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MECHANISM OF THE "ABNORMAL" PYROLYTIC 1, 3-ELIMINATION OF 2-ADAMANTYL METHANE SULPHONATE

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Abstract—Pyrolysis of *syn*-2-adamantyl-4-d$_1$ methane-sulphonate **8** in a silanised pyrex reactor leads to protoadamantene with about 0.25 atoms ^{2}H at each of C-2, -7 and -9 and little labelling elsewhere according to ^{2}H and ^{13}C NMR. This indicates complete epimerisation of **8** before elimination. In the concurrently formed dehydroadamantane, unequal partitioning of label between positions C-6/8, -9 and -10 suggests only limited epimerisation before elimination. Pyrolysis of the 4,4-dideuteriated sulphonate **11**, gave analogous results. The syntheses of **8** and **11** are described and the relevance of the analytical results to possible pyrolysis mechanisms is considered.

Pyrolysis of 2-adamantyl methanesulphonate **1** or its toluene-*p*-sulphonate **2** at 450–560° and 0.05–0.5 Torr in a Monel-type reactor affords a 2 : 3 mixture of protoadamantene **3** and 2,4-dehydroadamantane **4** in 95% yield.[1] The reaction is preparatively useful because it can be operated on a 10–50 g scale and because the two major hydrocarbons are readily separable by column chromatography. Formally, **3** and **4** can be regarded as being the products of homoretroene reactions (see **5** and **6**), to be compared with the formal retroene mechanism of normal ester pyrolysis (see **7**). It is generally accepted that the latter proceeds *via* a cyclic transition state (as **7**),[2–4] although the possible involvement of ionic intermediates has repeatedly surfaced in the literature.[5–7] Considerable efforts have been made[4,8,9] to gain an insight into the nature of the transition state for ester pyrolysis. We and others[10–13] have investigated analogous problems for the homo-retroene reaction and we have previously published[14] our findings in the noradamantane and diamantane series. We report here on the mechanism of the "abnormal" pyrolytic 1,3-elimination of 2-adamantyl methanesulphonate **1**. In particular, this work set out to establish whether C$_\gamma$-H bond cleavage was subject to a deuterium isotope effect. Detection of such an effect would indicate intervention of a cyclic concerted process.[15,16] A decision should be obtainable in principle from an intramolecular competition experiment[17,18] in which the *syn*-2-adamantyl-4-d$_1$ methane-sulphonate **8** is pyrolysed. The choice between the geometrically equivalent H$_\gamma$ and D$_\gamma$ atoms (see **8**) leading to products **4** or **9** and **3** or **10** will be governed by the isotope effect, whose magnitude should be available directly for each reaction from the ratios of **9** : **10** and **11** : **12**. In practice these should be readily obtainable from g. c.-m. s. analysis of the pyrolysis products. However, a more searching procedure would be analysis of the separated products by ^{2}H and ^{13}C NMR spectroscopy, since this will reveal not only the *proportion* of ^{2}H : ^{1}H in each product, but also whether ^{2}H is *located* at the sites predicted by the proposed mechanism.

We first describe the synthesis of the specifically deuteriated esters **8**, **11** and **12**, then discuss the NMR analysis of the pyrolysis products obtained from them and finally draw some conclusions regarding the mechanism of the pyrolysis process.

Synthesis of the deuteriated 2-adamantyl methanesulphonates **8**, **11** *and* **12**

Our initial approach to the synthesis of **8** was to proceed by deuteriolysis (LAD) of the diol-monotoluenesulphonate **13**. Baeyer–Villiger oxidation of adamantan-2-one and rearrangement of the resulting lactone **14** with 50% sulphuric acid[19] afforded the epimeric ketols **15** and **16** (8 : 1) (15% unchanged **14**). Reduction of the major ketol **15** with LAH[19] OR Li/NH$_3$ gave diols **17** and **18** (19 : 1[19] or 99 :1); the minor ketol **16** gave with LAH diols **18** and **19** (3 : 2). Jones oxidation of the ketol mixture afforded adamantan-2,4-dione, reduction of which with LAH furnished the diols **17–19** (2 : 2 : 1), while Meerwein–Ponndorf–Verley reduction gave different proportions (2 : 7 : 3) of the same diols. Equilibration of the diols with aluminium isopropoxide disappointingly furnished more than 95% of **17**. Attempts to separate the required unsymmetrical diol **18** from **17** and **19** proved troublesome. The diaxial diol **17** was readily separated by either column or preparative layer chromatography. However, **18** and **19** were not separable and neither were their diacetates or di-3,5-dinitrobenzoates. One of the

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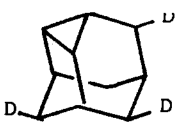
D at C-5; the latter value was obtained by comparison of the intergrals for the C-5 (δ 136.7) and C-4 (δ 136.2) absorptions.

Discussions of the spectra for the dehydroadamantanes **46** and **47** obtained concurrently with the protoadamantenes **44** and **45** must be prefaced by the caution that these compounds could not be separated from deuterioadamantane formed during the pyrolyses. Certain features of both the qualitative and quantitative analyses of **46** and **47** were thereby unavoidably obscured.

In the ^{13}C spectrum of **46** (Fig. 5), the absorptions for C-6/8 (δ 33.0), C-9 (δ 52.0) and C-10 (δ 28.4) contain the characteristic triplets for carbon bearing deuterium ($J_{CD} \sim 20$ Hz, $\Delta\delta - 0.4$), as does the pattern for the methylene carbons of adamantane (δ 37.5). Again, location of deuterium at these major sites in **46** is corroborated by secondary effects at geminal and vicinal carbons, e.g. C-1/5 (δ 32.1), C-2/4 (δ 23.6), C-3 (δ 20.3) and C-7 (δ 26.8). A notable feature, apparent from both qualitative and quantitative analyses, is that deuterium is not equally distributed over the labelled sites, C-6/8, -9 and -10. The C-D triplet is most pronounced for C-9, indicating significantly more D at C-9 than at either C-6/8 or -10. This inequality is further borne out by comparing the intensity of the isotope-shifted components of C-1/5 (*gem* to C-9 and C-6/8) with those for C-3 (gem to C-10) and C-7 (*gem* to C-10 and C-6/8). Broadening of the C-6/8 signal (*vicinal* and *antiperiplanar* to C-9 and C-10) is more marked than for C-2/4 (*vic* and *antipp* to C-10) or C-9 (*vic* and *antipp* to C-6/8). Integration of the methine signals (C-1/5, -2/4, -3 and -7) indicated the absence of deuterium at these positions. For the methylene signals accurate integration is difficult because (a) the methine carbon of adamantane overlaps C-10; (b) adamantane bears D at the methylene carbon, hence it is difficult to make an allowance for its contribution to C-10; (c) each methylene site of dehydroadamantane bears D, thus a direct measurement of intensity for CH_2 is impossible. However, a crude estimate would place 2-3 times as much D at C-9 as at C-6/8 and C-10.



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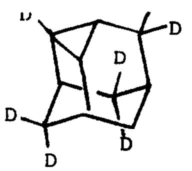

47

The ^{13}C spectrum of dehydroadamantane-d_2 **47** (Fig. 6) exhibits some notable supporting features. The C-3 signal has two isotope-shifted components arising from geminal deuterium at C-2/4 and C-10. Strikingly, the less shifted component, from monodeuteration at C-2/4, is more than twice as intense as the more shifted component (from dideuteration at C-10), clearly indicating higher D content at C-2/4 than at C-10. The reverse situation obtains for C-1/5 geminal to dideuteriated C-6/8 and -9 with mono-deuteration at C-2/4. The C-7 absorption contains only a doubly-shifted component, which is more intense than that for C-3.

CONCLUSIONS

A number of mechanistic conclusions can be justifiably drawn from the foregoing data in spite of their numerical imprecision.

(1) Formation of dehydroadamantane *via* a carbenoid intermediate[11] is excluded for the present experiments, since there was virtually no loss of D in dehydroadamantene or protoadamantene formed from 2-adamantyl-2-d_1 methane-sulphonate (ms.).

(2) Protoadamantene cannot be formed via dehydroadamantane by a [$_\sigma2 + _\sigma2$] cyclo-reversion process.[24] This has already been demonstrated for pyrolysis of

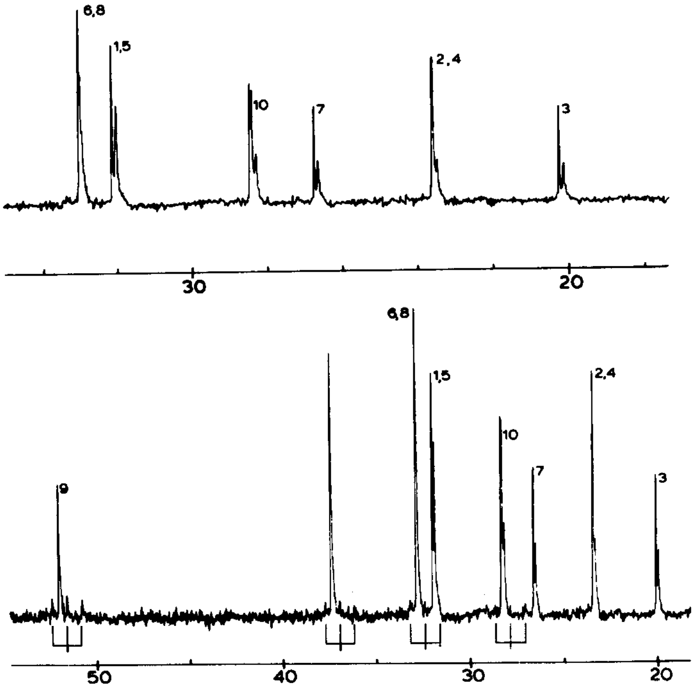

Fig. 5. 25.2 MHz ^{13}C NMR spectrum of dehydroadamantane (**46**).

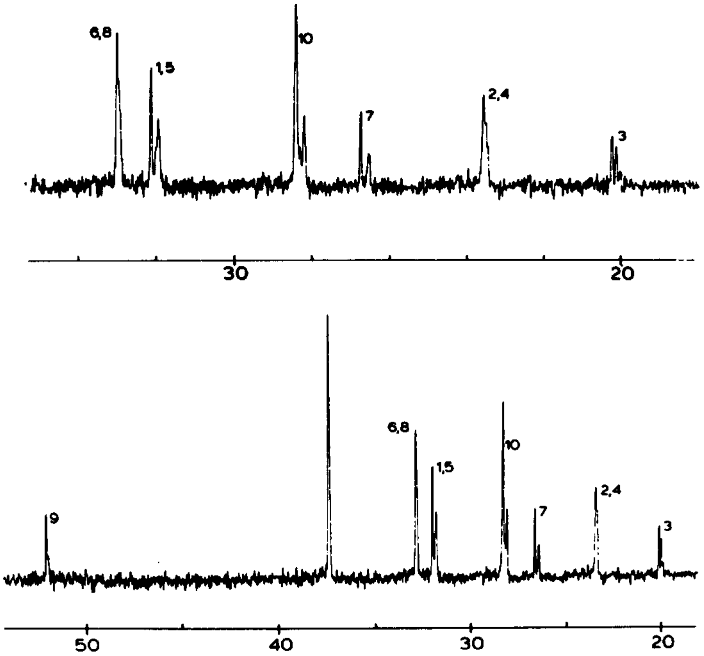

Fig. 6. 25.2 MHz ^{13}C NMR spectrum of dehydroadamantane (47).

2-adamantyl-2-d_1 methanesulphonate in the gold reactor[14] and is borne out in the present experiments with *syn*-4-d_1- and 4,4-d_2-labelled adamantyl methanesulphonates. In particular, such a process would require the presence of D labels in protoadamantene at C-2, -5 and -10, where there are none.

(3) Formation of protoadamantenes **44** and **45** must be preceded by fast epimerisation of the methanesulphonate residue, presumably *via* an ion pair. Thus approximately 0.25 atoms D is located at each of the positions C-2, -7 and -9, as predicted by a concerted process of the kind previously proposed,[1] and, according to both the ^{2}H and ^{13}H NMR spectra, very little ($<5\%$ D) is located elsewhere.

(4) By contrast with protoadamantene, formation of dehydroadamantane is preceded by less epimerisation. Not surprisingly, since molecular reorganisation in the transition state leading to dehydroadamantane is less extensive, the rate of its formation competes favourably with epimersisation and in fact a preponderance of product is formed, presumably concertedly, from the original *syn*-4d_1-ester, rather than from the *anti*-epimer.

EXPERIMENTAL

General. The following instruments were used: IR Perkin-Elmer 225 and 257; ^{1}H NMR, Varian T60 and HA100; mass spectrometry, A. E.I. MS9 for high resolution and MS12 for low resolution spectra; g.c.m.s., LKB 900A; glc, Perkin-Elmer F11. Unless otherwise stated, solvents for spectroscopy were: IR, CCl_4; NMR, $CDCl_3$ with internal tetramethylsilane standard. Merck Kieselgel HF_{254} was used for tlc and Woelm alumina or Koch-Light silica gel 200–300 mesh, deactivated to the appropriate Brockmann grade, for column chromatography. All m. ps recorded are uncorrected.

^{2}H and ^{13}C spectra. A Varian XL-100-15 system operating in the Fourier transform mode at 15.4 and 25.2 MHz, respectively, was employed with square-wave modulated proton decoupling at 100 MHz. The samples were dissolved in CCl_4/C_6F_6 (3 : 1) to provide a ^{19}F lock signal; the same solutions were utilized for both ^{2}H and ^{13}C spectra to avoid reisolation of the solutes which were available in relatively small amounts. The shielding data, differing slightly from those reported previously[14] because of the solvent change, are judged to have precisions of ± 0.05 ppm while the J_{CD} values are ± 1 Hz. For the ^{2}H spectra, 1500–2500 transients with sweep widths of 500 Hz in 8 K data points were collected using a 30° flip angle and an acquisition time of 4 s. For the ^{13}C spectra, spectral widths of 1250 Hz (sp^3 region only) in 8 K data points with a 22° flip angle and a 6 s repetition rate were employed. At least 12 K transients were obtained for **44** and **45** (60 and 70 mg, respectively) while >40 K scans were collected for **46** and **47** (40 and 20 mg, respectively). A comparable sample of normal protoadamantene was examined under the same operating conditions to calibrate the integration results. Under these conditions, the intensities of the methylene ^{13}C signals were $25 \pm 2\%$ greater than those for methine carbons. Careful integration of the ^{13}C spectra for **44** and **45** provided the data discussed in the text. Corresponding data for **46** and **47** were obtained but the precision was reduced for the reasons given in the text.

Pyrolysis experiments. Initial test pyrolyses were carried out with 2-adamantyl-2-d_1 methanesulphonate (**12**) in a previously described[25] flow reactor (carrier gas helium, 1 bar), modified for preparative scale work. For this purpose a solution of **12** in toluene was injected, evaporated and transferred by helium to the electrically heated pyrex reactor (contact time 20 sec). The pyrolysate was condensed in a cold trap. The redbrown condensate was worked up by treatment with isopentane, filtration over aluminum oxide (basic, grade 2) and concentration, and analysed by glc (1.5 m 3% SE 30, column temp. 60°). Since a mixture of four products in a total yield of only 20% was obtained, the pyrolysis was repeated under reduced pressure in a redesigned flow reactor.

The assembly (Fig. 7) consisted of a distillation flask connected by a ball joint to the coiled reactor made from Pyrex glass tubing (total length 95 cm; e.d. 6 mm, i.d. 4 mm) connected in turn to a cold trap. The reactor itself was enclosed in a steel cylinder filled with copper powder to provide good thermal conduction. The whole unit was heated electrically by a heating jacket wrapped around the outside. The temperature was measured at the centre of the reactor coil with a Pt-100 resistance thermometer. The volume of the pyrex reactor coil was 12 ml. For purification and

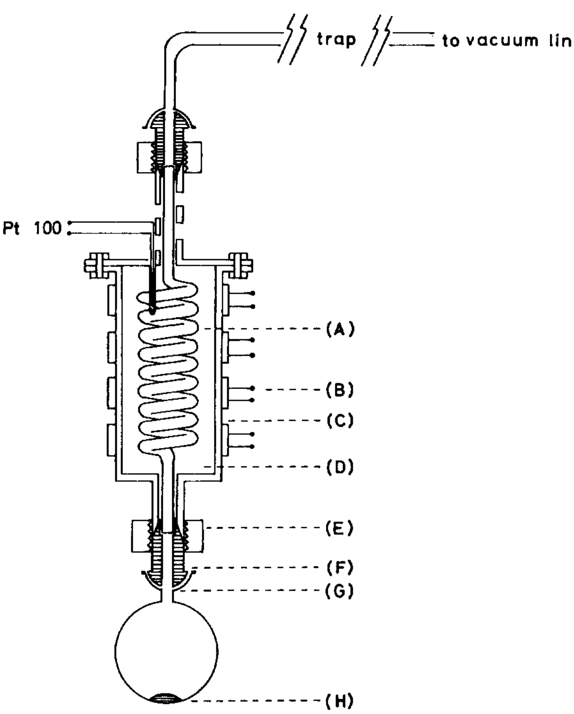

Fig. 7. Flow reactor for the gas phase pyrolysis of adamantyl methane sulphonates: (A), pyrex reactor coil; (B), electrical heating coils; (C), stainless steel cylinder; (D), copper powder filling; (E), connecting screw cap; (F), PTFE ball joint; (G), flask with ball joint; (H), sample to be pyrolised.

deactivation the pyrex coil was rinsed with AR acetone (250 ml), dried by passing a stream of air for 5 min at 450° washed with aqueous Na_2HPO_4 (250 ml), carefully rinsed with distilled water, dried again and then silanised twice with portions (100 ml) of bis(trimethylsilyl) acetamide. Finally 1 ml of cyclohexane was pyrolyzed at 500°. The silylation procedure was repeated prior to each pyrolysis run.

In a typical vacuum pyrolysis experiment (0.01 torr) up to 300 mg of the appropriate adamantyl methanesulphonate **12**, **8** or **11** was sublimed into the hot zone during 1 hr by heating the distillation flask in an oil bath at 180°. The pyrolysate was worked up as described above. Yields of crude hydrocarbon mixture were approx. 60%.

Analytical glc on 3% SE30 (1.5 m, 60°) showed two peaks: (protoadamantene + adamantane) and dehydroadamantane in the ratio 8 : 1. The combined dehydroadamantane + adamantane fraction obtained from preparative chromatography over $AgNO_3$-Al_2O_3 (see below) was separable into its components by analytical glc on 5% Dexoil 300 on 80–100 Gaschrom Q (1.3 m, 90°). This showed the ratio of dehydroadamantane to adamantane to be 3 : 2. The hydrocarbon fraction from each pyrolysis was separated into saturated (dehydroadamantane + adamantane) and unsaturated (protoadamantene) fractions on $AgNO_3$-Al_2O_3 as previously described.[1] The saturated fraction was used for the NMR experiments without further separation.

4-Oxohomoadamantan-5-one **14** *from adamantanone.* Adamantanone (12.0 g; Aldrich Chemical Co. Ltd.) was converted into 4-oxohomoadamantan-5-one **14** by the method Faulkner and McKervey.[19] Yield 12.2 g, m.p. 284–286° (sublimation) (Lit.[19] 286–289°), ν_{max} 1734, 1723, 1264, 1169, and 1083 cm^{-1}, δ 4.45 (1H, m), 3.04 (1H, m), and 1.64–2.16 (12H, m), *m/e* (relative intensity) 166 (2, M^+), 122(18), and 80(100).

Conversion of 4-oxohomoadamantan-5-one **14** *into 4-hydroxyadamantan-2-ones* **15** *and* **16**. 4-Oxohomoadamantan-5-one **14** (12.0 g) was rearranged with 50% v/v sulphuric acid, as described by Faulkner and McKervey.[19] Chromatography over silica gel (100 g) and elution with light petroleum-acetone (10 : 1) gave the starting material **16** (1.8 g) followed by 4*e*-hydroxyadamantan-2-one **16** (0.8 g), m.p. 324–332° (sublimation), (Lit.[19] 320–322°), ν_{max} 3632, 3450 (broad), and 1732 cm^{-1}, δ 3.97 (1H, m) 2.60(1H, m), 2.48(1H, m), and 1.52–2.40 (1H, m) *m/e* (relative intensity) 166 (32, M^+), 148 (16), 138 (53), 96 (76), and 79 (100). Further elution gave 4*a*-hydroxyadamantan-2-one **15** (6.2 g), m.p. 321–329° (sublimation), (Lit. 316–320°), ν_{max} 3622, 3510 (broad), 1755, and 1715 cm^{-1}, δ 4.28 (1H, m), 2.65 (1H, m), 2.48(1H, m), and 1.74–2.50 (10H, m), *m/e* (relative intensity) 166 (20, M^+), 148 (18), 138 (31), 96 (44), and 79 (100).

Lithium-ammonia reduction of 4a-hydroxyadamantan-2-one **15**. To a stirred slurry of lithium (0.03 g) in refluxing ammonia (distilled from sodium; 20 ml) was added a solution of **15** (0.05 g) in ether (10 ml). After stirring the reaction mixture under reflux for 1 hr, solid ammonium chloride (0.6 g) was added. The ammonia was evaporated and the residue extracted with ether. Evaporation of the ethereal extract to dryness gave a solid (0.03 g) which was shown by glc analysis of the bistrimethylsilyl ether and diacetate derivatives to contain **17** and **18** in the ratio 99 : 1.

Lithium aluminium hydride reduction of 4e-hydroxyadamantan-2-one **16**. Lithium aluminium hydride (*ca.* 0.002 g) was added to a stirred solution of **16** (0.01 g) in ether (5 ml). The mixture was boiled under reflux overnight. The usual work-up gave a solid (0.008 g) which was shown by glc analysis of the bistrimethylsilyl ether and diacetate derivatives to contain **18** and **19** in the ratio of 3 : 2.

Adamantan-2,4-dione. A mixture of **15** and **16** (4.8 g; 5 : 1) in acetone (100 ml) was treated dropwise with Jones reagent until the first permanent red colour appeared. The usual work-up afforded the dione (4 g), m.p. 292–294° (sublimation), (Lit. 280–282°) ν_{max} ($CHCl_3$) 1780 and 1708 cm^{-1}, δ 3.37 (1H, m), 2.77 (1H, m), 2.40 (2H, m) and 1.62–2.62 (7H, m), *m/e* (relative intensity) 164(84, M^+), 136 (19), 118 (30), 108 (26), 92 (61), and 79 (100). (Found: C, 73.45; H, 7.6. Calc. for $C_{10}H_{12}O_2$ C, 73.15; H, 7.35%).

Lithium aluminium hydride reduction of adamantane-2,4-dione. To a stirred solution of the dione (4 g) in ether (250 ml), was added a slurry of lithium aluminium hydride (1 g) in ether (100 ml). The mixture was boiled under reflux overnight. The usual work-up gave a solid (3.8 g), showing two spots on tlc [methanol-chloroform (1.9)]. This was adsorbed on to silica gel (40 g) and the adsorbate was added to a column of silica gel (400 g). Elution [methanol–cholroform (1 : 50)] afforded adamantane-2*a*, 4*a*-diol **17** (1.5 g), m.p. 332–334° (sublimation), ν_{max} (*ca.* 3×10^{-3} *M*) 3656 and 3552 cm^{-1}, δ 4.31 (2H, d, disappeared on shaking with D_2O), 3.90 (2H, m), and 1.30–2.50 (12H, m), *m/e* (relative intensity) 168 (5, M^+), 150 (100), 132 (10), and 79 (82). Further elution of the column gave on removal of solvent a solid diol mixture (2.1 g) which showed only one spot on tlc in the following solvent systems: methanol-chloroform (1 : 9), acetone-light petroleum (1 : 1), methanol–ether (1 : 9), three times with ethyl acetate, and four times with acetone–light petroleum (1 : 4). The trimethylsilyl ethers of the diols (0.01 g) were prepared by the usual method, revealing two compounds on glc (4m 2.5% SE30 capillary column, 180°), retention times 10, 11 min, in the ratio of 7 : 3 respectively. The acetates of the diols were prepared by the usual method, and while homogeneous on tlc, they showed as two compounds (7 : 3) on glc (retention time 18.3 and 21.4 min). These diol derivatives, on glc comparison with those of the separated pure diols obtained later, showed that the major diol is adamantan-2*e*, 4*a*-diol **18** and the minor adamantane-2*e*, 4*e*-diol **19**. The bis(3,5-dinitrobenzoyl)-derivatives of the diols (0.01 g), prepared in the usual way, were also homogeneous on tlc.

Meerwein-Ponndorf-Verley reduction of adamantane-2,4-dione. A stirred solution of the dione (0.84 g) and aluminium isopropoxide (2 g) in isopropanol (10 ml) was distilled through a Vigreux column at a rate of *ca.* 1–4 drops per min. Isopropanol was added dropwise at the same rate. At the end of *ca.* 0.5 hr when the distillate was found free of acetone, most of the isopropanol was removed under reduced pressure. The cooled residue was hydrolysed with 5% aqueous hydrochloric acid (20 ml), saturated with sodium chloride, and then extracted with chloroform (3 × 20 ml). The chloroform extract was dried and evaporated giving a diol mixture (0.65 g) separated by preparative tlc [methanol–chloroform (1 : 9)] into **17** (0.08 g), identical with an authentic sample (IR, NMR, and tlc), and a mixture of **18** and **19** (0.4 g) in the ratio of 7 : 3 (glc comparisons of bistrimethylsilyl ethers and diacetates).

Attempted equilibrium of adamantan-2,4-diols

(*a*) *Adamantan-*2a, 4a-*diol* **17**. Acetone (0.0005 ml) was added to a solution of **17** (0.018 g) and aluminium isopropoxide (0.04 g) in isopropanol (0.2 ml) in an ampoule which was sealed and kept at 150° for 168 hr. The cooled contents were poured into 5*M* aqueous hydrochloric acid (5 ml) which was saturated with sodium chloride and then extracted with chloroform (3 × 5 ml). The chloroform extract, after being dried and concentrated, gave a mixture containing *ca.* 95% of the starting material (glc of diacetates and tlc).

(*b*) *Adamantan-*2e, 4a- *and* 2e, 4e-*diols* **18** *and* **19**. Equilibration as in (a) of a mixture of **18** and **19** (4 : 1, 0.018 g) gave the same product mixture as in (a).

*Mono-*3, 5-*dinitrobenzoylation of the mixture of adamantan-*2e, 4a- *and* 2e, 4e-*diols* **18** *and* **19**. 3,5-Dinitrobenzoyl chloride (3.3 g) in pyridine (50 ml) was added slowly during 5 hr to a stirred solution of the above diol mixture (2.0 g) in pyridine (100 ml) at 60°. After 1 hr at this temperature, the reaction mixture was poured into ice-water (200 ml) and extracted with ether (3 × 150 ml). The ether extract was washed with 15% hydrochloric acid, saturated aqueous sodium carbonate, water, and dried. The solid mixture (4.0 g) obtained upon evaporation of the ether, was separated by preparative tlc developed twice in ethyl acetate-chloroform (1 : 9). The first band ($R_f = 0.9$) afforded a mixture of 2*e*, 4*a*- and 2*e*, 4*e*-bis(3,5-dinitrobenzoyloxy)adamantanes (0.3 g), ν_{max} 3103, 1736, 1343, 1268, 1160, 1073, and 920 cm^{-1}, δ 9.13–9.32 (6H, m), 5.90 (0.6H, m), 5.48 (0.6H, m), 5.32 (2 × 0.4H, m), and 1.48–2.66 (12H, m). The second band (R_f = 0.51) gave 4*a*-(3,5-dinitrobenzoyloxy)adamantan-2e-ol (**20**)(0.6 g), m.p. 115–118° (from acetone–light petroleum), ν_{max} 3640, 3105, 1736, 1343, 1270, 1165, 1084, 1072, 1020, 970, and 920 cm^{-1}, δ 9.18–9.32 (3H, m), 5.44 (1H, m), 4.26 (1H, m) 2.15 (1H, s, disappeared when shaken with D_2O), and 1.50–2.40 (12H, m) (Found: C, 56.3; H, 5.3; N, 7.55. $C_{17}H_{18}O_7N_2$ requires C, 56.35; H, 5.0; N, 7.75%). The compound **20** (0.01 g) on reduction with lithium aluminium hydride followed by acetylation in the usual way gave a single peak on glc, retention time 18.3 min. The third band ($R_f = 0.41$) afforded a mixture of at least two mono-3, 5-dinitrobenzoates (2.0 g), ν_{max} 3624, 3010, 1736, 1340, 1270, 1165, 1090, 1070, 1050, 1020, 970, 958, and 920 cm^{-1}. The mixture (0.01 g) on reduction with lithium aluminium hydride followed by acetylation in the usual way gave an acetate mixture shown by tlc to be **18**-diacetate and **19**-diacetate in the ratio of 3 : 2. The fourth band ($R_f = 0.05$)) gave the starting material (0.3 g), whose acetate on glc analysis was shown to be a mixture of **18**- and **19**-diacetate in the ratio of 4 : 1.

Lithium aluminium hydride reduction of monobenzoate **20**: *Adamantan-*2*e*, 4a-*diol* **18**. To a stirred solution of **20** (0.1 g) in ether (100 ml), was added a slurry of lithium aluminium hydride (0.06 g) in ether (50 ml). The mixture, boiled under reflux overnight, was treated by successive dropwise addition of water (0.06 ml), 15% aqueous sodium hydroxide (0.06 ml), and water (0.16 ml) and then filtered. The filtrate was washed with 15% hydrochloric acid (2 × 50 ml) and then dried over anhydrous sodium sulphate and sodium carbonate. Evaporation of the ether gave a pale yellow solid which on further purification by preparative tlc [methanol–chloroform (1 : 9)] gave **18** (0.025 g), m.p. 321–325° (sublimation), ν_{max} (*ca.* $3 \times 10^{-3} M$) 3620 cm^{-1}, δ (pyridine) 4.89 (1H, m), 4.34 (1H, m), and 1.20–2.80 (12H, m), *m/e* (*relative intensity*) 168 (< 0.5, M^+), 150 (100), 107 (43), and 79 (55). (Found: C, 71.6; H, 9.7. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.6%).

2e-*Toluene-*p-*sulphonoxy-*4a-(3, 5-*dinitrobenzoyloxy*)-*adamantane* **23**. Toluene-*p*-sulphonyl chloride (0.1 g) was added to **20** (0.072 g) in pyridine (2 ml) at 0°, and the reaction mixture kept at room temperature for 72 hr. The usual work-up gave **23** (0.095 g), m.p. 200–201° (from acetone–light petroleum), ν_{max} 3010, 1738, 1343, 1269, 1187, 1178, 1162, 974, 935, and 858 cm^{-1}, δ 9.13 (2H, d), 9.33 (1H, dd), 7.84 (2H, d), 7.32 (2H, d), 5.34 (1H, m), 4.88 (1H, m), 2.37 (3H, s), and 1.44–2.40 (12H, m). (Found: C, 55.8; H, 4.6; N, 5.3. $C_{24}H_{24}O_9N_2S$ requires C, 55.8; H, 4.7; N, 5.4%).

Lithium aluminium deuteride reduction of 2e-*toluene-*p-*sulphonoxy-*4a-(3,5-dinitrobenzoyloxy) adamantane **23**. To a solution of **23** (0.09 g) in ether (20 ml), was added a slurry of lithium aluminium deuteride (Isotopic Products Canada, isotopic purity > 99 atom% ^2H, 0.1 g) in ether (10 ml) and the mixture refluxed overnight. The usual work-up afforded a pale yellow oil (0.025 g) which was purified by preparative tlc [ethyl acetate-light petroleum (1 : 3)] to give bicyclo [3.3.1] non-2-ene-7α-deuteromethanol (**24d**) (0.018 g), δ 5.90 (1H, m), 5.58 (1H, m), 3.34 (1H, d, $J = 6$ Hz), and 1.24–2.50 (12H, m), identical by glc and tlc with the protio-compound **24a** obtained subsequently.

2e, 4e-*Bis*(*toluene-*p-*sulphonoxy*) *adamantane* **29**. Toluene-*p*-sulphonyl chloride (0.03 g) was added to a solution of **28** (0.03 g) in pyridine (1 ml) at 0° which was then kept at room temperature overnight. The usual work-up afforded **29** (0.03 g), m.p. 115–117° (from ether-light petroleum), ν_{max} 1370, 1187, 1176, and 927 cm^{-1}, δ 7.74 (4H, d), 7.30 (4H, d), 4.44 (2H, m), 2.45 (6H, s), and 1.36–2.16 (12H, m). (Found: C, 60.3; H, 5.85. $C_{24}H_{28}O_6S_2$ requires C, 60.5; H, 5.9%).

2e, 4a-*Bis*(*toluene-*p-*sulphonoxy*) *adamantane* **30**

(a) *From* 2e-*Toluene-*p-*sulphonoxyadamantan-*4a-*ol* **13**. Toluene-*p*-sulphonyl chloride (0.03 g) was added to a solution of **13** (0.03 g) in pyridine (1 ml) at 0° which was then kept at room temperature overnignt. The usual work-up gave **30** (0.03 g), m.p. 97–99° (from ether–light petroleum), ν_{max} 1370, 1188, 1178, 946, 925, and 858 cm^{-1}, δ 7.77 (2H, d), 7.73 (2H, d), 7.32 (4H, d), 4.82 (1H, m), 4.67 (1H, m), 2.45 (6H, s), and 1.28–2.22 (12H, m). (Found: C, 60.65; H, 5.9. $C_{24}H_{28}O_6S_2$ requires C, 60.5; H, 5.9%).

(b) *From* 4a-*Toluene-*p-*sulphonoxyadamantan-*2e-*ol* **27**. The compound **27** (0.03 g) on similar toluene-*p*-sulphonation as in (a) gave **30** (0.03 g), m.p. 97–99°, identical with **30** obtained in (a) (IR and NMR comparisions).

Lithium aluminium deuteride reduction of 4a-*toluene-*p-*sulphonoxyadamantan-*2e-*ol* **27**. To a solution of **27** (0.08 g) in ether (10 ml), was added a slurry of lithium aluminium deuteride (0.04 g) in ether (5 ml) which was then boiled under reflux overnight. The usual work-up gave a mixture shown by glc analysis to contain **24d** and adamantan-2-ol in the ratio of 3 : 7. G.c.m.s. analysis (3m × 3mm Carbowax 1540 column, 140°) showed that both compounds contain one deuterium (M^+ 153, $M^+ - 15$ 135) when compared with unlabelled compounds. The mixture was separated by preparative tlc [developed twice in 25% ethyl acetate–light petroleum (1 : 3)] to give 4*e*-deuterio-adamantan-2*e*-ol **31** (0.013 g), m.p. 294–296° (sublimation), ν_{max} 3632, 2162, 2145, 1052, and 1020 cm^{-1}, identified by Eu(dpm)$_3$-shifted NMR; and **27d** (*ca.* 0.006 g), identified by NMR and MS comparisons.

Lithium aluminium hydride reduction of 4e-*toluene-*p-*sulphonoxyadamantan-*2e-*ol* **28**. To a solution of **28** (0.433 g) in ether (30 ml), was added a slurry of lithium aluminium hydride (0.2 g) in ether (10 ml). The mixture was boiled under reflux overnight. The usual work-up afforded bicyclo-[3.3.1) non-2-ene-7α-methanol **24a** (0.21 g) as an oil, homogeneous on tlc [ethyl acetate–light petroleum (3 : 7)] and glc (50 m × 0.5 mm capillary 5% Carbowax 1540 column, 120°), ν_{max} 3640, 3020, 1643, 1430, 1032, and 1020 cm^{-1}, δ 5.78 (1H, m), 5.49 (1H, m), 3.51 (2H, d, J = 6Hz), and 1.20–2.50 (12H, m), *m/e* (relative intensity) 152 (<1, M^+), 151 (2), 150 (1.5), 134 (40), 92 (53), and 79 (100). (Found: C, 79.1; H, 10.55. Calc. for $C_{10}H_{16}O$: C, 78.9; H, 10.6%).

Lithium aluminium hydride reduction of 2e-*toluene-*p-*sulphonoxyadamantan-*4a-*ol* **13**. Lithium aluminium hydride (0.005 g) was added to a stirred solution of **13** (0.01 g) in ether (2 ml) which was then boiled under reflux overnight. The usual work-up afforded an oil, shown by glc to contain **24a** [identical with **24a** obtained as above (IR and tlc comparisons)] and adamantan-2-ol in the ratio of 93 : 7.

*Monotoluene-*p-*sulphonation of the mixture of adamantan-*2e, 4a- *and* 2e, 4e-*diols* **18** *and* **19**. Toluene *p*-sulphonyl chloride (1.75 g) in pyridine (10 ml) was added to the mixture of **18** and **19** (3 : 2, 1.5 g) in pyridine (10 ml) over 5 hr at 0° with stirring which was continued at room temperature for 16 hr. The usual work-up gave a *mixture of mono- and bis-toluene-p-*sulphonates (2.7 g), which was separated by preparative tlc developed four times in ethyl acetate-light petroleum (3 : 7). The first band ($R_f = 0.72$) afforded a mixture of 2*e*, 4*a*- and 2*e*, 4*e*-bis-(toluene-*p*-sulphonoxy) adamantane **30** and **29** (0.8 g), ν_{max} 1370, 1190, and 1180 cm^{-1}, δ 7.86 (4H, d), 7.34 (4H, d), 4.73 (0.6H, m), 4.59 (0.6H, m), 4.45 (2 × 0.4H, m), 2.46 (6H, s), and 1.25–2.20 (12H, m). The second band ($R_f = 0.48$) gave 4*a*-toluene-*p*-sulphonoxyadamantan-2*e*-ol **27** (0.25 g), m.p. 68–70° (from ether–light petroleum), ν_{max} 3626, 1372, 1190, and 1180 cm^{-1}, δ 7.77 (2H, d), 7.30 (2H, d) 4.77 (1H, m), 4.12 (1H, m), 2.44 (3H, s), 1.78 (1H, s, disappears on shaking with D_2O), and 1.26–2.33 (12H, m). (Found: C, 63.1; H, 7.05. $C_{17}H_{22}O_4S$ requires C, 63.35; H, 6.9%).The *third band* ($R_f = 0.43$) gave 2*e*-toluene-*p*-sulphonoxy-adamantan-4*a*-ol **13** (0.6 g), m.p. 83–85° (from ether-light petroleum), ν_{max} 3622, 1369, 1189, and 1179 cm^{-1}, δ 7.78 (2H, d), 7.30 (2H, d), 4.99 (1H, m), 3.99 (1H, m), 2.43 (3H, s), 1.29 (1H, s disappears on shaking with D_2O), and 1.20–2.26 (12H, m). (Found: C, 63.4; H, 6.7. $C_{17}H_{22}O_4S$ requires C, 63.35; H, 6.9%). The fourth band ($R_f = 0.36$) gave 2*e*-toluene-*p*-sulphonoxyadamantan-4*e*-ol **28** (0.6 g), m.p. 87–90° (from ether–light petroleum) ν_{max} 3622, 1369, 1189, and 1179 cm^{-1}, δ 7.82 (2H, d), 7.33 (2H, d), 4.53 (1H, m), 3.71 (1H,m), 2.40 (3H, s), 1.79 (1H, s, exchangeable with D_2O), and 1.32–2.18 (12H, m). (Found: C, 63.45; H, 6.95. $C_{17}H_{22}O_4S$ requires C, 63.35; H, 6.9%).

4a - *Tetrahydropyranoxy*-2e - *toluene*-p-*sulphonoxyadamantane* **32**. Dihydropyran (0.04 g) and phosphoryl chloride (0.01 ml) were added under nitrogen to a stirred solution of **15** (0.127 g) in benzene (3 ml) at 20° and stored overnight. The usual work-up gave **32** (0.155 g), m.p. 119–121° (from light petroleum–ether), ν_{max} 1369, 1188, 1178, 1021, and 927 cm^{-1}, δ 7.81 (2H, d), 7.29 (2H, d), 4.96 (2/3H, m), 4.80 (1/3H, m) 4.64 (2/3H, m), 4.45 (1/3H, m), 3.25–3.92 (3H, m), 2.42 (3H,s) and 1.28–2.26 (18H, m). (Found: C, 65.35; H, 7.35. $C_{22}H_{30}O_5S$ requires C, 65.0; H, 7.45%).

Lithium aluminium hydride reduction of 4a-*tetrahydropyranoxy*-2e-*toluene*-p-*sulphonoxyadamantane* **32**.

(a) *With a slight excess of lithium aluminium hydride.* Lithium aluminium hydride (0.014 g) was added to a stirred solution of **32** (0.083 g) in ether (10 ml) and the solution boiled under reflux overnight. The usual work-up gave a mixture shown by tlc [ethyl acetate–light petroleum (1 : 4)] to contain the starting material and a more polar product in the ratio of *ca.* 3 : 7. Separation by preparative tlc [ethyl acetate–light petroleum (1 : 1)] afforded the starting material, identified by IR and 4*a*-tetrahydropyranoxyadamantan-2*e*-*ol* **33** (0.028 *g*) as an oil, ν_{max} 3628 and 1022 cm^{-1}, δ 4.68 (1H, m), 3.30–4.24 (4H, m), 1.20–2.37 (19H, m), *m/e* (relative intensity) 252 (4, M^+), 251 (23), 235 (23), 167 (23), 150 (10), 133 (17), 91 (22), 85 (100), and 79 (23). (Found: C, 71.5; H, 9.7. $C_{15}H_{24}O_3$ requires C, 71.4; H, 9.6%).

(b) *With a large excess of lithium aluminium hydride.* Lithium aluminium hydride (0.025 g) was added to a stirred solution of **32** (0.011 g) in ether (3 ml) which was then boiled under reflux overnight. The usual work-up gave **33** identified by IR and tlc comparisons.

Acid hydrolysis of 4a-*tetrahydropyranoxyadamantan*-2e-*ol* **33**. Hydrochloric acid (5 *M*, 1 drop) was added to a solution of **33** (0.01 g) in methanol (1 ml) which was stirred at room temperature overnight. The usual work-up gave **18** (0.005 g), m.p. 321–325° (sublimation), identified by tlc and IR comparison.

Synthesis of syn-4d-, *and* 4d$_2$-*Adamantan-2-ols from hydroxyketone* **15**.

Acetylation of 4*a-hydroxyadamantan-2-one* **15**. Pyridine (2 ml) was added to a stirred solution of **15** (2.7 g) in acetic anhydride (200 ml) which was then kept at 20° for 48 hr. The usual work-up gave 4*a-acetoxyadamantan-2-one* **15a** (2.35g) as an oil, ν_{max} 1737, 1730, 1243, 1235, 1225, and 1035 cm^{-1}, δ 5.22 (1H, approx. q), 2.71 (1H, m), 2.54 (1H, m), 2.03 (3H, s), and 1.80–2.42 (10H, m), *m/e* (relative intensity) 208 (26, M^+), 166 (54), 165 (52), 148 (35), 138 (33), 120 (63), 96 (58), and 79 (100). (Found: C, 69.25; H, 7.55. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.75%).

Sodium borodeuteride reduction of 4a-*acetoxyadamantan*-2-*one* **15a**. Sodium borodeuteride (Koch-Light, isotopic purity > 98 atom % ^2H, 0.5 g) in aqueous 1,4-dioxan (1 : 1, 150 ml) was added with stirring to a solution of **15a** (2.35 g) in 1,4-dioxan (150 ml) and the solution kept at room temperature for 2 hr. The mixture was then saturated with sodium chloride and the organic layer separated. The aqueous layer was extracted with ether (3 × 50 ml). The combined organic extracts were dried and concentrated to give a mixture shown by glc (4m 2.5% SE30 capillary column, 180°) to contain two compounds in the ratio of 17 : 3. Further acetylation and glc comparison (similar conditions) with unlabelled samples showed that the mixture contained 4a-*acetoxy*-2e-*deuterioadamantan*-2a-*ol* **34** and 4a-*acetoxy*-2a-*deuterioadamantan*-2e-*ol* **35**, **34** being the major component, Separation by preparative tlc [methanol-chloroform (1 : 50)] gave **34** (1.40 g) as an oil, ν_{max} 3610, 2150, 1745, 1222, 1118, 1083, 1060, 1022, 969, 940, and 890 cm^{-1}, δ 5.00 (1H, approx. q), 3.63 (1H, broad s), 2.04 (3H, s), and 1.34–2.32 (12H, m), *m/e* (*relative intensity*) 211 (5, M^+), 193 (4), 152 (13), 151 (100), 150 (13), 109 (16), 93 (18), and 79 (23). (Found: M^+ 211.131. $C_{12}H_{17}O_3D$ requires M^+ 211.131); and **38** (0.25 g), m.p. 78–82° (sublimation), ν_{max} 3632, 1738, 1236, 1109, 1089, 1030, 1020, 975, and 933 cm^{-1}, δ 5.04 (1H, m), 3.77 (1H, broad s), 2.05 (3H, s), and 1.22–2.22 (12H, m), *m/e* (relative intensity) 152 (8), 151 (77), 150 (100), 109 (19), 93 (20), and 79 (18). (Found: C, 68.25; H(D), 8.9 $C_{12}H_{17}O_3D$ requires C, 68.2; H(D) 9.05%).

4a - *Acetoxy*-2e-*deuterio*-2a-*toluene*-p-*sulphonoxyadamantane* **36**. Toluene-*p*-sulphonyl chloride (2.5 g) was added to **34** (1.38 g) in pyridine (20 ml) at 0°. The mixture was then kept at room temperature for 72 hr. The usual work-up gave pure **36** (2.37 g), m.p. 83–85° (from ether), ν_{max} 2192, 1738, 1365, 1245, 1232, 1176, 1100, 1092, 1058, 1030, 1022, 960, 930, and 854 cm^{-1}, δ 7.75 (2H, d), 7.29 (2H, d), 4.79 (1H, m), 2.43 (3H, s), 2.00 (3H, s), and 1.34–2.40 (2.40 (12H, m). (Found: C, 62.5; H (D), 6.7. $C_{19}H_{23}O_5SD$ requires C, 62.45; H (D), 6.9%).

Lithium aluminium hydride reduction of 4a-*acetoxy*-2e-*deuterio*-2a-*toluene*-p-*sulphonoxyadamantane* **36**. To a solution of **36** (1.2 g) in ether (200 ml), a slurry of lithium aluminium hydride (0.8 g) in ether (20 ml) was added and the suspension was boiled under reflux overnight. The usual work-up gave a mixture containing (tlc) three products having the same R_f values as adamantan-2-ol, **24a** and **17**. The mixtures was absorbed on to alumina (10 g) and the adsorbate deposited on an alumina column (50 g). Elution with ether-pentane. (3 : 7) afforded 4*a*-deuterioadamantan-2*a*- ol **37** (0.4 g), m.p. 292–296° (sublimation), ν_{max} 3628, 2155, 1048, and 1020 cm^{-1}, identical with 2-adamananol on tlc and glc comparisions. Further elution of the column with ether-pentane (1 : 1) gave 2-deuterio-bicyclo-[3.3.1] non-2-ene-7*α*-menthanol **24b** as an oil (0.03 g), ν_{max} 3637, 3020, 2240, 1634, and 1020 cm^{-1}, δ 5.55 (1H, m), 3.55 (2H, d, $J = 7$ Hz), and 1.24–2.50 (12H, m) *m/e* (relative intensity) 153 (6, M^+), 152 (4), 151 (3), 135 (97), 120 (22), 106 (14), 93 (74), and 80 (100), identical with **24a** on tlc and glc comparisons. The third compound was not eluted.

Lithium aluminium deuteride reduction of 4a-*acetoxy*-2e-*deuterio*-2a-*toluene*-p-*sulphonoxyadamantane* **36**. To a solution of **36** (1.14 g) in ether (200 ml), was aded a slurry of lithium aluminium deuteride (0.8 g) in ether (20 ml) and the suspension boiled under reflux overnight. The usual work-up gave a mixture similar (tlc) to the reduction products of **36** with LAH, which was chromatographed over alumina. Elution with ether–pentane (3 : 7) afforded 4,4-*dideuterioadamantan*-2a-*ol* **38** (0.4 *g*), m.p. 292–295° (sublimation), ν_{max} 3628, 2200, 2088, 1048, and 1020 cm^{-1}, identical with 2-adamantanol on tlc and glc comparisons. Further elution of the column with ether–pentane (1 : 1) gave 2-*deuteriobicyclo*[3.3.1] *non-2-ene-7α-deuteriomethanol* **24c** as an oil (0.03 g), ν_{max} 3650, 3205, 2240, 2140, 1630, and 1042 cm^{-1}, δ 5.55 (1H, m), 3.55 (1H, d, $J = 7$ Hz), and 1.24–2.50 (12H, m) identical with **24a** and **24b** on tlc and glc comparisons. The third compound was not eluted.

4*a-Deuterio*-2a-*adamantyl methanesulphonate* **8**. Methanesulphonyl chloride (0.6 ml) was added with stirring to a solution of **37** (0.1 g) in pyridine (6 ml) at 0° and the mixture stirred at room temperature for 72 hr.The usual work-up afforded **8** (0.14 g), m.p. 65.5–66.5° (from pentane), ν_{max} 2170, 1174, 922, and 916 cm^{-1}, identical with 2-adamantyl methanesulphonate by tlc.

4,4-Dideuterio-2a-adamantyl methanesulphonate **11**. Methanesulphonyl chloride (1 ml) was added with stirring to a solution of **38** (0.15 g) in pyridine (10 ml) at 0° and the mixture stirred at room temperature for 72 hr. The usual work-up gave **13** (0.21 g), m.p. 66–67° (from pentane), ν_{max} 2200, 2120, 2100, 2085, 1365, 1340, 1174, and 920 cm^{-1}, identical with 2-adamantyl methanesulphonate by tlc.

2-Deuterio-2-adamantyl methanesulphonate **12**. To a stirred solution of adamantanone (3.0 g) in ether (250 ml), was added a slurry of lithium aluminium deuteride (0.8 g) in ether (50 ml). The mixture was boiled under reflux overnight. The usual work-up gave *2-deuterioadamantan-2-ol* (3.0 g), m.p. 295–297° (sublimation), ν_{max} 3632, 2135, 2123, 2105, 1110, 1050, 1022, and 936 cm^{-1}, δ 1.48–2.26 (m), identical with adamantan-2-ol glc and tlc comparisons.

Methane sulphonyl chloride (15 ml) was added with stirring to a solution of 2-deuterioadamantan-2-ol (3.0 g) in pyridine (60 ml) at 0° and the mixture was stirred at room temperature for 72 hr. The usual work-up afforded **12** (3.9 g), m.p. 66–67° (from ether-isopentane), ν_{max} 2182, 1360, 1343, 1176, and 917 cm^{-1}, δ 3.00 (3H, s) and 1.48–2.24 (1H, m), identical with 2-adamantyl methanesulphonate on tlc.

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