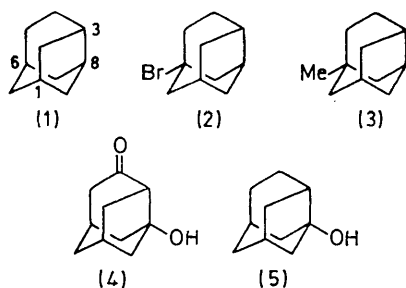


Bridgehead Reactivity in Proadamantane. Ionic Bromination.

By Anna Karim and M. Anthony McKervey,* Department of Chemistry, The Queen's University, Belfast BT9 5AG

In agreement with computer molecular mechanics calculations, the preponderant product of bromination of protoadamantane (tricyclo[4.3.1.0^{3,8}]decane) is the 6-bromo-derivative. The structure elucidation is based on the finding that 6-methylprotoadamantane is significantly less reactive in bromination than is protoadamantane. 6-Bromoprotoadamantane reacts readily in several nucleophilic substitution reactions.

THE bridgehead positions of protoadamantane (1),¹ unlike those of adamantane, differ structurally and should be of unequal chemical reactivity. Computer molecular mechanics calculations of bridgehead reactivity in polycyclic systems,² which assess the change in strain energy in going from the ground state of the hydrocarbon to the transition state (approximated by the structure of the appropriate cation), predict that of the four bridgehead positions of protoadamantane, the 6-position should be the most reactive in ionic substitution reactions, appreciably more reactive than the 3-position and much more reactive than either the 1- or the 8-position.³ We have found that treatment of protoadamantane with hot bromine (conditions known to promote ionic bromination of diamondoid hydrocarbons⁴) yields a monobromoprotoadamantane (ca. 95%) with traces of two other substances one of which is thought to be 1-bromoadamantane. That the preponderant product contained the protoadamantyl skeleton was established by catalytic debromination and n.m.r. spectroscopy revealed its tertiary character, though which bridgehead position bore the substituent was not obvious from the spectrum. Accordingly, the structure elucidation was undertaken by chemical methods.



If the product was indeed 6-bromoprotoadamantane (2) then under similar reaction conditions 6-methylprotoadamantane (3) should be appreciably less reactive in bromination than was protoadamantane, if we make the reasonable assumption that replacement of a bridgehead hydrogen atom by a methyl group should have a negligible effect on the relative reactivities of the three remaining bridgehead positions. In practice, it was

¹ B. R. Vogt, *Tetrahedron Letters*, 1968, 1575.

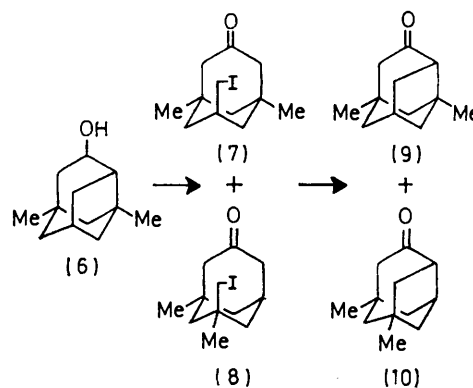
² J. L. Fry, E. M. Engler, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 4628, and references therein.

³ Preliminary account, A. Karim, M. A. McKervey, E. M. Engler, and P. von R. Schleyer, *Tetrahedron Letters*, 1971, 3987. Further details of the reactivity of protoadamantan-6-yl derivatives in solvolytic reactions will be published elsewhere (P. von R. Schleyer, personal communication).

⁴ H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.

more convenient to have methyl groups at both the 6- and the 8-position; the latter was readily excluded as the bromination site since Wolff-Kishner reduction of 8-hydroxyprotoadamantan-4-one (4)⁵ yielded an alcohol (5) different from the alcohol produced by hydrolysis of the bromide whose structure we sought.

Treatment of 3,5-dimethyladamantan-1-ol (6)⁶ with lead tetra-acetate and iodine⁷ in benzene afforded a



mixture of iodo-ketones (7) and (8), which was transformed, without purification, by methanolic sodium hydroxide into a 9 : 1 separable mixture of two dimethylprotoadamantan-4-ones in 33% yield. The structures of these tricyclic ketones were not apparent from the n.m.r. spectrum of the mixture of iodo-ketones; the latter were but two components of a complex mixture of products (and starting material) and attempts to purify them invariably led to cyclisation. The positions of the methyl groups in the preponderant dimethylprotoadamantanone were located by another approach. The ketone was reduced with lithium aluminium hydride and the mixture of epimeric alcohols so produced was exposed to hot 25% sulphuric acid, whereupon a protoadamantane \rightarrow adamantane rearrangement⁸ occurred, yielding a mixture of new alcohols. Oxidation of this mixture with chromic acid furnished 1,5-dimethyladamantan-2-one (13) as the preponderant product (94%). None of the intermediates in this sequence was isolated and scrutinised; however, their structures, (11) and (12), must be reasonably secure in view of the identity of the ultimate product which was independently synthesised by oxidation of 1,3-dimethyladamantane

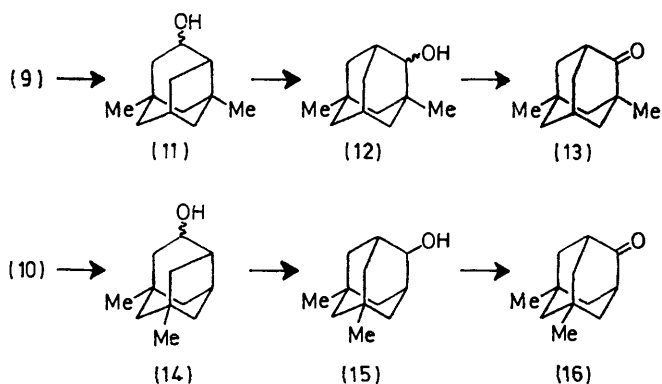
⁵ J. R. Alford and M. A. McKervey, *Chem. Comm.*, 1970, 615.

⁶ S. Landa, J. Vais, and J. Burkherd, *Z. Chem.*, 1967, **7**, 233.

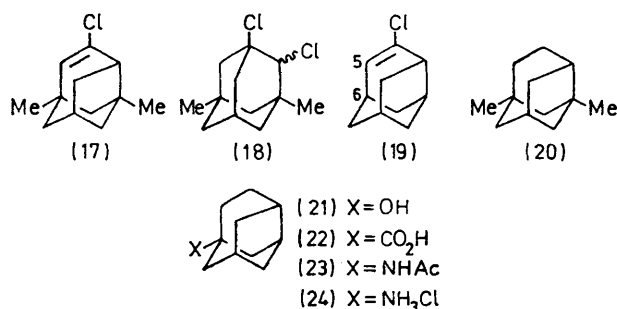
⁷ W. H. W. Lunn, *J. Chem. Soc. (C)*, 1970, 2134; R. M. Black and G. B. Gill, *Chem. Comm.*, 1970, 972.

⁸ Cf. D. Lenoir, R. Glaser, P. Mison, and P. von R. Schleyer, *J. Org. Chem.*, 1971, **36**, 1821; B. D. Cuddy, D. Grant, and M. A. McKervey, *J. Chem. Soc. (C)*, 1971, 3173.

with 96% sulphuric acid.⁹ This result fixes the position of the 8-methyl group in the ketone (9).



The location of the second methyl group followed from the observation that treatment of the ketone (9) with $\text{PCl}_5\text{-PCl}_3$ yielded a mixture of 4-chloro-6,8-dimethylprotoadamantan-4-ene (17) and 1,2-dichloro-3,7-dimethyladamantane (18); the former could be converted into the latter by the action of hot hydrochloric acid.⁸ The ^1H n.m.r. spectrum of the chloro-olefin (17) was very similar to that of 4-chloroprotoadamantan-4-ene (19),⁸ but, significantly, it lacked the 5,6-coupling present in the latter, thereby establishing (i) that the preponderant ketone (9) was 6,8-dimethylprotoadamantan-4-one and (ii) that the action of lead tetra-acetate-iodine on the alcohol (6) gave predominantly the iodo-ketone (7) (which can cyclise in only one direction). Steric effects may be responsible for the preferential formation of the iodo-ketone (7) in as much as the oxyl radical, presumed to be an intermediate in the reaction, fragments towards the bridgehead position not encumbered with a methyl group; in this arrangement steric interaction between the incipient carbon radical and an iodine molecule is minimised. To complete the picture the minor tricyclic ketone (10) was subjected to the reduction-rearrangement-oxidation sequence (10) → (14) → (15) → (16), and the final product was identified as 5,7-dimethyladamantan-2-one (16) by direct comparison with an



authentic sample obtained by oxidation of 1,3-dimethyladamantane with 96% sulphuric acid.⁹ This result established that the ketone (10) was 1,6-dimethylprotoadamantan-4-one.

Wolff-Kishner reduction of the ketone (9) furnished

⁹ R. E. Moore, B. W. Warren, and A. Schneider, *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, 1970, **15**, B43.

6,8-dimethylprotoadamantane (20) in good yield. When this hydrocarbon was exposed to bromine under conditions which resulted in complete bromination of protoadamantane (1), only 6% reaction was observed and the remainder of the starting material could be recovered. On the basis of this evidence and that cited earlier we concluded that the 6-position of protoadamantane is the most reactive in ionic bromination, in agreement with the molecular mechanics result. However, essentially complete reaction was observed when 6,8-dimethylprotoadamantane was exposed to hot bromine for 6 days. To facilitate identification, the crude product was exposed to hot aqueous dimethylformamide-hydrochloric acid whereupon partial hydrolysis occurred. Chromatography over alumina yielded two unidentified monobromides (13%), presumed to be dimethyl bromoprotoadamantanes, followed by an alcohol (55%) identified as 3,5-dimethyladamantan-1-ol (6). The preponderant product of prolonged exposure of (20) to bromine is therefore 1-bromo-3,5-dimethyladamantane. Apparently bromine is a sufficiently powerful Lewis acid to cause rearrangement of (20) to 1,3-dimethyladamantane more rapidly than direct bromination of the 1- and 3-positions. Similar behaviour was observed when attempts were made to brominate 6-methylprotoadamantane (3). This hydrocarbon, readily prepared from 6-bromoprotoadamantane (2) and methylmagnesium iodide,¹⁰ was treated with hot bromine for 6 days. The crude product was then partially hydrolysed and chromatographed over alumina, yielding a mixture of three unidentified monobromides (5%), presumed to be methylbromoprotoadamantanes, followed by traces of materials containing three bromo-substituents, and finally, 3-methyladamantan-1-ol (22) (55%).

The protoadamantane → adamantane rearrangement was also observed when protoadamantan-6-ol (21), prepared by hydrolysis of the bromide (2), was briefly exposed to 98% sulphuric acid. The product was adamantan-1-ol almost exclusively. However, in the presence of formic acid (Koch-Haaf carboxylation conditions) rearrangement of the alcohol (21) in sulphuric acid was suppressed and protoadamantan-6-carboxylic acid (22) was obtained in good yield. But when this acid was treated with 98% sulphuric acid alone for 5 h, partial rearrangement (to adamantane-1-carboxylic acid) was observed. A Ritter reaction between the alcohol (21) and acetonitrile yielded the unrearranged amide (23) which could be hydrolysed to 6-aminoprotoadamantane (24).

EXPERIMENTAL

M.p.s were determined for samples sealed in capillary tubes. Unless otherwise stated i.r. spectral data relate 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

¹⁰ Cf. E. Osawa, Z. Majerski, and P. von R. Schleyer, *J. Org. Chem.*, 1971, **36**, 205.

following columns: (A) 2 m Silicone Gum Rubber on Chromosorb W (5% w/w); (B) 2 m Silicone Nitrile Fluid (XF-1150) on Chromosorb W (10% w/w); (C) 2 m 2-Cyanoethyl Methyl Silicone on Chromosorb G (2½% w/w); (D) 50 m Apiezon L capillary. Spence type H activated alumina and Whatman SG31 silica gel were used for adsorption chromatography. Light petroleum used had b.p. 40–60°. The drying agent employed was magnesium sulphate.

Protoadamantan-4-one was prepared in 65% yield from adamantan-1-ol according to the published procedure.⁷

Protoadamantane (Tricyclo[4.3.1.0^{3,8}]decane) (1).—A solution of protoadamantan-4-one (5.0 g) and hydrazine (30 ml; 98–100%) in triethylene glycol (250 ml) containing glacial acetic acid (15 ml) was heated at 80–90° under nitrogen for 24 h. The flask was then fitted with a flash head attached to a condenser with a receiving flask cooled in an ice-bath. Potassium hydroxide (50 g) was added and the mixture was heated at 190–210° for 6 h. During this time a sublimate collected in the flash head. After cooling, the apparatus was washed with pentane and water. The organic layer and pentane extracts of the aqueous solution were combined, washed with water and aqueous sodium chloride, then dried. The solution was concentrated by careful distillation through a fractionation column and the residue was sublimed, yielding the hydrocarbon (4.3 g, 94%), m.p. 205–206° (lit.,¹ 210.5–212.0°).

6-Bromoprotoadamantane (6-Bromotricyclo[4.3.1.0^{3,8}]decane) (2).—A mixture of protoadamantane (2.0 g) and bromine (20 ml) was heated under reflux with stirring for 5 h. The cooled mixture was dissolved in carbon tetrachloride (20 ml) and poured into water (200 ml). After removal of the excess of bromine with sodium disulphite the organic layer and dichloromethane extracts (4 × 25 ml) of the aqueous layer were combined, washed with water, and dried. Evaporation left a solid (3.2 g, 100%) which was shown by g.l.c. analysis on column (B) at 120° to be a mixture of one major (95%) and several minor components (5%). Sublimation of the product followed by crystallisation from ethanol gave the *bromide*, m.p. 80–81° (Found: C, 55.6; H, 7.3; Br, 37.2. C₁₀H₁₆Br requires C, 55.8; H, 6.95; Br, 37.2%), τ (CDCl₃) 7.30–7.65 (3H, m, bridgehead) and 7.65–8.67 (12H, m), *m/e* 215 (1%, M⁺), 136 (12), 135 (100), 107 (16), 105 (2), 93 (18), 91 (7), 79 (20), 67 (11), 41 (9), and 39 (7).

Bromination of Protoadamantane at Room Temperature.—A mixture of protoadamantane and bromine was stirred at room temperature for 5 h then worked up as described above, yielding a mixture of 6-bromoprotoadamantane (70%) and unchanged hydrocarbon (30%).

Hydrogenolytic Debromination of 6-Bromoprotoadamantane.—A mixture of the bromide (0.1 g) in methanol (5 ml) containing potassium hydroxide (0.2 g) and 5% palladium-carbon (25 mg) was exposed to hydrogen at atmospheric pressure for 5 h. The mixture was filtered and the filtrate was diluted with water (20 ml) and extracted with dichloromethane (3 × 15 ml). The extract was washed with water, dried, and evaporated, yielding protoadamantane (52 mg, 86%).

Protoadamantan-6-ol (6).—A solution of 6-bromoprotoadamantane (3.0 g) in dimethylformamide (7.5 ml) containing hydrochloric acid (8 ml; 0.67N) was stirred and heated at 105–107° for 1.5 h. The cooled solution was poured into water (50 ml) and extracted with dichloromethane (3 × 25 ml). The extract was washed with water, dried, and evaporated to yield the *alcohol* (1.92 g, 90%), m.p.

235–236° (after sublimation and crystallisation from light petroleum) (Found: C, 79.15; H, 10.35. C₁₀H₁₆O requires C, 78.95; H, 10.5%), τ [(CD₃)₂SO] 5.85 (1H, s, OH), 7.70–8.10br (3H, m, bridgehead), and 8.10–8.90 (12H, m), *m/e* 152 (38%, M⁺), 151 (2), 134 (4), 109 (42), 96 (33), 95 (100), 81 (11), 79 (13), 67 (13), 41 (22), and 39 (15).

Rearrangement of Protoadamantan-6-ol in Sulphuric Acid.—A solution of the alcohol (0.1 g) in 96% sulphuric acid (15 ml) was stirred at room temperature for 20 min then poured onto ice and extracted with dichloromethane (3 × 15 ml). The extract was washed with water, dried, and evaporated yielding a solid (0.09 g). Crystallisation from light petroleum yielded adamantan-1-ol, m.p. 286–287° (lit.,¹¹ 287.2–288.5°).

Protoadamantane-6-carboxylic Acid (22).—A solution of protoadamantan-6-ol (0.2 g) in formic acid (3 ml, 98%) was added dropwise with stirring to sulphuric acid (25 ml; 98%) at 0° during 1½ h. The mixture was stirred for a further 1 h at 0° then poured onto ice and extracted with carbon tetrachloride (3 × 50 ml). The extract was shaken with aqueous potassium hydroxide (2 × 20 ml; 1N) and the alkaline solution was made strongly acidic with 5N-hydrochloric acid. The precipitated acid was taken up in dichloromethane (2 × 50 ml) and the extract was washed with water and dried. Evaporation gave the *acid* (0.18 g, 74%), m.p. 89–90° (from aqueous methanol) (Found: C, 73.15; H, 8.55. C₁₁H₁₆O₂ requires C, 73.35; H, 8.9%), τ (CDCl₃) –0.80br (1H, s, CO₂H), 7.60–7.86 (3H, m, bridgehead), and 7.86–8.80 (12H, m), *m/e* 180 (52%, M⁺), 136 (14), 135 (100), 93 (17), 81 (7), 79 (17), 77 (7), 67 (10), and 41 (10). G.l.c. analysis of the methyl ester on column (B) at 130° showed that the product was *ca.* 99% pure.

Carboxylation of Protoadamantan-6-ol at Room Temperature.—The alcohol was carboxylated exactly as described above except that the sulphuric acid solution was kept at 23° throughout the reaction. Work-up gave protoadamantane-6-carboxylic acid (69% yield; *ca.* 99% purity).

Rearrangement of Protoadamantane-6-carboxylic Acid.—A solution of the acid (0.1 g) in 98% sulphuric acid (15 ml) was stirred at room temperature for 5 h. Work-up as described above gave a product (0.04 g) which after esterification with methanol was shown by g.l.c. analysis on column (B) at 130° to consist of starting material (73%) and adamantane-1-carboxylic acid (27%), identified by direct comparison with an authentic sample.

N-Protoadamantan-6-ylacetamide (23).—To a solution of protoadamantan-6-ol (1.0 g) in carbon tetrachloride (15 ml) containing acetonitrile (5 ml) at 0° was added sulphuric acid (15 ml; 98%) during 1 h. The mixture was stirred for an additional 1 h at 0° then poured onto ice and extracted with dichloromethane (3 × 25 ml). The extract was washed with water, dried, and evaporated, yielding a solid (1.12 g) which was placed on a column of silica gel. Elution with light petroleum-ether (6 : 4) afforded starting material (0.22 g, 22%). Further elution with light petroleum-ether (4 : 6) afforded the *amide* (0.82 g, 62%), m.p. 99.5–100° (from light petroleum) (Found: C, 74.4; H, 9.9; N, 7.15. C₁₂H₁₉NO requires C, 74.6; H, 9.85; N, 7.15%), τ (CDCl₃) 4.59br (1H, s, NH), 7.62–8.62 (15H, m), and 8.12 (3H, s, CH₃), *m/e* 193 (69%, M⁺), 151 (15), 150 (38), 136 (85), 135 (31), 134 (100), 122 (15), 109 (38), 95 (69), 94 (62), 81 (46), 57 (69), and 41 (62).

¹¹ S. Landa, S. Kriebel, and E. Knobloch, *Chem. listy*, 1954, **48**, 61.

Protoadamantan-6-ylammonium Chloride (24).—A solution of the amide (23) (1.0 g) in diethylene glycol (10 ml) containing sodium hydroxide (1.0 g) was heated under reflux for 12 h. The cooled solution was poured into water (20 ml) and extracted with dichloromethane (3 × 25 ml). The extract was washed with water, dried, and evaporated, yielding a solid (0.7 g). The product was taken up in dry ether and hydrogen chloride gas was passed into the solution for 10 min. Filtration yielded the *hydrochloride*, m.p. 313° (by differential thermal analysis) (Found: C, 64.05; H, 9.8; N, 8.15. $C_{10}H_{18}ClN$ requires C, 64.0; H, 9.6; N, 7.45%), *m/e* 151 (20%, M^+ of amine), 109 (10), 108 (50), 95 (50), 94 (100), 91 (10), 77 (15), and 57 (45).

Attempted hydrolysis of the amide with potassium hydroxide in ethanol yielded protoadamantan-6-ol quantitatively, whereas use of hot concentrated hydrochloric acid produced 6-chloroprotoadamantane as the sole product.

6,8-Dimethylprotoadamantan-4-one (9) and *1,6-Dimethylprotoadamantan-4-one* (10).—A mixture of 3,5-dimethyladamantan-1-ol (6) (9.4 g), lead tetra-acetate (35.0 g; dried at 10 mmHg immediately before use), and iodine (20.0 g) in dry benzene (200 ml) was heated at 60–65° for 3 h with vigorous stirring. The cooled mixture was filtered and the filtrate and benzene (50 ml) and ether (50 ml) washings of the solids were combined, washed with aqueous sodium disulphite (3 × 50 ml) and water, and dried. Evaporation at reduced pressure left an oil. This product (11.2 g) was dissolved in methanol (40 ml) containing sodium hydroxide (4.0 g) and the solution was stirred at room temperature overnight, then diluted with water (150 ml), and extracted with dichloromethane (6 × 50 ml). The extract was washed with water, dried, and evaporated, yielding an oil (7.6 g) which was shown by g.l.c. analysis on column (B) at 180° to consist of starting material (60%) and product (40%). The product contained two components in the ratio *ca.* 9:1. The entire mixture was taken up in light petroleum and placed on a column of activated alumina (1500 g). Elution with ether–light petroleum (7:3) gave *6,8-dimethylprotoadamantan-4-one* (2.5 g, 27%), b.p. 48–49° at 0.15 mmHg (Found: C, 88.4; H, 10.3. $C_{12}H_{18}O$ requires C, 88.9; H, 10.1%), τ (CDCl₃) 7.31–8.73 (12H, m), 8.89 (3H, s, CH₃), and 9.03 (3H, s, CH₃), *m/e* 178 (57%, M^+), 163 (26), 145 (14), 135 (14), 120 (100), 93 (43), and 43 (57); 2,4-dinitrophenylhydrazone, m.p. 162–163° (from ethanol). Further elution with ether–light petroleum (7:3) gave a mixture of the ketone (9) and *1,6-dimethylprotoadamantan-4-one* (0.5 g, 6.4%) in the ratio 1:4. Preparative g.l.c. on column (B) at 180° yielded the minor ketone of *ca.* 98% purity, τ (CDCl₃) 7.20–8.80 (12H, m), 8.93 (3H, s, CH₃), and 9.03 (3H, s, CH₃), *m/e* 178 (83%, M^+), 163 (50), 145 (16), 135 (17), 120 (100), 107 (53), 93 (37), and 41 (27); 2,4-dinitrophenylhydrazone, m.p. 171–172° (from ethanol) (Found: C, 60.4; H, 6.4; N, 15.6. $C_{18}H_{22}N_4O_4$ requires C, 60.35; H, 6.15; N, 15.65%). Further elution of the column with ether–methanol (95:5) gave the starting alcohol (3.2 g).

6,8-Dimethylprotoadamantane (20).—When subjected to the Wolff–Kishner procedure described for the preparation of protoadamantane, *6,8-dimethylprotoadamantan-4-one* (5.0 g) yielded the *hydrocarbon* (20) (4.0 g, 87%), b.p. 67° at 12 mmHg (Found: C, 87.9; H, 12.25. $C_{12}H_{20}$ requires C, 87.7; H, 12.1%).

Rearrangement of 6,8-Dimethylprotoadamantan-4-one (9).—A solution of the ketone (0.2 g) in ether (5 ml) was added dropwise to a stirred slurry of lithium aluminium hydride

(0.08 g) in ether (5 ml). The mixture was stirred for 1 h and water was then added dropwise. The ether layer and ethereal extracts (3 × 20 ml) of the aqueous layer were combined, washed with water, dried, and concentrated, yielding a crystalline solid (0.2 g). G.l.c. analysis on column (C) at 150° revealed the presence of two components, ratio 3:7, to which were assigned the epimeric alcohol structures (11).

The entire product was treated with 25% sulphuric acid (10 ml) at 110° for 4 h. The cooled solution was diluted with water (50 ml) and extracted with ether (3 × 25 ml). The extract was washed with water, dried, and concentrated, yielding a solid (0.10 g, 50%) which was shown by g.l.c. analysis on column (C) at 150° to consist largely (94%) of one component, assigned structure (12).

To a solution of the product (0.10 g) in acetone (5 ml) was added Jones reagent until the first permanent red colour appeared. The solution was stirred for 15 min and several drops of isopropyl alcohol were added. Water (20 ml) and ether (10 ml) were added and the ether layer and ethereal extracts of the aqueous layer were combined, washed with water, dried, and concentrated, yielding *1,5-dimethyladamantan-2-one* (13) (0.08 g, 80%) of *ca.* 95% purity. The product was identified by direct comparison with an authentic sample prepared by oxidation of *1,3-dimethyladamantane* in 96% sulphuric acid.

Rearrangement of 1,6-Dimethylprotoadamantan-4-one (10).—The ketone was subjected to the same procedure as that described for the ketone (9), and the major product (82%) was identified as *5,7-dimethyladamantan-2-one* (16) by direct comparison with an authentic sample prepared by oxidation of *1,3-dimethyladamantane* in 96% sulphuric acid.

4-Chloro-6,8-dimethylprotoadamantan-4-one (17).—A mixture of *6,8-dimethylprotoadamantan-4-one* (1.5 g), phosphorus trichloride (6 ml), and phosphorus pentachloride (5.0 g) was stirred at 0° for 10 h and then was allowed to warm to room temperature. The mixture was poured onto ice and extracted with dichloromethane (3 × 50 ml). The extract was washed with water (3 × 100 ml), dried, and concentrated, yielding an oil. The product was placed on a column of silica gel (300 g). Elution with light petroleum gave the *chloride* (0.9 g, 53%), b.p. 42° at 0.2 mmHg (Found: C, 73.55; H, 8.9; Cl, 18.2. $C_{12}H_{17}Cl$ requires C, 73.55; H, 8.65; Cl, 18.05%), τ (CDCl₃) 4.11–4.21 (1H, d, $J_{5,3}$ 2 Hz, vinylic), 7.50–8.66 (10H, m), 8.81 (3H, s), and 9.03 (3H, s), *m/e* 198 (16%, M^+), 197 (37, M^+), 181 (21), 161 (100), 141 (21), 140 (32), 119 (42), 105 (95), and 91 (47). Further elution of the column gave a small amount of dichloride (18).

1,2-Dichloro-3,7-dimethyladamantane (18).—The crude product obtained from chlorination of *6,8-dimethylprotoadamantan-4-one* (9) (0.5 g) as above was heated under reflux in concentrated hydrochloric acid (50 ml) for 16 h. The cooled solution was diluted with water and extracted with dichloromethane (4 × 25 ml). The extract was washed with water, dried, and evaporated, yielding an oil which was placed on a column of silica gel (200 g). Elution with light petroleum gave a small amount of material which was discarded. Further elution with light petroleum–ether (85:18) gave the *dichloride* (0.3 g, 50%), b.p. 98° at 1.0 mmHg (Found: C, 61.85; H, 7.85; Cl, 30.3. $C_{12}H_{18}Cl_2$ requires C, 61.8; H, 7.7; Cl, 30.45%), τ (CDCl₃) 6.00 (1H, s), 7.50–8.81 (11H, m), 8.95 (3H, s), and 9.10 (3H, s), *m/e* 234 (5%, M^+), 232 (7, M^+), 199 (38), 197 (100), 161 (17), 107 (38), and 77 (12).

6-Methylprotoadamantane (3).—A solution of methylmagnesium iodide [from methyl iodide (23 g) and magnesium (4 g)] in ether (40 ml) was concentrated at reduced pressure at 20°. The resulting thick paste was transferred under nitrogen to 1 l screw-cap 'Coca Cola' bottle. 6-Bromoprotoadamantane (2.0 g) was added and the bottle was then flushed with nitrogen, closed tightly and heated, with stirring, at 98–99° for 30 min. The cooled mixture was diluted with light petroleum (30 ml) and water (30 ml) dropwise, and the layers were separated. The organic layer and light petroleum extracts (3 × 20 ml) of the aqueous layer were combined, washed with water, and dried. Careful removal of the solvent at atmospheric pressure yielded the *hydrocarbon* (1.4 g, 99%), m.p. 65–68° after sublimation at atmospheric pressure (Found: C, 87.9; H, 12.2. C₁₁H₁₈ requires C, 88.0; H, 12.0%), *m/e* 150 (90%, M⁺), 136 (10), 135 (90), 121 (10), 108 (40), 96 (30), 95 (50), 93 (100), 91 (10), 81 (20), 79 (50), 67 (40), 41 (40), and 39 (20).

Bromination of 6,8-Dimethylprotoadamantane (20).—(a) A mixture of the hydrocarbon (0.05 g) and bromine (3 ml) was heated under reflux for 5 h. The cooled mixture was dissolved in carbon tetrachloride (20 ml) and poured into water (20 ml). After removal of the excess of bromine with sodium disulphite the organic layer and dichloromethane extracts (2 × 5 ml) of the aqueous layer were combined, washed with water, and dried. Removal of the solvent left an oil (0.05 g) which was shown by g.l.c. analysis on column (B) at 125° to be a mixture of two components in the ratio 94 : 6. The major component was identified as starting material by its retention time and by co-injection with an authentic sample.

(b) A mixture of the hydrocarbon (0.5 g) and bromine (10 ml) was heated under reflux for 6 days and then was processed as described under (a), yielding an oil (0.73 g). The crude product was taken up in dimethylformamide (5 ml) and hydrochloric acid (0.67N; 5 ml) and heated at 110° with stirring for 1.5 h. The cooled solution was diluted with water and extracted with dichloromethane (5 × 20 ml). The extract was washed with water, dried, and concentrated, yielding a solid (0.62 g) which was taken up in light petroleum and placed on a column of alumina (150 g). Elution with light petroleum gave a mixture of two compounds (0.1 g), presumed to be monobromodimethylprotoadamantanes from mass spectral analysis. Further elution with light petroleum–ether (90 : 10) gave an unidentified material (0.07 g). Elution with ether–methanol (99 : 1) gave 3,5-dimethyladamantan-1-ol (6) ⁶ (0.3 g, 55%).

Bromination of 6-Methylprotoadamantane (3).—A mixture of the hydrocarbon (0.75 g) and bromine (15 ml) was heated under reflux for 6 days and then was processed and hydrolysed as described in (b) above. The entire crude product was placed on a column of alumina (150 g). Elution with light petroleum gave a mixture of three components (0.08 g, 5%) presumed to be monobromomethylprotoadamantanes from mass spectral analysis. Further elution with light petroleum gave an unidentified material (0.12 g) containing three bromo-substituents. Elution with ether gave 3-methyladamantan-1-ol ⁶ (0.45 g, 55%).

We thank the S.R.C. for a postdoctoral fellowship to A. K.

[4/1203 Received, 20th June, 1974]