The π-Route to Substituted Adamantanes. Part II.[1]

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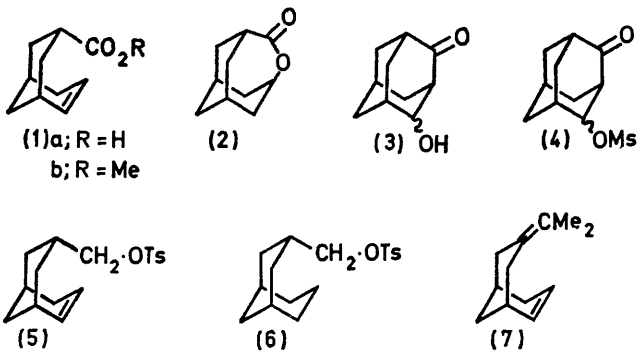
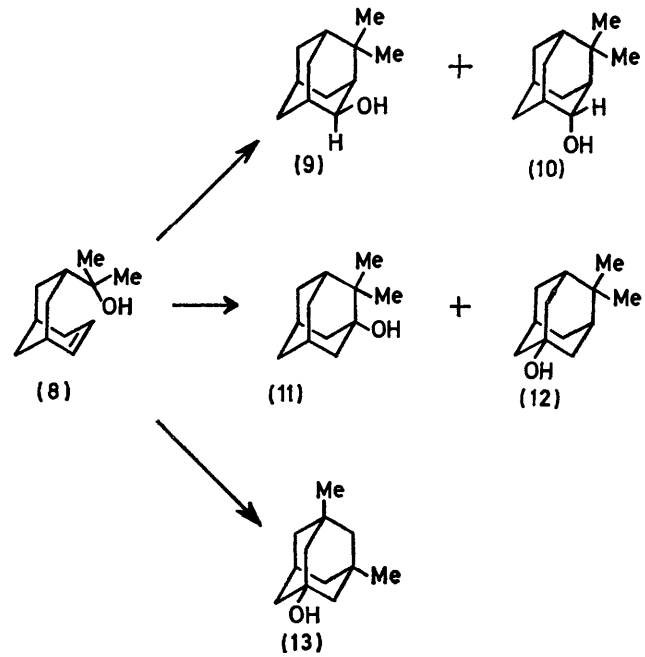
Cyclisation of 2-(*endo*-bicyclo[3,3,1]non-6-en-3-yl)propan-2-ol in hot formic acid yields, after hydrolysis of the initial product, a mixture of 4,4-dimethyladamantan-2*ax*- and -2*eq*-ol of which the latter, derived from *trans*-addition to the double bond, predominates by a factor of 6:1. These stereochemical assignments are based on the n.m.r. spectra of the isomers in pyridine solution as compared with dimethyl sulphoxide solution and on the production of the axial alcohol by reduction of 4,4-dimethyladamantan-2-one with lithium aluminium hydride. Cyclisation of 2-(*endo*-bicyclo[3,3,1]non-6-en-3-yl)propan-2-ol in 98% sulphuric acid at 20° yields a 1:3 mixture of 2,2-dimethyladamantan-1-ol and 4,4-dimethyladamantan-1-ol, whereas in this medium at 50° the major product is 3,5-dimethyladamantan-1-ol; these products are formed by intermolecular hydride transfer and skeletal rearrangement reactions after π-route cyclisation has occurred. In hot formic acid, α-(*endo*-bicyclo[3,3,1]non-6-en-3-yl)benzyl alcohol yields, after hydrolysis of the formate, 2-phenyladamantan-1-ol.

CYCLISATION processes involving nucleophilic participation of the double bond in cations produced by ionisation of certain *endo*-bicyclo[3,3,1]non-6-en-3-yl derivatives form the mechanistic basis of a useful route to non-bridgehead difunctionalised adamantanes which are otherwise difficult to obtain.[2] For example, *endo*-bicyclo[3,3,1]non-6-ene-3-carboxylic acid (1a) [or the corresponding lactone (2)] on treatment with 50% sulphuric acid or methanesulphonic acid yields 4-hydroxyadamantan-2-one (3) or 4-methylsulphonyloxyadamantan-2-one (4).[1]



These π-route cyclisations have several commendable features. In the first place, in the bicyclo[3,3,1]nonene series there is usually a large driving force for ring closure: for example, in 80% acetone, solvolysis of the unsaturated tosylate (5) proceeds about 10^4 times faster than does that of the saturated analogue (6); and the product is exclusively adamantan-2-ol.[3] Second, bicyclo[3,3,1]nonene precursors can be easily prepared from the unsaturated acid (1a); and third, the route is capable of considerable extension, as we now illustrate.†

Exposure of the acid (1a) to ethereal diazomethane furnished the methyl ester (1b), which with methylmagnesium iodide in ether yielded 2-(*endo*-bicyclo-[3,3,1]non-6-en-3-yl)propan-2-ol (8). Cyclisation of the alcohol (8) was attempted under various acidic conditions. Cold dilute sulphuric acid was an ineffectual catalyst, and although use of 50% sulphuric acid at 50° did produce two saturated alcohols (ratio 5 : 1) in 43% yield, it was otherwise unsatisfactory since it also catalysed the formation of an appreciable amount of material tentatively characterised as a dimeric ether from its i.r. and mass spectrometric data. Use of 98% formic acid was much more satisfactory, for in this medium for 4 h at 100° alcohol (8) yielded a mixture of saturated formates in *ca.* 90% yield. Although the formates could be easily cleaved with lithium aluminium hydride in ether, it was more convenient to hydrolyse the mixture on a column of alumina (elution with ether–methanol) to give a mixture of two alcohols in 82% yield. About 1% of a mixture of several other



substances, of which the diene (7) was thought to be the chief component, was also isolated. G.l.c. analysis indicated that the alcohols were identical with those

† The π-route to 3,5-disubstituted diamantanes has been described.[4]

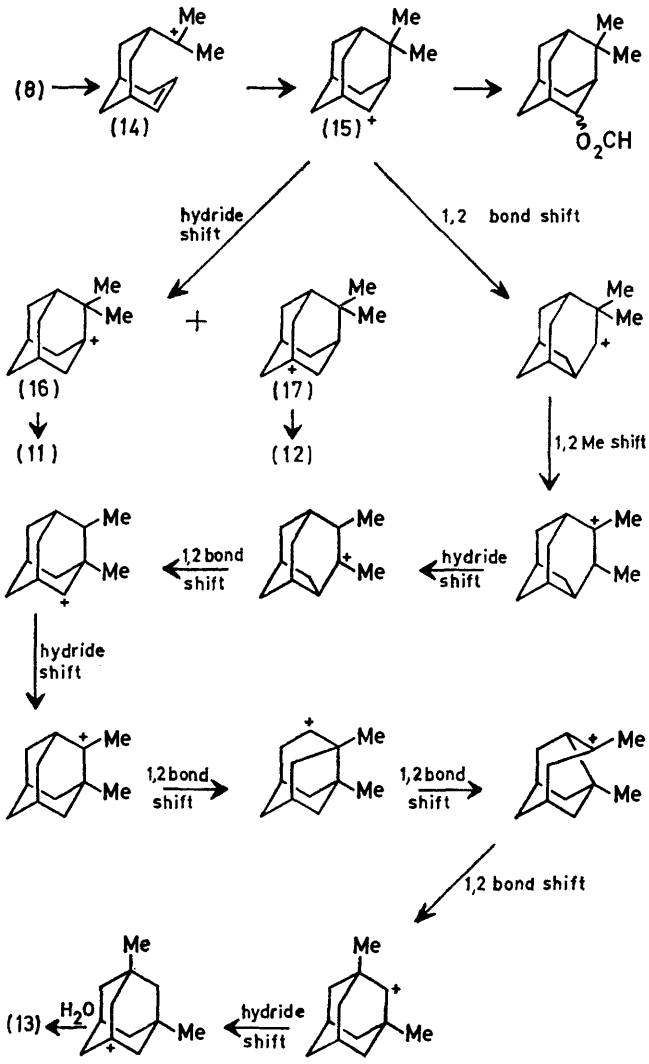
[1] Part I, D. Faulkner and M. A. McKervey, *J. Chem. Soc.* (*C*), 1971, 3906.

[2] M. A. McKervey, D. Faulkner, and H. Hamill, *Tetrahedron Letters*, 1970, 1971.

[3] D. J. Raber, G. J. Kane, and P. von R. Schleyer, *Tetrahedron Letters*, 1970, 4117.

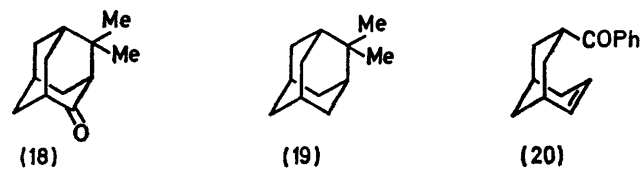
[4] D. E. Johnston, D. Faulkner, R. A. Glendinning, and M. A. McKervey, *Tetrahedron Letters*, 1971, 1671.

produced from the unsaturated alcohol in 50% sulphuric acid and that the isomer ratio was 6 : 1. Careful chromatography of the mixture over alumina gave the preponderant isomer, m.p. 176—177°, whose n.m.r. spectrum [$(CD_3)_2SO$] displayed sharp singlets for the methyl groups, at τ 8·95 and 9·01, and a broad singlet at τ 6·00 (>C*H*·OH). The minor isomer was more conveniently obtained from another reaction (see later).



SCHEME

Consideration of the mechanism of this π-route cyclisation led to the conclusion that the products were 4,4-dimethyl-2-adamantyl derivatives, resulting from addition of the olefinic bond to the cationic centre in the intermediate (14) with subsequent capture of the cyclised cation (15) by formic acid. Oxidation of the alcohol mixture with chromic acid in acetone gave 4,4-dimethyladamantan-2-one (18). This structural assignment is based on the n.m.r. spectrum, which revealed that the methyl groups were non-equivalent, and on Wolff–Kishner reduction to 2,2-dimethyladamantane (19).[5] The relative stereochemistry of the alcohols was elucidated as follows. Reduction of the ketone (18) with lithium aluminium hydride yielded essentially (>99%) a single product, which was identical with the minor isomer isolated from cyclisation of the unsaturated alcohol, and which on any reasonable steric argument should be assigned the 4,4-dimethyladamantan-2*ax*-ol structure (9).* This was substantiated by comparison of the changes induced in the n.m.r. spectra of the alcohol (9) and its epimer (10) by changing the solvent from dimethyl sulphoxide to pyridine. In dimethyl sulphoxide, the alcohol (9) exhibited singlets at τ 8·80 and 9·03 τ ($\Delta\tau$ 0·23 p.p.m.) for the axial



and equatorial methyl groups, respectively. The corresponding $\Delta\tau$ value for isomer (10) was 0·06 p.p.m. In pyridine, on the other hand, the axial methyl group absorption in the spectrum of isomer (9) was shifted substantially ($\Delta\tau$ 0·52 p.p.m.), whereas with isomer (10) the change from dimethyl sulphoxide to pyridine produced essentially no effect on the relative positions of the methyl singlets ($\Delta\tau$ 0·04 p.p.m.).[6] We concluded that π-route cyclisation of alcohol (8) proceeded predominantly by a normal *trans*-addition of the solvent and the cation across the olefinic bond.

In adapting the π-route approach to the synthesis of other types of polysubstituted adamantanes we were able to take advantage of two characteristic reactions of some 2-substituted derivatives. The first of these is exemplified by the rapid isomerisation [7] of adamantan-2-ol into adamantan-1-ol in 96% sulphuric acid at room temperature. The second is a feature of the isomerisation of 2-methyladamantane into the 1-isomer catalysed by aluminium chloride [8] or sulphuric acid; [9] that of 2-methyladamantan-2-ol into 3-methyladamantan-1-ol in 96% sulphuric acid at 50°; [9,10] and that of 2,2-dimethyladamantane into 1,3-dimethyladamantane with aluminium halide catalysis.[11] There is

* The symbols *ax* and *eq* denote the axial and equatorial positions with respect to that cyclohexane ring of the adamantane skeleton to which all the substituents are attached.

[5] C. Wentworth, V. Buss, and P. von R. Schleyer, *Chem. Comm.*, 1968, 569; J. Vais, J. Burkhard, and S. Landa, *Z. Chem.*, 1968, **8**, 303.

[6] For a discussion of pyridine-induced n.m.r. chemical shift changes in alcohols see P. V. Demarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, 1968, **90**, 5480.

[7] H. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, 1968, **24**, 5361.

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

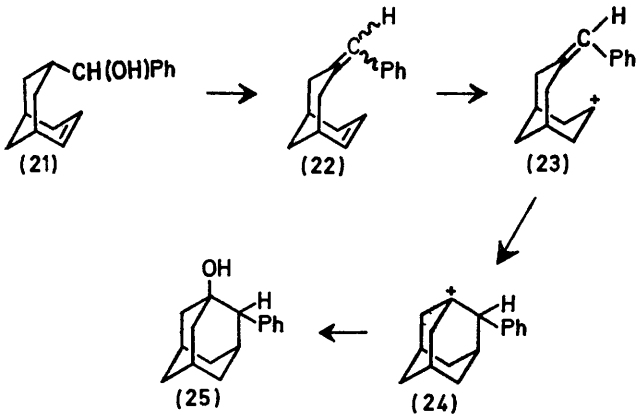
[9] M. A. McKervey, J. R. Alford, J. F. McGarrity, and E. J. F. Rea, *Tetrahedron Letters*, 1968, 5165; B. D. Cuddy, D. Grant, A. Karim, M. A. McKervey, and E. J. F. Rea, following paper.

[10] H. W. Geluk and J. L. M. A. Schlatmann, *Rec. Trav. chim.*, 1969, **88**, 13.

[11] P. von R. Schleyer, *Angew. Chem.*, 1969, **81**, 539.

evidence from dilution studies that the former isomerisation proceeds by way of intermolecular hydride transfer;[12] in the latter type, the simple 1,2-methyl shift mechanism has been excluded,[8] the most likely alternative being a skeletal reorganisation involving protoadamantyl intermediates.[13] With these reactions in mind, we examined the behaviour of the alcohol (8) in concentrated sulphuric acid at room temperature and at 50° in the hope that cyclisation at the lower temperature might be followed by hydride transfer reactions only, yielding the bridgehead cations (16) and (17), but that the higher temperature might further cause skeletal rearrangement. In the event, brief treatment of the alcohol (8) with 98% sulphuric acid at 20° yielded a 1 : 3 mixture of 2,2-dimethyladamantan-1-ol (11)[14,15] and 4,4-dimethyladamantan-1-ol (12).[14] At 50° in 98% sulphuric acid for 5 min alcohol (8) yielded 3,5-dimethyladamantan-1-ol (13) (35% yield). The mechanisms of these reactions are summarised in the Scheme.

While attempting to extend the π-route method to the synthesis of an adamantanol having a non-bridgehead phenyl substituent we observed yet another mode of cyclisation, which leads exclusively to a 1,2-disubstituted derivative. Exposure of the unsaturated ester (1b) to phenylmagnesium bromide yielded *endo*-bicyclo[3,3,1]non-6-en-3-yl phenyl ketone (20) (87%), which on reduction with lithium aluminium hydride furnished the alcohol (21) as a viscous oil; the n.m.r. spectrum of this material indicated the existence of diastereoisomers (ratio 1 : 1), though these were not separated. A solution of the alcohol in 98% formic acid was heated at 100° for 48 h, and to effect hydrolysis of the formate, as with the dimethyl analogue, the



crude product was eluted from a column of alumina. Initially a mixture of four components (24%) was obtained, two of which were thought to be the isomeric dienes (22) on the basis of n.m.r. and g.l.c. analysis (see later). Further elution yielded 2-phenyladamantan-1-ol (25) (73%), whose identification is based on analytical and spectral data. The n.m.r. spectrum of the alcohol (25) [$(CD_3)_2SO$] established that cyclisation had taken place, that the hydroxy-substituent was tertiary, and that the phenyl group was attached to a methylene position. The i.r. spectrum established the 1,2-relationship of the two substituents: at high dilution in carbon tetrachloride the compound exhibited free and hydrogen-bonded OH absorptions with a spectral shift of 20 cm^{-1}; a shift of this magnitude lies with the accepted range for intramolecular hydrogen bond formation between a phenyl ring and a hydroxy-substituent.[16]

The formation of a 1,2-disubstituted product in the reaction of the alcohol (21) with formic acid instead of a 2,4-derivative, as was observed with the dimethyl alcohol (8), reflects differences in reactivity of the cations and olefins involved in each case. With the phenyl alcohol, dehydration to the diene mixture (22) apparently proceeds much faster than does direct cyclisation. Protonation of the dienes can then occur at the endocyclic olefinic bond and the resulting cation (23) can cyclise to the cation (24), which combines with formic acid and yields 2-phenyladamantan-1-ol after hydrolysis. We prepared a 1 : 1 mixture of dienes (22) by dehydration of the alcohol (21) in phosphoryl chloride and observed that they react with formic acid exactly as did the unsaturated alcohol, to yield 2-phenyladamantan-1-ol (25) (72%).

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. ^1H 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) 50 m capillary column coated with Apiezon L; (B) 2 m Versamid 930 on Chromosorb W (3% w/w); (C) 2 m Silicone Nitrile XF-1150 on Chromosorb W (5% w/w). Light petroleum had b.p. 40—60°. The drying agent employed was magnesium sulphate.

endo-*Bicyclo*[3,3,1]*non*-6-*ene*-3-*carboxylic Acid* (1a).—The

[12] P. von R. Schleyer, L. K. M. Lam, D. J. Raber, J. E. 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; D. J. Raber, R. C. Fort, jun., E. Wiskott, C. W. Woodsworth, P. von R. Schleyer, J. Weber, and H. Stetter, *Tetrahedron*, 1971, **27**, 3; H. W. Geluk and J. L. M. A. Schlatmann, *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, 1970, **15**, B40; J. R. Alford, B. D. Cuddy, D. Grant, and M. A. McKervey, *J.C.S. Perkin I*, 1972, 2707.

[13] (*a*) H. W. Whitlock, jun., and M. W. Siefken, *J. Amer. Chem. Soc.*, 1968, **90**, 4929; (*b*) M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Comm.*, 1969, 1000; (*c*) J. R. Alford and M. A. McKervey, *ibid.*, 1970, 615; (*d*) D. Lenoir and P. von R. Schleyer, *ibid.*, p. 941; (*e*) J. R. Alford, D. Grant, and M. A. McKervey, *J. Chem. Soc.* (*C*), 1971, 880; (*f*) B. D. Cuddy, D. Grant, and M. A. McKervey, *ibid.*, p. 3173; (*g*) D. Lenoir, R. Glaser, P. Mison, and P. von Schleyer, *J. Org. Chem.*, 1971, **36**, 1821.

[14] V. Buss, R. Gleiter, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 3927.

[15] B. Ree and J. C. Martin *J. Amer. Chem. Soc.*, 1970, **92**, 1660.

[16] L. J. Bellamy, ' Advances in Infra-red Group Frequencies,' Methuen, London, 1968, p. 246.

reaction of sodium azide with adamantanone in methanesulphonic acid followed by treatment of the reaction mixture with concentrated aqueous hydroxide gave the acid in 84% yield.[1]

Methyl endo-*Bicyclo*[3,3,1]*non*-6-*ene*-3-*carboxylate* (1b).—An ethereal solution of diazomethane was added slowly to an ice-cold solution of bicyclo[3,3,1]non-6-ene-3-carboxylic acid (25 g) in ether (500 ml) until nitrogen evolution had ceased and the first permanent yellow colour appeared. Evaporation of the solvent followed by distillation gave the *ester* as an oil, b.p. 102—104° at 4·5 mmHg (Found: M^+, 180·115. $C_{11}H_{16}O_2$ requires M, 180·115), $\nu_{max.}$ (film) 1740 and 715 cm^{-1}, τ ($CDCl_3$) 4·46 (2H, m, on C-6 and C-7), 6·49 (3H, s, CH_3), and 7·42—8·58 (11H, m), *m/e* 180 (14%, M^+), 149 (14), 148 (70), and 78 (100).

2-(endo-*Bicyclo*[3,3,1]*non*-6-*ene*-3-*yl*)*propan*-2-*ol* (8).—A solution of the ester (1b) (24·5 g) in dry ether was added during 1 h to a stirred solution of methylmagnesium iodide [from magnesium (34 g) and methyl iodide (200 g)] in ether (300 ml). The mixture was heated under reflux for 12 h, cooled, and treated with saturated aqueous ammonium chloride, and the organic layer and ethereal extracts (3 × 100 ml) of the aqueous layer were combined, washed with water, and dried. Evaporation left an oil which was taken up in light petroleum and placed on a column of alumina. Elution with light petroleum afforded material (1·3 g) which was discarded. Further elution, with light petroleum–ether (5 : 2), afforded unchanged ester, and elution with ether–methanol (19 : 1) yielded the *alcohol* (13·5 g, 64%), m.p. 56·5—58·0° (after sublimation at 50°) (Found: C, 79·8; H, 11·15. $C_{12}H_{20}O$ requires C, 79·95; H, 11·2%), $\nu_{max.}$ 3400 and 725 cm^{-1}, τ [$(CD_3)SO$] 4·19—4·52 (2H, m, on C-6 and C-7), 6·06 (1H, s, OH), 7·58—9·20 (11H, m), 9·02 (3H, s, CH_3), and 9·06 (3H, s, CH_3), *m/e* 180 (<5%, M^+), 162 (6), 122 (25), 79 (53), and 59 (100).

Cyclisation of the Alcohol (8) *in Hot Formic Acid.*—A solution of the alcohol (7·0 g) in 98% formic acid (100 ml) was stirred and heated at 100° for 4 h, cooled, poured into cold water, neutralised with 50% aqueous sodium hydroxide, and extracted with ether (3 × 100 ml). The extract was washed with water, then dried. Evaporation yielded an oil (7·2 g), $\nu_{max.}$ (film) 1720 and 1170 cm^{-1}. The product was placed on a column of alumina. Elution with light petroleum gave a fraction (0·06 g) which was discarded. Further elution, with ether–methanol (19 : 1), yielded a mixture of 4,4-dimethyladamantan-2*ax*- and 2*eq*-ol [(9) and (10)] (5·75 g, 82%). G.l.c. analysis on column (C) at 120° revealed that the isomer ratio was 6 : 1 in favour of alcohol (10). The alcohol mixture was subjected to a second chromatography on alumina. Elution with ether–light petroleum (3 : 1) yielded mainly the minor isomer (9), identical (m.p., i.r., n.m.r., and g.l.c.) with the alcohol obtained by lithium aluminium hydride reduction of 4,4-dimethyladamantan-2-one (18). Further elution with the same solvent mixture gave the preponderant isomer (10) of >98% purity by g.l.c. analysis. Sublimation gave 4,4-*dimethyladamantan*-2eq-*ol* (10) as flakes, m.p. 176—177° (Found: C, 80·2; H, 11·05. $C_{12}H_{20}O$ requires C, 79·95; H, 11·2%), $\nu_{max.}$ 3300 cm^{-1}, τ [$(CD_3)_2SO$] 5·62 (1H, d, OH), 6·00br (1H, s, >CH–O–), 7·85—8·87 (12H, m), 8·95 (3H, s, CH_3), and 9·01 (3H, s, CH_3), *m/e* 180 (21%, M^+), 165 (13), 162 (100), and 147 (81).

4,4-*Dimethyladamantan*-2-*one* (18).—A mixture of alcohols (9) and (10) (4·0 g) in acetone (100 ml) was treated with Jones reagent with stirring until the first permanent red colour appeared. Excess of oxidant was removed by addition of isopropyl alcohol; the solution was diluted with ether (200 ml), and then neutralised with sodium hydrogen carbonate. The solids were filtered off and the filtrate was dried and concentrated to yield a solid which was taken up in light petroleum and placed on a column of alumina. Elution with light petroleum–ether (3 : 1) gave the *ketone* (3·7 g, 93%), m.p. 174—175° (after sublimation at 130°) (Found: C, 81·1; H, 9·85. $C_{12}H_{18}O$ requires C, 80·85; H, 10·15%), $\nu_{max.}$ 1720 and 1710 cm^{-1}, τ ($CDCl_3$) 7·48—8·55 (12H, m), 8·86 (3H, s, CH_3), and 9·09 (3H, s, CH_3), *m/e* 178 (100%, M^+), 163 (39), 135 (44), and 79 (30).

2,2-*Dimethyladamantane* (19).—A mixture of 4,4-dimethyladamantan-2-one (0·5 g), 98% hydrazine (1·0 g), potassium hydroxide (1·0 g), and diethylene glycol (40 ml) was heated at 140° for 2 h, and then at 180° for 12 h. The cooled solution was poured into water and extracted with pentane (4 × 30 ml). The extract was washed with water, dried, and concentrated, yielding a product which was then chromatographed over alumina. Elution with pentane gave the hydrocarbon (0·06 g, 13%), m.p. 143—144° (after sublimation) (lit.,[5] 144—145°).

4,4-*Dimethyladamantan*-2ax-*ol* (9).—A solution of 4,4-dimethyladamantan-2-one (1·0 g) in ether (15 ml) was added dropwise to a stirred slurry of lithium aluminium hydride (0·38 g) in ether (10 ml). The mixture was then heated under reflux for 4 h, cooled, and treated with water and 10% sulphuric acid. The ether layer and ethereal extracts of the aqueous layer were combined, washed with saturated aqueous sodium hydrogen carbonate, and dried. Evaporation yielded the *alcohol* (0·96 g, 96%) m.p. 194—196° (after sublimation at 135°) (Found: C, 79·85; H, 11·05%). $\nu_{max.}$ 3350 cm^{-1}, τ [$(CD_3)_2SO$] 5·46 (1H, d, OH), 6·20 (1H, s, >CH–O–), 7·60—8·80 (12H, m), 8·80 (3H, s, CH_3), and 9·03 (3H, s, CH_3), *m/e* 180 (9%, M^+), 162 (100), 147 (67), and 79 (35). G.l.c. analysis of the product on column (C) at 120° showed that it contained less than 1% of its epimer (10).

Cyclisation of the Alcohol (8) *in* 98% *Sulphuric Acid.*—(a) *At* 50°. The alcohol (1·0 g) was added in one portion to 98% sulphuric acid (15 ml) at 50°; the solution was stirred rapidly for 5 min then poured on ice. The aqueous solution was neutralised with 50% aqueous sodium hydroxide and extracted with ether (3 × 50 ml). The extract was washed with water, dried, and concentrated to an oil. The product was placed on a column of alumina. Elution with light petroleum–ether (19 : 1) gave material (0·26 g) which was shown by g.l.c. analysis to be a complex mixture and which was not further investigated. Elution with ether–methanol (19 : 1) gave 3,5-dimethyladamantan-1-ol (13) (0·33 g, 35%), m.p. 97—98°, identical (i.r. and n.m.r. spectra, m.p.) with a sample independently synthesised from 1,3-dimethyladamantane.[17]

(b) *At* 20°. The alcohol (1·76 g) was added in one portion to 98% sulphuric acid (30 ml) at 18°. The solution was stirred rapidly for 20 min, then poured on ice. Work-up in (a) gave a 1 : 3 mixture (1·52 g, 86%) of 2,2-dimethyladamantan-1-ol (11) and 4,4-dimethyladamantan-1-ol (12). Fractional crystallisation of the mixture gave the preponderant isomer (12), m.p. 145—148°. These products were identified by direct comparison (i.r. and n.m.r. spectra, m.p.s, and retention times) with samples prepared by literature methods.[14,15]

[17] S. Landa, J. Vais, and J. Burkhard, *Z. Chem.*, 1967, **7**, 233.

Reaction of Phenylmagnesium Bromide with Methyl endo-*Bicyclo*[3,3,1]*non*-6-*ene*-3-*carboxylate* (1b).—A solution of the ester (7·5 g) in dry ether (150 ml) was added during 1 h to a stirred solution of phenylmagnesium bromide [from magnesium (16 g) and bromobenzene (105 g)] in ether (100 ml). The mixture was heated under reflux for 18 h, cooled, and treated with saturated aqueous ammonium chloride, and the ethereal solution was decanted off. The solid residue was then dissolved in dilute sulphuric acid. The aqueous solution was extracted with ether (3 × 100 ml) and the combined ethereal solutions were washed with water and dried. Evaporation yielded an oil which was placed on a column of alumina. Elution with light petroleum gave material which was discarded. Further elution, with light petroleum–ether (9 : 1), gave endo-*bicyclo*[3,3,1]*non*-6-*en*-3-*yl phenyl ketone* (20) (8·1 g, 86%), b.p. 148—150° at 0·85 mmHg (Found: C, 84·85; H, 8·0. $C_{16}H_{18}O$ requires C, 84·9; H, 8·0%), $\nu_{max.}$ (film) 1670, 1590, 715, and 690 cm^{-1}, τ ($CDCl_3$) 2·09—2·53 (5H, m, Ph), 4·10 (2H, m, on C-6 and C-7), 6·21 (1H, m, on C-3), and 7·40—8·40 (10H, m), *m/e* 226 (35%, M^+), 105 (100), 79 (24), and 77 (32).

α-(endo-*Bicyclo*[3,3,1]*non*-6-*en*-3-*yl*)*benzyl Alcohol* (21).—A solution of the ketone (20) (5·0 g) in ether (50 ml) was added dropwise to a stirred slurry of lithium aluminium hydride (1·0 g) in ether (50 ml). The mixture was heated under reflux for 4 h, cooled, and treated with water, and the organic layer and ethereal extracts of the aqueous layer were combined and dried. Evaporation gave the *alcohol* (4·9 g, 98%) as a viscous oil (Found: C, 84·4; H, 8·95. $C_{16}H_{20}O$ requires C, 84·15; H, 8·85%), $\nu_{max.}$ (film) 3400, 1600, and 710 cm^{-1}, τ [$(CD_3)_2SO$] 2·75 (5H, m, Ph), 4·31 (2H, m, on C-6 and C-7), 4·97 (s) and 5·02 (s) (1H, OH, ratio 1 : 1, diastereoisomeric), 5·80 (1H, m, >CH–O–), and 7·64—9·00 (11H, m).

Cyclisation of the Alcohol (21) *in Formic Acid.*—A solution of the alcohol (0·43 g) in 98% formic acid (7 ml) was stirred at 100° for 48 h, then cooled, diluted with water, neutralised with 45% aqueous sodium hydroxide, and extracted with ether (4 × 15 ml). The extract was washed with water, dried, and evaporated, and the crude product was placed on a column of alumina. Elution with light petroleum–ether (3 : 1) yielded a mixture (0·09 g, 24%). G.l.c. analysis on column (C) at 170° showed the presence of four components; the n.m.r. spectrum indicated that the isomeric dienes (22) were present in the ratio 1 : 1. Further elution, with ether–methanol (19 : 1), gave 2-*phenyladamantan*-1-*ol* (0·31 g, 73%), m.p. 55—57° (after sublimation) (Found: C, 84·0; H, 8·9. $C_{16}H_{20}O$ requires C, 84·15; H, 8·85%); $\nu_{max.}$ 3400, 1100, 1090, and 700 cm^{-1}, τ [$(CD_3)_2SO$] 2·40—2·90 (5H, m, Ph), 5·66 (1H, s, OH), 7·04br (1H, s, on C-2), and 7·60—8·80 (13H, m), *m/e* 228 (100%, M^+), 171 (59), and 95 (93).

Dehydration of the Alcohol (21) *with Phosphoryl Chloride.*—A solution of the alcohol (1·0 g) in dry pyridine (20 ml) containing phosphoryl chloride (2·5 ml) was stirred at 18° for 48 h, then poured on ice and extracted with ether (3 × 25 ml). The extract was washed with 15% hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, then dried. Evaporation gave the dienes (22) as an oil (0·36 g, 40%) which slowly crystallised, m.p. 49—54°. The crude product was used without further purification; τ ($CDCl_3$) 2·67 (5H, s, Ph), 4·22 (2H, vinyl, endocyclic), 5·32 and 5·46 (1H, d, vinyl, ratio 1 : 1), and 7·40—9·00 (10H, m), *m/e* 210 (72%, M^+), 121 (100), 93 (44), 91 (84), 79 (100), and 67 (54).

Cyclisation of the Dienes (22) *in Formic Acid.*—Exposure of the dienes to hot formic acid exactly as described for the alcohol (21) yielded 2-phenyladamantan-1-ol (72%) after chromatography.

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