The Chemistry of Diamantane. Part I.[1] Synthesis and Some Functionalisation Reactions

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Rearrangement of the tetrahydro-derivative of the heptacyclotetradecane Binor-S in the gas phase in hydrogen chloride over a chlorinated platinum–alumina catalyst at 150° or in solution in dichloromethane containing aluminium chloride gives diamantane in high yields. Methods for functionalisation of diamantane have been developed. Chlorination at 0° with aluminium chloride–acetyl chloride yields equal amounts of 1- and 4-chlorodiamantane (the so-called zonal and apical derivatives) whereas use of chlorosulphonic acid at −5° yields mainly the 1-chloro-isomer. Hydrolysis of the chlorides yields the corresponding alcohols, which are separable by chromatography over alumina. The chlorides and alcohols can be equilibrated with aluminium chloride and with concentrated sulphuric acid, respectively. Oxidation of diamantane with 96% sulphuric acid at 75° yields diamantanone, 9-hydroxydiamantan-3-one, and diamantane-4,9-diol. Treatment of diamantan-3-ol with 70% sulphuric acid yields a mixture of mono-ols, 9-hydroxydiamantan-3-one, diamantane-3,9-diol, and diamantane-4,9-diol.

A SUBSTANTIAL improvement in the technology of adamantane production was recently reported.[2] In this new approach conventional batch techniques are replaced by a gas-phase flow system in which the hydrocarbon precursor in a stream of hydrogen chloride is passed over a chlorinated platinum-alumina catalyst at 168°. The advantages of the method lie in the greatly improved yields of adamantane and in the almost total elimination of destructive side reactions. We have now achieved similar improvements in the efficiency of rearrangements leading to diamantane (1) (formerly called congressane), the second member of the diamondoid hydrocarbon homologous series.

Schleyer and his co-workers [3] were the first to discover that diamantane could be synthesised from the [2 + 2] norbornene photodimer (2) by rearrangement with an aluminium bromide 'sludge' catalyst in yields of 1—10% depending on which stereoisomer of the starting material was employed. Disproportionation and fragmentation reactions predominate with these dimers, no doubt because of the presence of the highly labile cyclobutane ring.

Various other dimers containing the norbornene skeleton are known; we have investigated the efficacy of two of these, the Katz dimer (3)[4] and Binor-S (5),[5] as precursors for diamantane formation; these substances are not isomeric with diamantane but their tetrahydro-derivatives are. Low pressure hydrogenation of the Katz dimer (3) in glacial acetic acid over Adams catalyst cleaved the cyclopropane ring and removed the olefinic bond to yield a tetrahydro-derivative (4) of undetermined structure. When subjected to the gas-phase isomerisation procedure at 150° hydrocarbon (4) yielded diamantane in 45% yield. Much greater improvements were achieved with Binor-S (5) as starting material. The use of Binor-S as a synthetic precursor for diamantane was discovered independently by Schleyer and his co-workers,[6a] who have also described some functionalisation reactions of diamantane.[6b,c]

Preparation of Binor-S from norbornadiene by use of dibromobistriphenylphosphinecobalt(II) and boron trifluoride–ether catalysts and a published procedure was a capricious reaction; more often than not a polymer was formed instead of the dimer. The difficulty evidently

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

[2] D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Amer. Chem. Soc.*, 1971, **93**, 2798.

[3] C. Cupas, P. von R. Schleyer, and D. J. Trecker, *J. Amer. Chem. Soc.*, 1965, **87**, 919.

[4] J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, 1966, **88**, 4012.

[5] G. N. Schrauser, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, 1966, **88**, 4890; G. N. Schrauser, R. K. Y. Ho. and G. Schlesinger, *Tetrahedron Letters*, 1970, 543.

[6] (a) T. M. Gund, V. Z. Williams, jun., E. Osawa, and P. von R. Schleyer, *Tetrahedron Letters*, 1970, 3877; (b) T. M. Gund, M. Nomura, V. Z. Williams, jun., P. von R. Schleyer, and C. Hoogzand, *ibid.*, p. 4875; (c) T. M. Gund, P. von R. Schleyer, and C. Hoogzand, *ibid.*, 1971, 1583.

lies in the high exothermicity of the process, and if at the initial stages provision is not made for rapid cooling of the system polymerisation occurs. However, by conducting the reaction in solution in hot dry toluene this difficulty could be overcome, and 80% yields of pure
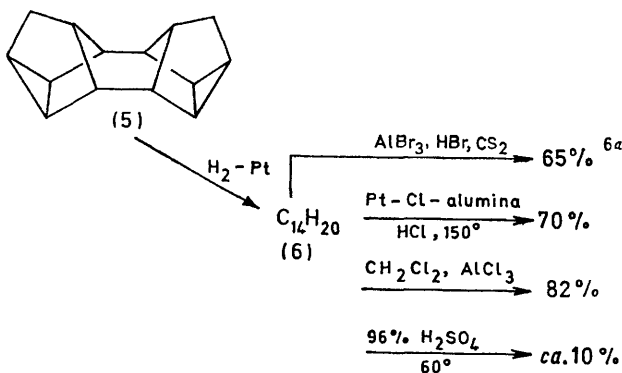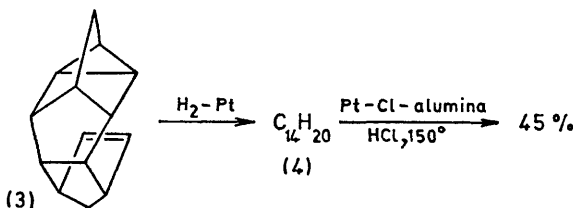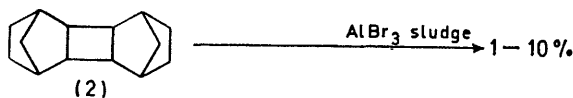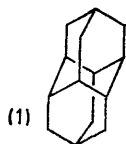

(1)

AlBr₃ sludge → 1 — 10%

(2)

(3)

H₂-Pt → C₁₄H₂₀ (4) Pt-Cl-alumina / HCl,150° → 45%

(5)

H₂-Pt → C₁₄H₂₀ (6)

AlBr₃, HBr, CS₂ → 65% 6a

Pt-Cl-alumina / HCl, 150° → 70%

CH₂Cl₂, AlCl₃ → 82%
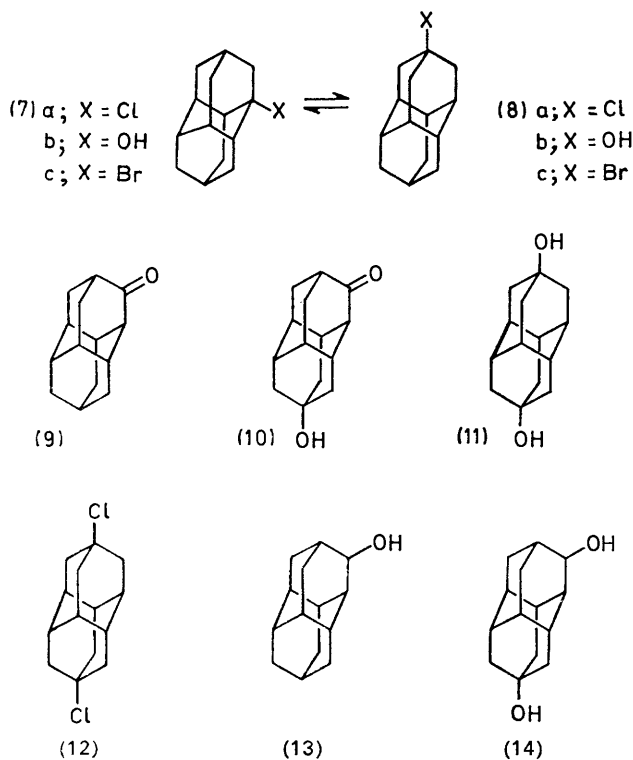
96% H₂SO₄ / 60° → ca. 10%

Binor-S were routinely obtained. Hydrogenolytic opening of both cyclopropane rings of Binor-S proceeded smoothly at low pressure on Adams catalyst in glacial acetic acid at room temperature, furnishing a tetrahydro-derivative (6) in essentially quantitative yield. The structure of this hydrocarbon has not been elucidated; g.l.c. analysis indicated that it was a single compound. Exposure of tetrahydro-Binor-S to the gas phase isomerisation procedure gave diamantane in 70% yield. Although this result represents a substantial improvement in diamantane methodology, it was not our method of choice for large-scale preparative work, particularly when we wished to functionalise the hydrocarbon. Sulphuric acid was also an active catalyst for the formation of diamantane from tetrahydro-Binor-S, but the yield was poor (ca. 10%).

* For an indirect route to 4-substituted diamantanes see ref. 6b.
† We thank Dr. H. Mackle and Mr. T. Clark for this purity and m.p. determination.

In an earlier study of the 2,3-tetramethylenenorbornane–1-methyladamantane rearrangement [7] (which proceeds quantitatively by the gas-phase method [2]) we developed a convenient procedure whereby in essentially a single operation the product could be monochlorinated in high yield at a bridgehead position by simply treating a solution of the hydrocarbon precursor with aluminium chloride in dichloromethane, followed after several hours by acetyl chloride. The application of this procedure to the preparation and functionalisation of diamantane proved so successful that it now constitutes the simplest route to both 1- and 4-substituted derivatives.*

A solution of tetrahydro-Binor-S (6) in dichloromethane containing aluminium chloride was heated under reflux while the progress of the reaction was monitored by g.l.c. After 12 h the product was composed of diamantane (95%) and several minor components, two of which were later found to be 1- and 4-chlorodiamantane. Diamantane of >98% purity was obtained in 82% yield after chromatography and recrystallisation; a zone-refined sample of 99·99% purity had m.p. 251° (by differential thermal analysis).† Functionalisation of the molecule was accomplished easily. The rearrangement procedure was conducted as before and after 12 h the cooled solution was treated with acetyl chloride, to yield a 1 : 1 mixture of 1-chlorodiamantane (7a) and 4-chlorodiamantane (8a). The individual isomers were not isolated as such from this reaction but were hydrolysed directly to a mixture of diamantan-1-ol (7b) and diamantan-4-ol (8b) (52% yield from tetrahydro-Binor-S), which were separable by chromatography over alumina, the former isomer being the more easily eluted. Chlorides (7a) and (8a) were then obtained by the action of either thionyl chloride or hot concentrated hydrochloric acid on the individual alcohols

Two distinct types of bridgehead monosubstitution are possible with diamantane since the substituent can occupy either the apical 4-position or the zonal 1-position; and there exists an interesting structural difference between apical and zonal derivatives. In the zonal arrangement the substituent is axially disposed with respect to one cyclohexane ring of the diamantane skeleton whereas in an apical derivative the substituent is exclusively equatorial. The effects of this difference on the n.m.r. spectra of the tertiary chlorides and alcohols were used in making the structural assignments. With cyclohexane compounds it is known that some substituents can cause pronounced downfield n.m.r. shifts when in 1,3-diaxial configurations with respect to protons,[8] and with the zonal alcohol and chloride this effect was clearly discernible in the spectra of solutions in pyridine. The assignments were supported by a chemical correlation. Bromination of diamantane with liquid bromine under mild conditions is known to yield

[7] M. A. McKervey, D. Grant, and H. Hamill, Tetrahedron Letters, 1970, 1975; H. Hamill, A. Karim, and M. A. McKervey, Tetrahedron, 1971, 27, 4317.
[8] Cf., L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 237.

exclusively the zonal bromide (7c) in a kinetically controlled process.[6c,9] We prepared bromide (7c) by this method and found that its hydrolysis product and the alcohol to which we had assigned the zonal configuration (7b) were identical. Functionalisation of diamantane could also be achieved by use of chlorosulphonic acid at −5°; the product was a 3 : 1 mixture of chlorides (7a) and (8a).

The product ratio of *ca.* 1 : 1 in the chlorination of diamantane with acetyl chloride–aluminium chloride was particularly interesting since subsequent equilibration studies with the individual chlorides (aluminium chloride as the catalyst in chloroform) revealed that at 27° the two isomers were of equal thermodynamic stability. Similarly, with aluminium bromide as the catalyst in dibromomethane, we showed that the equilibrium constant for equilibration of bromides (7c) and (8c) was unity at 98°. The isomeric diamantanols (7b) and (8b) were brought to equilibrium in 98% sulphuric acid and were found to be equally thermodynamically stable at 48°. These equilibrations probably all proceed *via* an intermolecular hydride transfer mechanism of the type

(7) a; X = Cl
b; X = OH
c; X = Br

(8) a; X = Cl
b; X = OH
c; X = Br

(9)

(10)

(11)

(12)

(13)

(14)

proposed to account for related rearrangements in the adamantane series.[10] The thermodynamic data for

each of these systems show that whereas the apical isomers are of lower enthalpy than the zonal isomers by 1·1 (ref. 11), 0·68 (ref. 12), and 0·59 * kcal mol^{-1} for the hydroxy-, chloro-, and bromo-substituents, respectively, there is a counterbalancing entropy factor due to symmetry differences in favour of the zonal isomers. The higher enthalpies of the zonal isomers reflect the unfavourable 1,3-interactions between the axial substituent and the axial hydrogen atoms on C-3 and C-14; no such interactions exist in the apical isomers.

Oxidation with concentrated sulphuric acid proved to be most effective for functionalising diamantane at a non-bridgehead position. Geluk and Schlatmann [13] discovered that treatment of adamantane with 96% sulphuric acid at 75° produced adamantanone in high yield. When applied to diamantane, this procedure furnished diamantanone (9) (54%), 9-hydroxydiamantan-3-one (10) (6%), diamantane-4,9-diol (11) (5%), and an unidentified compound (2%) (tetrahydro-Binor-S yielded 5% of diamantanone when similarly treated). The minor products were separated by chromatography over silica gel and characterised by their spectral data. The hydroxy-ketone was assigned structure (10) since its n.m.r. spectrum (pyridine) revealed the presence of two protons α to the carbonyl group and Wolff-Kishner reduction yielded only diamantan-4-ol. The simplicity of the n.m.r. spectrum of the diol (a single absorption at τ 8·03 with a slight shoulder at τ 8·10) was consistent with the 4,9-structure (11), and this was confirmed by converting it with hot concentrated hydrochloric acid into 4,9-dichlorodiamantane (12); the n.m.r. spectrum of the dichloride in pyridine consisted of a twelve-proton broad singlet at τ 7·94 and a six-proton broad singlet at τ 8·26 for the α and zonal protons, respectively.

Substantial amounts of disubstituted diamantanes were also produced from diamantan-3-ol (13) in sulphuric acid. The alcohol, prepared from the ketone and lithium aluminium hydride, was exposed to 70% sulphuric acid at 90° for 2·5 h, to yield a mixture of seven compounds which, in order of elution from an alumina chromatography column, were diamantane (42·7%), diamantanone (6·3%), diamantan-1-ol (1·1%), diamantan-4-ol (1·3%), diamantan-3-ol (5·6%), 9-hydroxydiamantan-3-one (10) (4·6%), diamantane-3,9-diol (14) (9·4%), and diamantane-4,9-diol (11) (4·0%). The 3,9-diol (14) was identified by direct comparison with the product of reduction of 9-hydroxydiamantan-3-one (10) with lithium aluminium hydride. The tertiary mono-alcohols produced in 70% sulphuric acid probably result from intermolecular rearrangement [14] of the 3-alcohol, whereas the diols and the keto-alcohol arise through disproportionation and/or oxidation reactions

* Details of the thermodynamics of the bromodiamantane equilibrations will be described separately.

[9] R. C. Fort, jun., and P. von R. Schleyer, *Adv. Alicyclic Chem.*, 1966, **1**, 283; see also ref. 6b.

[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] D. E. Johnston, M. A. McKervey, and J. J. Rooney, *Chem. Comm.*, 1972, 29.

[12] M. A. McKervey, D. E. Johnston, and J. J. Rooney, *Tetrahedron Letters*, 1972, 1547.

[13] H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, 1968, **24**, 5361, 5377.

[14] *Cf.* ref. 10; J. R. Alford, B. D. Cuddy, D. Grant, and M. A. McKervey, *J.C.S. Perkin I*, 2707.

of the type which have been described for adamantan-2-ol in sulphuric acid.[13] Rearrangements and equilibrations of a variety of disubstituted diamantanes will be described in a subsequent paper.

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 60 MHz with tetramethylsilane as internal standard. Mass spectrometric data were obtained with an A.E.I. MS 902 spectrometer with an ionising beam energy of 70 eV. G.l.c. refers to analysis on one of the following columns: (A) 2 m Silicone Gum Rubber on Chromosorb G (2% w/w); (B) 2 m 2-Cyanoethyl Methyl Silicone (XE-60) on Chromosorb W (2% w/w); (C) 2 m Versamid 930 on Chromosorb W (3% w/w). Light petroleum had b.p. 40—60°. The drying agent employed was magnesium sulphate.

Binor-S (5).—Boron trifluoride–ether complex (0·8 ml) was added dropwise to a stirred mixture of freshly distilled norbornadiene (77·2 g), dry toluene (150 ml) and dibromo-bistriphenylphosphinecobalt(II) (3·0 g). After all the boron fluoride–ether complex had been added the mixture was warmed gently until a visible reaction commenced; heating was discontinued while the mixture boiled spontaneously and then continued for 12 h. The cooled mixture was diluted with dichloromethane (250 ml) and the organic solution was washed with water (3 × 250 ml), dried and evaporated, to yield an oil which soon solidified. Distillation gave Binor-S (61 g, 80%) of *ca.* 98% purity, b.p. 108° at 2·5 mmHg, m.p. 64—65° (lit.,[5] 65—66°).

Tetrahydro-Binor-S (6).—A suspension of Binor-S (30·0 g) in glacial acetic acid (150 ml) containing Adams catalyst (0·5 g) was exposed to hydrogen at room temperature and 3 atm pressure. When hydrogen uptake ceased the solution was filtered and neutralised with aqueous 10% sodium hydroxide. The solution was extracted with ether (3 × 200 ml) and the extract was washed with water (2 × 250 ml) and dried. Evaporation gave the hydrocarbon (30·1 g, 98%), b.p. 102—104° at 1·2 mmHg (Found: C, 89·05; H, 10·9. Calc. for $C_{14}H_{20}$: C, 89·3; H, 10·7%), τ (CDCl$_3$) 7·85—9·20 (m), *m/e* 188 (100%, *M*[+]), 147 (41), 146 (31), 145 (51), 134 (18), 133 (19), 131 (35), 119 (17), 105 (25), 93 (19), 92 (24), 91 (55), 80 (31), 79 (44), 77 (18), and 67 (28). G.l.c. analysis indicated that the product was a single component.

Diamantane (1).—A solution of tetrahydro-Binor-S (264 g) in dichloromethane (2·5 l) containing aluminium chloride (50 g) was heated under reflux for 12 h with the exclusion of moisture. The solution was allowed to cool and the crystals were filtered off, washed with cold dichloromethane (3 × 100 ml), and dried, to yield diamantane (151 g), m.p. 236—237°. Recrystallisation from dichloromethane gave material of m.p. 243—245° (lit.,[3] 244—246°). The mother liquor and the washings were combined with the original dichloromethane filtrate, and washed with aqueous 5% sodium hydroxide (3 × 500 ml) and water (4 × 500 ml). The dried solution was concentrated to 750 ml and activated alumina (250 g) was added. The remainder of the solvent was removed by slow evaporation and the dry residue was placed on a column of activated alumina (750 g). Elution with

light petroleum gave diamantane, m.p. 242—244°. The total yield of diamantane of >98% purity was 217 g (82%). Eight sublimations at reduced pressure and twenty zone-refinings gave a sample of m.p. 251° (by differential thermal analysis), of 99·99% purity. The spectral data were in close agreement with those published.[3]

Diamantan-1-ol (7b) *and Diamantan-4-ol* (8b).—A solution of tetrahydro-Binor-S (5·0 g) in dichloromethane (500 ml) containing aluminium chloride (5·0 g) was heated under reflux for 12 h then cooled to 0°. Acetyl chloride (2·4 g) and additional aluminium chloride (5·0 g) were added and the mixture was stirred at 0° for 22 h, then poured on ice. The organic layer and dichloromethane extracts (2 × 100 ml) of the aqueous layer were combined, washed with aqueous 5% sodium hydroxide (100 ml) and water (2 × 100 ml), then dried. Evaporation gave a mixture of chlorides (7a) and (7b) which was dissolved in a mixture of dimethylformamide (130 ml) and 0·67N-hydrochloric acid (150 ml) and heated under reflux for 6 h. The cooled solution was diluted with water (500 ml) and the precipitated solids were filtered off, washed with water, and dried. G.l.c. analysis on column (B) at 180° showed the presence of two major components in about equal amounts. The product in light petroleum was placed on a column of activated alumina (200 g). Elution with light petroleum gave diamantane (0·5 g, 10%). Further elution with light petroleum gave a mixture of dichlorides (0·1 g, 2%) whose structures will be discussed elsewhere. Further elution, with light petroleum–ether (2 : 3), gave *diamantan-1-ol* (1·3 g, 24%), m.p. 292·5—294·0° (lit.,[6b] 291—292°) (Found: C, 82·35; H, 10·05. $C_{14}H_{20}O$ requires C, 82·3; H, 9·85%), ν$_{max.}$ 3267 cm^{-1}, τ (pyridine) 7·40 (2H, q, axial protons on C-3 and C-14), 8·02 (1H, s, OH), and 8·15—8·73 (17H, m), *m/e* 204 (51%, *M*[+]), 186 (100, *M*[+] −H$_2$O), 130 (36), 129 (26), 95 (86), 94 (87), 92 (23), 91 (24), and 79 (21). Further elution of the column with ether–methanol (99 : 1) gave *diamantan-4-ol* (1·5 g, 28%), m.p. 206—208° (from benzene) (lit.,[6b] 204—206°) (Found: C, 82·2; H, 10·1%), ν$_{max.}$ 3280 cm^{-1}, τ (pyridine) 8·02 (1H, s, OH), 8·12 (9H, s, protons on C-2, C-3, C-5, C-6, C-12, and C-14), and 8·32 (10H, s), *m/e* 204 (100%, *M*[+]), 186 (3, *M*[+] −H$_2$O), 109 (18), 108 (15), 107 (17), and 96 (14).

1-Chlorodiamantane (7a).—A solution of thionyl chloride (1·3 g) in chloroform (10 ml) was added dropwise to a solution of diamantan-1-ol (1·3 g) in chloroform and the mixture was heated under reflux for 5 h. Evaporation under reduced pressure gave a solid which was taken up in light petroleum and placed on a short column of alumina. Elution with light petroleum gave the *chloride* (1·2 g, 87%), m.p. 250·5—252·5° (after sublimation) (Found: C, 75·65; H, 8·65; Cl, 16·15. $C_{14}H_{19}Cl$ requires C, 75·5; H, 8·6; Cl, 15·9%), ν$_{max.}$ 1068, 972, 881, 808, and 719 cm^{-1}, τ (pyridine) 7·58 (2H, q, axial protons on C-3 and C-14), 7·85 (2H, d, protons on C-13), 8·12 (5H, m, protons on C-2, C-7, C-11, C-9, and C-12), and 8·45—8·75 (10H, m), *m/e* 224 (7%, *M*[+]), 222 (21, *M*[+]), 188 (16), 187 (100, *M*[+] − Cl), 186 (28), 95 (13), 94 (11), and 91 (12). This chloride was also prepared in high yield by treatment of the alcohol with hot concentrated hydrochloric acid for 6 h.

4-Chlorodiamantane (8a).—Treatment of diamantan-4-ol with thionyl chloride as described for the 1-isomer gave the *chloride* (88%), m.p. 75·5—76·5° (after sublimation) (Found: C, 75·8; H, 8·85; Cl, 16·0%), ν$_{max.}$ 1078, 1069, 1049, 1044, 983, 969, 850, 829, 797, 708, and 529 cm^{-1}, τ (pyridine) 7·90 (6H, d, protons on C-5, C-14, and C-3), 8·27br (3H, s, protons

on C-12, C-6, and C-2), and 8·40 (10H, m), m/e 224 (7%, M^+), 222 (19, M^+), 188 (16), and 187 (100, M^+ — Cl).

4-Bromodiamantane (8c).—A mixture of diamantan-4-ol (1·02 g) and 48% hydrobromic acid (50 ml) was heated under reflux for 6 h, cooled, and extracted with ether (3 × 20 ml). The extract was washed with aqueous 5% sodium hydroxide (40 ml) and water (2 × 25 ml), and dried. Evaporation gave a solid which was placed on a column of alumina (20 g). Elution with light petroleum gave the *bromide* (1·24 g, 82%), m.p. 127—129° (lit.,[6b] 127—128·2°) (Found: C, 63·2; H, 7·35; Br, 29·75. $C_{14}H_{19}Br$ requires C, 62·94; H, 7·15; Br, 29·9%), $\nu_{max.}$ 2910, 1245, 1068, 980, 963, 813, and 501 cm^{-1}, τ (CDCl$_3$) 7·68 (6H, s, protons on C-5, C-14, and C-3), 8·16br (3H, s, protons on C-12, C-6, and C-2), and 8·26 (10H, m), m/e 268 (<1%, M^+), 266 (<1, M^+), 266 (<1, M^+), 188 (14), 187 (100, M^+ — Br), 91 (7), 79 (7).

1-Bromodiamantane (7c).—Treatment of diamantan-1-ol with 48% hydrobromic acid as described for the 4-isomer gave the *bromide* (82%), m.p. 207—209° (Found: C, 63·0; H, 7·25; Br, 30·05%), $\nu_{max.}$ 2910, 1463, 1444, 1070, 970, 887, 801, 791, and 712 cm^{-1}, τ (C$_6$H$_6$) 7·30 and 7·52 (2H, q, axial C-3 and C-14 protons), 7·59 (2H, d, C-13 protons), and 8·13—8·80 (m, 15H), m/e 268 (<1%, M^+), 266 (<1%, M^+), 188 (15), 187 (100, M^+ — Br), 105 (8), and 91 (11).

Bromination of Diamantane.—A mixture of diamantane (1·0 g) and bromine (25 ml) was stirred at 20° for 12 h then poured on ice and chloroform (10 ml) was added. Excess of bromine was removed by addition of solid sodium disulphite. The organic layer and chloroform extracts (3 × 10 ml) of the aqueous layer were washed with aqueous sodium hydrogen carbonate and water, then dried. Evaporation gave the 1-bromide (1·3 g, 90%), m.p. 207—209° (from methanol) (lit.,[6b] m.p. 209—211°). The compound was identical with the bromide prepared from diamantan-1-ol and hydrobromic acid.

Oxidation of Diamantane in 96% Sulphuric Acid.—A mixture of diamantane (6·02 g) and 96% sulphuric acid (50 ml) was stirred at 75° for 10 h. The cooled solution was poured on ice and extracted with ether (4 × 125 ml). The extract was washed with saturated aqueous sodium hydrogen carbonate and water, then dried. Evaporation gave a solid which was shown by g.l.c. analysis on column (A) at 180° to contain one major and two minor components and a trace of starting material. The product was placed on a column of activated alumina (250 g). Elution with light petroleum gave diamantane (0·15 g, 2%). Further elution with ether gave diamantanone (3·5 g, 54%), m.p. 248—249° (lit.,[6b] 249—250°) (Found: C, 83·2; H, 9·0. $C_{14}H_{18}O$ requires C, 83·1; H, 8·95%), $\nu_{max.}$ 1738, 1712, 1294, 1288, and 491 cm^{-1}, τ (CDCl$_3$) 7·55 (2H, s, C-2 and C-4 protons) and 8·04—8·16 (16H, m), m/e 203 (16%), 202 (100, M^+), 174 (4, M^+ — CO), 91 (17), and 79 (18). The remaining products were then stripped from the column with ether–methanol (49 : 1) and re-chromatographed on silica gel. Elution with light petroleum–acetone (93 : 7) gave an unidentified compound (0·1 g). Elution with light petroleum–acetone (8 : 1) gave 9-*hydroxydiamantan-3-one* (10) (0·42 g, 6%), m.p. 191—193° (from benzene) (Found: C, 77·05; H, 8·25. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·05%), $\nu_{max.}$ 3380, 2900, 1718, 1337, 1120, 1109, 1091, and 1040 cm^{-1}, τ (pyridine) 7·52br (2H, s, C-2 and C-4 protons) and 7·70—8·50 (16H, m), m/e 219 (16%), 218 (100, M^+), 190 (16, M^+ — CO), 107 (26), 95 (21), 94 (48), 91 (23), 81 (22), 79 (22), 78 (23), and 77 (21). Further elution, with acetone,

gave *diamantane-4,9-diol* (11) (0·4 g, 5%), m.p. 290—292° (from methanol) (Found: C, 76·1; H, 9·35. $C_{14}H_{20}O_2$ requires C, 76·35; H, 9·15%), $\nu_{max.}$ 3280, 2920, 2895, 2858, 1348, 1251, 1118, 1104, 1027, and 968 cm^{-1}, τ (pyridine) 8·01 (13H, s) and 8·12 (7H, s), m/e 221 (17%), 220 (100, M^+), 203 (2), 110 (10), 109 (11), 108 (11), 107 (21), and 95 (11).

Wolff-Kishner Reduction of 9-Hydroxydiamantan-3-one (10).—The ketone (0·065 g), hydrazine hydrate (0·25 ml), glacial acetic acid (4 drops), and triethylene glycol (4 ml) were heated at 80—90° under nitrogen for 24 h. Potassium hydroxide (0·5 g) was added and the solution was heated to 180—190° and maintained there for 6 h. The cooled solution was diluted with water (100 ml) and extracted with dichloromethane (5 × 10 ml). The extract was washed with saturated aqueous sodium chloride and dried. Evaporation gave a solid which on sublimation yielded diamantan-4-ol (0·05 g, 82%), identified by comparison (g.l.c., i.r. spectrum, and m.p.) with an authentic sample.

Oxidative Rearrangement of Tetrahydro-Binor-S in 96% Sulphuric Acid.—A vigorously stirred mixture of tetrahydro-Binor-S (26·64 g) and 96% sulphuric acid (200 ml) was heated at 75°. G.l.c. analysis of a sample withdrawn after 30 min revealed that the product contained *ca.* 10% diamantane. After 9·5 h at 75° the mixture was cooled, poured on ice, and steam-distilled. Extraction of the distillate with ether gave diamantanone (1·37 g, 5%), identified by comparison (g.l.c., i.r. spectrum, and m.p.) with an authentic sample.

Hydrogenation of the Katz Dimer (3).—A solution of the dimer (10·0 g) in glacial acetic acid (50 ml) containing platinum oxide (1·0 g) was exposed to hydrogen at room temperature and 3 atm pressure. When hydrogen uptake had ceased the solution was degassed, filtered, diluted with water (150 ml), and extracted with dichloromethane (3 × 100 ml). The extract was washed with aqueous 5% sodium hydrogen carbonate and water, then dried. Evaporation and distillation gave the hydrocarbon (4) (5·6 g, 55%), b.p. 92—93° at 1·0 mmHg (Found: C, 89·55; H, 10·8. Calc. for $C_{14}H_{20}$: C, 89·3; H, 10·7%), $\nu_{max.}$ (film) 2938, 2890, 2874, 1499, 1482, 1308, 1294, and 1120 cm^{-1}, m/e 189 (16%), 188 (100, M^+), 160 (36), 159 (36), 147 (80), 121 (64), 120 (31), 105 (30), 93 (40), 92 (30), 91 (71), 80 (89), 79 (81), and 77 (30).

Chlorination of Diamantane in Chlorosulphonic Acid.—Diamantane (0·5 g) was added slowly with stirring to chlorosulphonic acid (10 ml) at —10°. The temperature was kept between —10 and —5° for 2·5 h and the reaction was then quenched on ice. The aqueous solution was extracted with ether (3 × 20 ml) and the extract was washed with aqueous 5% sodium hydroxide and water, then dried. Evaporation gave a product which was taken up in light petroleum and passed down a short column of alumina, to give a mixture of 1- and 4-chlorodiamantane (0·54 g, 91%) as shown by i.r. and g.l.c. analysis. The mixture was completely hydrolysed in hot dimethylformamide–hydrochloric acid as already described, to give a 3 : 1 mixture of diamantan-1-ol (7b) and diamantan-4-ol (8b) in high yield.

Equilibration of Diamantan-1- and -4-ols.—The alcohol (0·1 g) was added to 98% sulphuric acid (10 ml) at 0° and the solution was stirred rapidly for 15 min, then poured on ice. The aqueous solution was extracted with ether (3 × 10 ml) and the extract was washed with aqueous 5% sodium hydroxide and water, then dried. G.l.c. analysis on column (B) at 180° of the solution after concentration

showed the presence of the 1-ol (44%) and the 4-ol (56%). The equilibrium was approached from either side.

Equilibration of 1- *and* 4-*Chlorodiamantane* [(7a) *and* (8a)].—A solution of the chloride (0·25 g) in dry chloroform (25 ml) containing aluminium chloride (*ca.* 0·25 g) was stirred at 0° for 30 h, then poured on ice and extracted with dichloromethane (3 × 25 ml). The extract was washed with aqueous 5% sodium hydroxide and water, then dried. Evaporation gave a mixture of chlorides which was hydrolysed for 4 days in dimethylformamide (13 ml) and 0·67N-hydrochloric acid (15 ml) under reflux. The cooled solution was diluted with water (250 ml) and the precipitate was filtered off and taken up in ether. The ethereal solution was dried and concentrated. G.l.c. analysis on column (B) at 180° gave the equilibrium concentrations of 1- and 4-chlorodiamantane as 46 and 54%. The equilibrium was approached from either side.

Equilibration of 1- *and* 4-*Bromodiamantane* [(7c) *and* (8c)].—A solution of the bromide (0·25 g) in dibromomethane (25 ml) containing aluminium bromide (0·25 g) was stirred at 0° for 24 h. The reaction was quenched on ice and the dibromomethane layer and dichloromethane extracts (2 × 25 ml) of the aqueous layer were combined, washed with aqueous 5% sodium hydroxide and water, then dried. Evaporation gave a mixture of bromides which was hydrolysed as described for the corresponding chlorides. G.l.c. analysis on column (B) at 180° gave the equilibrium concentrations of 1- and 4-bromodiamantane as 43 and 57%.

*Diamantan-*3-*ol* (13).—A solution of diamantanone (5·0 g) in ether (30 ml) was added dropwise to a stirred slurry of lithium aluminium hydride (1·0 g) in ether (30 ml). The mixture was heated under reflux for 12 h then cooled. Excess of reducing agent was removed by the addition of cold water, after which the mixture was poured into 5N-sulphuric acid (60 ml) and the product extracted with chloroform (3 × 60 ml). The extract was washed with water and dried. Evaporation gave the *alcohol* (4·87 g, 97%), m.p. 247—250° (from benzene) (lit.,[6b] 256—257°) (Found: C, 82·55; H, 9·9. $C_{14}H_{20}O$ requires C, 82·3; H, 9·85%), $\nu_{max.}$ 3180, 2890, 1362, 1088, 1060, 1052, and 1010 cm^{-1}, τ (pyridine) 5·99 (1H, t, CH–O–), 7·50 (1H, s), 7·57br (1H, s), 8·00br (2H, s), and 8·30—8·60 (15H, m), *m/e* 204 (7%, M^{+}), 186 (100), 131 (10), 117 (6), 105 (8), 104 (7), 96 (7), 95 (7), 94 (7), 93 (14), 92 (20), 91 (20), and 79 (20).

*Oxidation of Diamantan-*3-*ol in* 70% *Sulphuric Acid.*—A solution of the alcohol (4·77 g) in 70% sulphuric acid (50 ml) was stirred at 90° for 2·5 h, then cooled and poured on ice. The aqueous solution was neutralised with aqueous 50% potassium hydroxide then extracted with chloroform (3 × 500 ml). The extract was washed with water and dried. Evaporation gave a solid (4·09 g) which was shown by g.l.c. analysis on column (C) at 220° to consist of seven components. The mixture was placed on a column of alumina. Elution with light petroleum gave diamantane (2·04 g, 42·7%); further elution, with light petroleum–ether

(7 : 3), gave diamantanone (0·3 g, 6·3%). The column was then stripped with methanol–chloroform (1 : 33) and the material eluted was rechromatographed on silica gel (200 g). Elution with light petroleum–acetone (3 : 1) yielded diamantan-1-ol (0·05 g, 1·1%), diamantan-4-ol (0·06 g, 1·3%), and diamantan-3-ol (0·27 g, 5·6%). These products were identified by comparison (m.p., i.r. spectra, and g.l.c.) with authentic samples. Further elution with the same solvent mixture gave 9-hydroxydiamantan-3-one (0·22 g, 4·6%) (10), identical with the hydroxy-ketone obtained from oxidation of diamantane in 96% sulphuric acid, followed by a mixture of diamantane-3,9-diol (14) and diamantane-4,9-diol (12) (0·64 g). The diols were separated by trituration of the mixture with cold methanol. Filtration yielded the 4,9-isomer (0·19 g, 4·0%), identified by comparison (i.r. spectrum and m.p.) with the diol obtained by oxidation of diamantane with 96% sulphuric acid. Evaporation of the methanolic solution gave the 3,9-*isomer* (0·45 g, 9·4%), m.p. 222—224° (from benzene) (Found: C, 76·15; H, 9·25. $C_{14}H_{20}O_{2}$ requires C, 76·35; H, 9·15%), τ (pyridine) 5·86 (1H, t, $>$CH–O–), 7·30br (1H, s), 7·49 (1H, s), and 7·90—8·60 (17H, m), *m/e* 220 (4%, M^{+}), 203 (17), 202 (100), 147 (29), 111 (40), 110 (57), 95 (33), 94 (19), 93 (38), 92 (36), and 91 (26).

4,9-*Dichlorodiamantane* (12).—Diamantane-4,9-diol (0·05 g), dissolved in concentrated hydrochloric acid (15 ml), was heated under reflux for 6 h; during this time a white solid collected in the condenser. The cooled solution was poured into water (50 ml) and neutralised with aqueous 50% potassium hydroxide. The solid in the condenser was dissolved in chloroform and the aqueous solution was extracted with chloroform (3 × 60 ml). The combined organic solutions were washed with water and dried. Evaporation gave the *dichloride* (0·45 g, 77%), m.p. 308—310° (from pentane) (Found: C, 65·35; H, 6·85; Cl, 27·7. $C_{14}H_{18}Cl_{2}$ requires C, 65·4; H, 7·05; Cl, 27·55%), $\nu_{max.}$ 2930 1332, 1239, 1070, and 844 cm^{-1}, τ (pyridine) 7·94br (12H, s, C-3, C-5, C-14, C-8, C-10, and C-13 protons) and 8·26br (6H, s, C-1, C-2, C-6, C-7, C-11, and C-12 protons), *m/e* 258 (8%, M^{+}), 256 (13, M^{+}), 223 (35, M^{+} − Cl), 222 (17), 221 (100, M^{+} − Cl), 185 (10), 91 (14), and 77 (10).

*Diamantane-*3,9-*diol* (14).—9-Hydroxydiamantan-3-one (0·13 g) was added to a slurry of lithium aluminium hydride (0·20 g) in ether (25 ml). The mixture was heated under reflux for 4 days, cooled, treated cautiously with water, and then poured into 5N-sulphuric acid (30 ml) and extracted with chloroform (3 × 80 ml). The extract was washed with water and dried. Evaporation gave a solid (0·10 g) which was placed on a column of alumina. Elution with chloroform–ether (1 : 2) gave the diol, identical with that obtained from the reaction of diamantan-3-ol with 70% sulphuric acid.