan-1-ol (25·6%), 2-methyladamantan-2-ol (2·4%), and 3-methyladamantan-1-ol (5·9%) (by co-injection of authentic samples).

Isomerisation of 1-Bromo-2-methyladamantane in Dibromomethane.—A solution of the bromide (0·1 g) in dibromomethane (11 ml) containing aluminium bromide (0·2 g) was stirred at 0° for 2·5 min, then poured on ice and processed as in the preceding experiment. After hydrolysis, the product was composed of 4-methyladamantan-1-ol (52%), 2-methyladamantan-1-ol (20%), 3-methyladamantan-1-ol (25%), and 2-methyladamantan-2-ol (3%).

syn- *and* anti-*1-Bromo-4-methyladamantane* (8).—A 1 : 1 mixture of *syn-* and *anti-*4-methyladamantan-1-ol (0·07 g) in benzene was treated with thionyl bromide at 0° as described for compound (7). The bromide mixture was obtained as an oil (Found: C, 57·3; H, 7·85; Br, 35·25. Calc. for $C_{11}H_{17}Br$: C, 57·65; H, 7·4; Br, 34·95%), τ (CCl_4) 7·40—8·60 (14H, m) and 8·96(s) and 9·00(s) (3H, Me).

2-Bromo-2-dibromomethyladamantane (14).—A solution of 2-bromo-2-methyladamantane (1·0 g) in bromine (15 ml) at −5° was stirred for 3 h, then poured on ice. Excess of bromine was removed by addition of sodium disulphite, and the solution was extracted with carbon tetrachloride (2 × 100 ml). The extract was washed with water, dried, and evaporated, to give the *tribromide* (1·46 g, 87%), m.p. 95—96° (from light petroleum) (Found: C, 34·15; H, 3·9; Br, 62·2. $C_{11}H_{15}Br_3$ requires C, 34·1; H, 3·9; Br, 62·0%), τ ($CHCl_3$) 3·35 (1H, s, $CHBr_2$) and 7·24—8·40 (14H, m).

Dehydrobromination of the Tribromide (14).—A mixture of the tribromide (3·0 g), ethylene glycol (50 ml), and potassium hydroxide (2·5 g) was stirred at 140° for 3 h. From time to time the sublimate in the condenser was washed out with dichloromethane. The cooled solution was poured into water and extracted with dichloromethane (3 × 50 ml). The combined dichloromethane solutions were washed with water (3 × 100 ml) and dried. Evaporation gave *dibromomethyleneadamantane* (2·3 g, 97%), m.p. 89—90° (light petroleum) (Found: C, 43·15; H, 4·55; Br, 52·25. $C_{11}H_{14}Br_2$ requires C, 43·4; H, 4·55; Br, 52·3%), τ ($CDCl_3$) 6·83br (2H, s, C-1 and C-3 protons) and 7·88—8·35 (12H, m).

2-Phenyladamantan-2-ol (22).—Adamantanone (4·5 g) in ether (60 ml) was added during 30 min to a stirred solution of phenylmagnesium bromide [from magnesium (3·6 g) and bromobenzene (23·6 g)] in ether (120 ml). The mixture was heated under reflux for 3 h and then treated with saturated aqueous ammonium chloride. The ether layer and ether extracts of the aqueous layer were combined, washed with water, and dried. Evaporation left an oil which was placed on a column of alumina (260 g). Elution with light petroleum gave several fractions which were discarded. Further elution, with ether, gave the alcohol (4·5 g, 65%), m.p. 79·5—80·5° (from light petroleum) (lit.,[23] 80·5—81·0°), τ (CCl_4) 2·70 (5H, m, Ph), 7·58 (4H, m), 8·02—8·51 (10H, m), and 8·74 (1H, s, OH), $\nu_{max.}$ 3300, 2880, 765, and 695 cm^{-1}.

[23] H. Tanida and T. Tsushima, *J. Amer. Chem. Soc.*, 1970, **92**, 3397.

Attempted Isomerisation of 2-Phenyladamantan-2-ol in 98% Sulphuric Acid.—The alcohol (0·15 g) in 98% sulphuric acid (5 ml) was stirred rapidly for 1 h, then poured on ice and extracted with dichloromethane (3 × 10 ml). The extract was washed with aqueous sodium hydrogen carbonate and water, then dried. Evaporation left a solid (0·10 g, 66%), the i.r. spectrum of which was identical with that of the starting alcohol.

2,2-*Dichloroadamantane* (23).—To a solution of adamantanone (10 g) in phosphorus trichloride (20 ml) at 0° was added phosphorus pentachloride (17·5 g) in portions with stirring during 1 h. The mixture was stirred overnight at room temperature and then poured on ice and extracted with dichloromethane (3 × 50 ml). The extract was washed with water, dried, and evaporated to yield the *dichloride* (12·3 g, 90%), m.p. 203—204° (from light petroleum) (Found: C, 58·4; H, 6·7; Cl, 34·55. $C_{10}H_{14}Cl_2$ requires C, 58·55; H, 6·9; Cl, 34·55%), τ ($CDCl_3$) 7·35—7·85 (6H, m) and 7·90—8·40 (8H, m).

2,2-*Dibromoadamantane* (24).—To a solution of adamantanone (5 g) in phosphorus tribromide (10 ml) at 0° was added phosphorus pentabromide (14 g) in portions with stirring during 1 h. The mixture was stirred overnight at room temperature and then was processed as described for the dichloride, to yield the *dibromide* (8·7 g, 88%), m.p. 162—163° (from light petroleum) (Found: C, 41·15; H, 4·8; Br, 54·45. $C_{10}H_{14}Br_2$ requires C, 40·85; H, 4·8; Br, 54·35%), τ ($CDCl_3$) 7·28 (2H, m), 7·48 (4H, m), and 7·90—8·40 (8H, m).

Rearrangement of 2,2-*Dichloroadamantane.*—(i) *With aluminium chloride in nitromethane.* To a solution of aluminium chloride (10·5 g) in nitromethane (30 ml) was added 2,2-dichloroadamantane (1 g), and the solution was stirred overnight at room temperature, then poured on ice and extracted with dichloromethane (3 × 50 ml). The extract was washed with water, dried, and evaporated to give a product which consisted of three components [g.l.c. analysis on column (B) at 160°]. The two major components (*ca.* 85% of the total), ratio *ca.* 2 : 1, were identified as the isomeric 1,4-dichloroadamantanes (27) by g.l.c. (co-injection with an authentic sample). Although the minor component was not identified, it was shown by g.l.c. not to be 1,2-dichloroadamantane. The crude product was taken up in light petroleum and placed on a column of alumina. Elution with ether–light petroleum (1 : 9) gave a product (0·85 g, 85%) whose i.r. and n.m.r. spectral data were in close agreement with those of an authentic sample of 1,4-dichloroadamantane (mixture of isomers).[18]

(ii) *With aluminium chloride in carbon tetrachloride.* To a solution of the dichloride (1 g) in carbon tetrachloride (10 ml) was added powdered aluminium chloride (1 g) and the mixture was stirred at room temperature for 72 h. Work-up as described under (i) gave a crude product which was shown by g.l.c. analysis on column (B) at 160° to consist mainly of 1,3-dichloroadamantane (70%). The product was purified by chromatography on alumina as described under (i), to give a sample of the 1,3-dichloride; the spectral data and m.p. were in close agreement with the published data.[17]

Rearrangement of 2,2-*Dibromoadamantane* (24).—The dibromide (1 g) was dissolved in a stirred solution of aluminium bromide (1 g) in carbon disulphide. After 1 h, the solution was poured on ice and processed as for the dichloride rearrangement, to give a crude product which consisted mainly (75%) of 1,3-dibromoadamantane. The product was taken up in light petroleum and placed on a column of alumina. Elution with ether–light petroleum (1 : 9) gave a solid (0·9 g) which on recrystallisation from methanol yielded the 1,3-dibromide, identified by comparison (g.l.c., i.r. spectrum, and m.p.) with an authentic sample.[24]

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[24] E. R. Talaty, A. E. Cancienne, jun., and A. F. Depuy, jun., *J. Chem. Soc.* (*C*), 1968, 1902.