PYROLYTIC STUDIES IN THE ALICYCLIC SERIES

A Thesis
presented to the Faculty of Science
University of Glasgow
as requirement for the Degree of
Doctor of Philosophy

by

Kong LUK

Chemistry Department December 1974

ACKNOWLEDGEMENT

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I express my thanks to Professors R.A. Raphael, F.R.S. and G.W. Kirby for their interest.

My thanks are also due to Professor J.B. Stothers for the measurement of the ^{13}C n.m.r. spectra of deuterium-labelled protoadamantene and dehydroadamantane, Dr. A.P. Lane for helpful discussions with the construction of the furnace, and my wife Florence for typing this thesis. In addition, this thesis could not have been completed without the advice and assistance of other members of staff, academic and technical, of the University of Glasgow too numerous to list here.

K. Luk

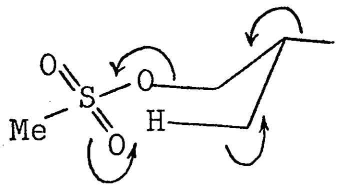
December 1974

CONTENTS

SUMMARY

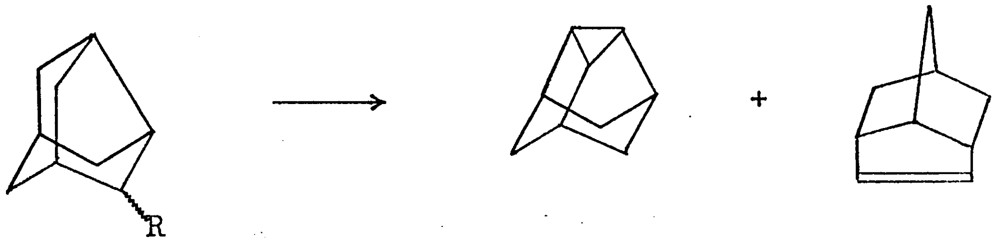
The work describe in this thesis is concerned with the vapour-phase pyrolysis of sulphonate esters resulting in 1,3-elimination with or without rearrangement.

This process is seen as going through a seven-membered transition state as in (1): the C—O and C—H bonds that cleave are coplanar while the C—C bond that migrates from the intermediate carbon is anti-periplanar to both.



(1)

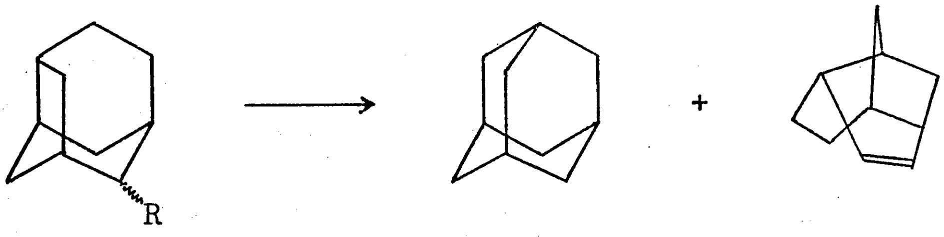
In order to test how rigid are the steric requirements for elimination to proceed, other systems have been pyrolysed in the course of this work. This thesis describes the pyrolysis of the two epimeric 2-noradamantyl mesylates (2) and (3) giving triaxane (4) and brendene (5), and the epimeric 10-protoadamantyl mesylates (6) and (7) giving adamantane (8) and the olefin (9).



(2) R = ax-OMs
(3) R = eq-OMs

(4)

(5)

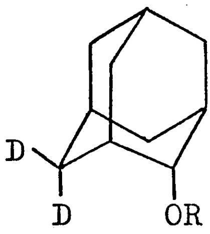


(6) R = *ax*-OMs
(7) R = *eq*-OMs

(8)

(9)

The *cis*-γ-deuterium kinetic isotope effect in the pyrolysis of 2-adamantyl esters has been investigated. This thesis describes the synthesis of (10), (11), and (12) and the analysis of the products obtained from their pyrolysis.



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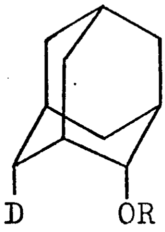

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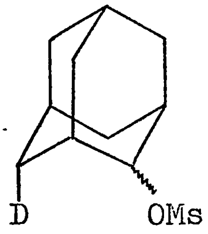
R = SO_3Me or $COCF_3$



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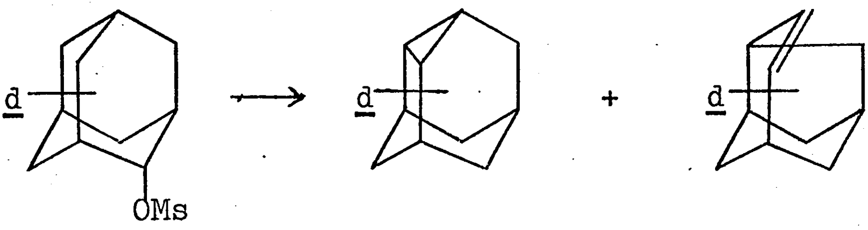


(13)

(14)

Two methods were used for analysing the partially labelled protoadamantene (14) and dehydroadamantane (13) products obtained from the pyrolyses, namely, g.c.m.s. and

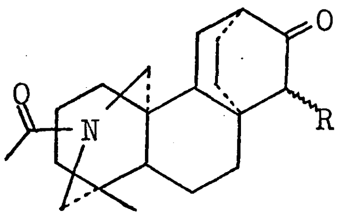
^{13}C n.m.r. spectroscopy. The results thus obtained indicate that the pyrolyses do not go through a simple concerted mechanism as depicted in (1).

The pyrolysis of (11) and (12) gave products with the same deuterium content, indicating an ion-pair intermediate causing an epimerisation of the ester function prior to or during pyrolysis. The subsequent elimination with or without rearrangement then proceed stepwise. A deuterium isotope effect is not observed for fission of the γ-C--H bond, so that this process presumably plays no part in the rate determining step.

INTRODUCTION

The work described in this thesis is concerned with the vapour-phase pyrolysis of sulphonate esters resulting in 1,3-elimination with or without rearrangement.

In this laboratory, the first pyrolysis of this kind was used[1] to convert the atisane skeleton of (1) and (2) into that of the aconane derivative (4) to provide a laboratory analogy for the supposed biosynthetic pathway. Pyrolysis of the epimeric tosylates (1) and (2) at 500° afforded respectively the olefins (3) and (4).



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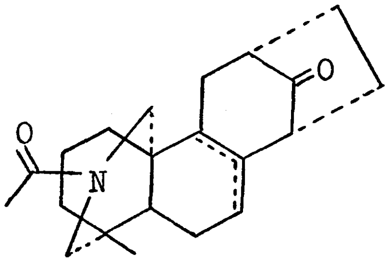
(2) R = α-OTs



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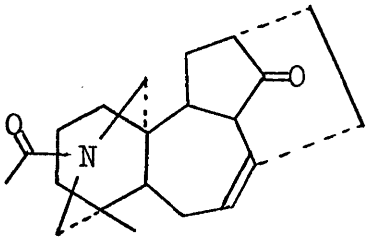
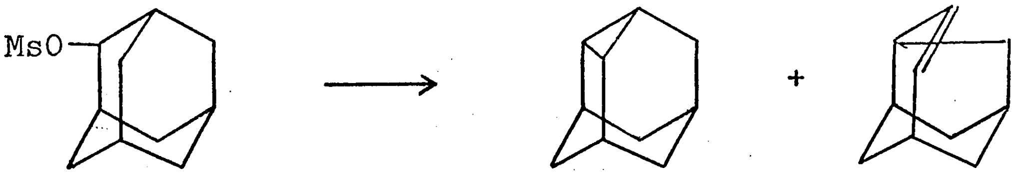
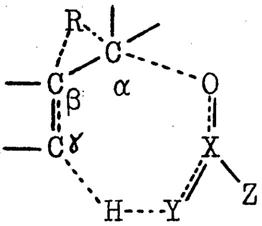


(4)

This work was followed by a qualitative study[2] of the pyrolysis of 2-adamantyl mesylate (5) in which dehydroadamantane (6) and protoadamantene (7) were obtained in essentially quantitative yield. The process[2,3] is visualised



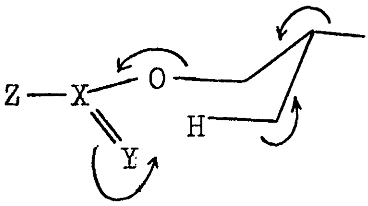
(5) (6) (7)



(8)

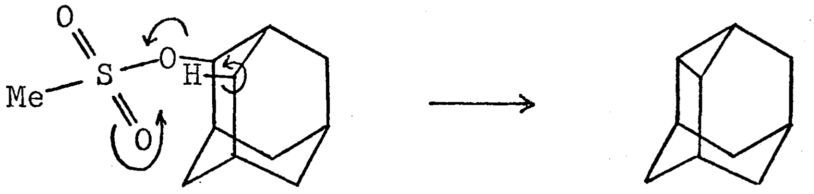
as going through a seven-membered transition state [as (8)] and comprises (a) abstraction by the ester function of hydrogen attached at a γ-carbon atom; (b) formation of a $\beta\gamma$-double bond; (c) $\beta\rightarrow\alpha$ migration of a β-substituent; and (d) α-C--O fission.

A comprehensive survey of anomalous ester pyrolyses[3] showed that carboxylic esters [X=C, Y=O, Z=R(Ar)], sulphonic esters [X=S, Y=O, Z=:O,R(Ar)], and xanthates (X=C, Y=S, Z=SR) exhibit this behaviour. Furthermore, the existing examples in the literature[3] of this 1,3-elimination with rearrangement involve a common steric situation as in (9);



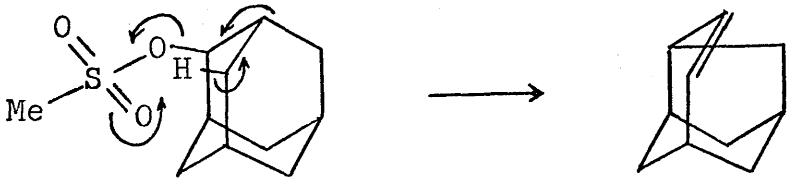
(9)

the C--O and C--H bonds that cleave are coplanar while the C--C bond that migrates from the intermediate carbon is anti-periplanar to both. Thus Scheme 1 shows the conversion of (5) into (6) and (7) where the geometry for these processes is optimal.



(5) (6)

Without rearrangement

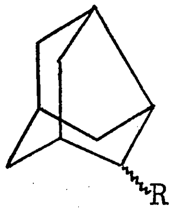


(5) (7)

With rearrangement

Scheme 1

In order to test how rigid are the steric requirements for elimination to proceed, other systems have been pyrolysed in the course of this work. These pyrolyses have also given hydrocarbons which are difficult to prepare otherwise, and therefore the pyrolysis itself becomes a useful synthetic method. This thesis describes the pyrolyses of the two epimeric 2-noradamantyl mesylates (10) and (11), the epimeric 10-protoadamantyl mesylates (12) and (13), and 2,6-adamantyl bismesylate (14) and the bistrifluoroacetate (15).



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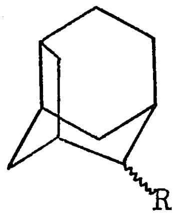
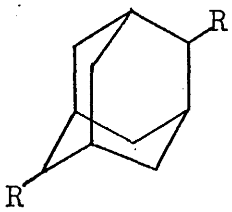
(11) R = *eq*-OMs



(12) R = *ax*-OMs
(13) R = *eq*-OMs



(14) R = OMs
(15) R = $OCOCF_3$

In another section of this thesis, evidence has been sought for a *cis*-γ-deuterium kinetic isotope effect and hence for C--H bond breaking in the transition state [see (9)].

The magnitude of the primary kinetic isotope effect has been used in the past two decades as a criterion of transition state structure in the study of organic reaction mechanisms. Based on the difference of the vibrational zero-point energy between a C--H bond and a C--D bond, and using the absolute rate theory,[4] Wiberg[5] deduced the expression (I) for the maximum isotope effect at moderate

$$\underline{k}_H/\underline{k}_D = e^{(h\nu_H - h\nu_D)/2RT} \qquad \text{(I)}$$

temperatures (0 - 500°). He concluded that the maximum isotope effect will be obtained when the bond to hydrogen or deuterium is completely cleaved in the activated complex, and the isotope effect will diminish the more bonding persists.

This treatment was, however, oversimplified because it considered only the C--H and C--D vibrations alone in the reactant. In a second approximation, Westheimer used a linear transition state A···H····B as in Fig. 1 where A and B are reactant and product respectively. By a simplified mathematical treatment,[6] he showed that a symmetrical transition state would give a maximum isotope effect while asymmetric transition states, either more product- or more reactant-like, would tend to exhibit smaller isotope effect. This was supported by a more elaborate mathematical treatment.[7] The validity of this correlation has been questioned since a number of parameters affecting the kinetic isotope effect have not been taken into account.

$$AH + B \rightleftharpoons A\cdots H\cdots B \rightleftharpoons A + HB$$

Fig. 1

To allow for the wave nature of hydrogen, quantum statistics has to be used instead of classical statistical mechanics and that introduces the possibility of 'tunnelling'.[8] This effect would be predicted to be less probable for deuterium than hydrogen. Using a coulombic model to calculate the curvatures of the energy surface for the transition state of proton transfer reactions as in Fig. 1, Bell[9] showed the contribution of the transverse vibration to the isotope effect will be exactly cancelled by that of the 'tunnel' effect, provided that both contributions are small. When this is not the case, the 'tunnel' effect will be the more important of the two.

Exploring the curvature of the potential barrier for the transition state, Willi and Wolfsberg[10] suggested that the amount of 'unsymmetry' in the transition state, causing $\underline{k}_H/\underline{k}_D$ to fall off, depends on the curvature parameter and high $\underline{k}_H/\underline{k}_D$ values can result even if the transition state is quite 'unsymmetric'. However, they explained the low experimental values could also result from high hydrogen bending force constants in the transition state.

Bader[11] has emphasised the occurrence of small isotope effects, whether in symmetrical or unsymmetrical transition states as resulting from large antisymmetrical vibrations. Saunders,[12] in his theoretical calculation of isotope effects in bimolecular elimination reactions, has developed a model of the transition state for proton transfer which suggests that proton coupling with other atomic motions has a significant influence on the isotope effect, a conclusion which is at variance with previous derivations.[6,7]

Another model calculation by More O'Ferrall and Kouba[13] appears to provide strong support for the correlation of transition state symmetry with deuterium isotope effect, provided that the proton is transferred from carbon. The claim is made that in the transfer of proton from oxygen, the bending vibrations in the transition state are too large to be ignored. For symmetrical transition states which are non-linear, More O'Ferrall has published model calculations[14] which show that the deuterium isotope effect is dependent on the angle A---H---B in Fig. 1, and is a maximum for the linear symmetrical transition state. Besides, the isotope effect remains small and only slightly dependent on the degree of asymmetry in the transition state.

For a simple proton transfer as in Fig. 1, Bell and Goodall[15] suggested that the most symmetrical transition state should occur when A and B are of approximately equal basicity and this has been supported by other investigations.[16] A recent communication by Bordwell and Boyle[17] challanges this conclusion and proposes that either $\underline{k}_H/\underline{k}_D$ is relatively insensitive to the symmetry of the transition state, or that the symmetry does not change over wide ranges of differences in the basicities of A and B.

In a recent investigation of the kinetic deuterium isotope effect in 'retro-ene' reactions shown in Fig. 2, Kwart and Latimore[18] concluded that no serious effects arise from changes in hybridisation and valence geometry of the carbon to which the proton is transferred. Moreover, the

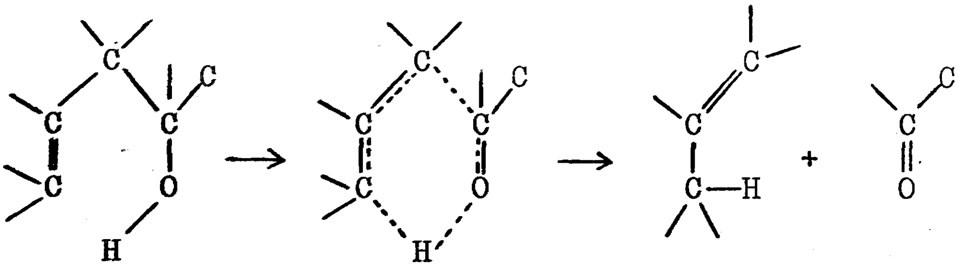


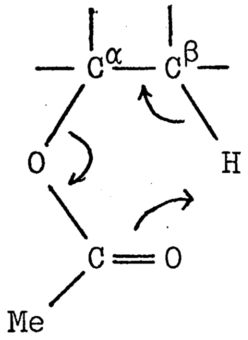
Fig. 2

ionic character of the O--H bond and the hybridisation of other atoms involved in the cyclic transition state do not appear to be of primary consequence in determining the $\underline{k}_H/\underline{k}_D$ magnitude in <u>concerted</u> proton transfer mechanism.

The significance of the magnitude of the primary deuterium kinetic isotope effect as a criterion of the transition state structure is still currently under debate. However, a determination of the magnitude of $\underline{k}_H/\underline{k}_D$ in sulphonate ester pyrolysis at different temperatures leading to 1,3-elimination would give valuable information towards an understanding of the mechanism of this reaction.

There have been investigations of the β-deuterium kinetic isotope effect in 1,2-eliminations during acetate pyrolysis in the past ten years and these have been reviewed.[19,20]

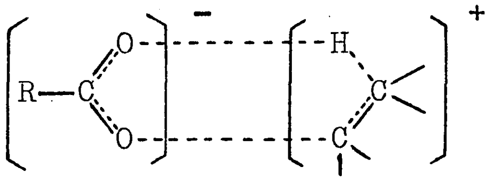
Acetate pyrolysis was originally portrayed to proceed <u>via</u> a six-membered transition state as a fully concerted process[21] (16). This could not explain the observed effect of substituents at the α- and β-carbon atoms and it appeared[22]



(16)

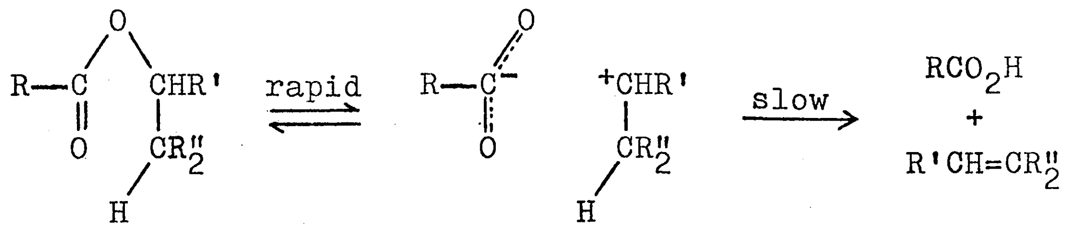
that electron supply at the α-carbon atom speeds up the reaction, while at the β-carbon electron supply speeds the reaction for secondary and tertiary esters and slows it for primary esters.

Smith <u>et al</u>. showed conclusively that the α-carbon possessed carbonium ion character in the transition state,[23] and this was later confirmed by Scheer <u>et al</u>.[24] and by Emovon and Maccoll[25] who suggested an ionic transition state for the reaction (17).



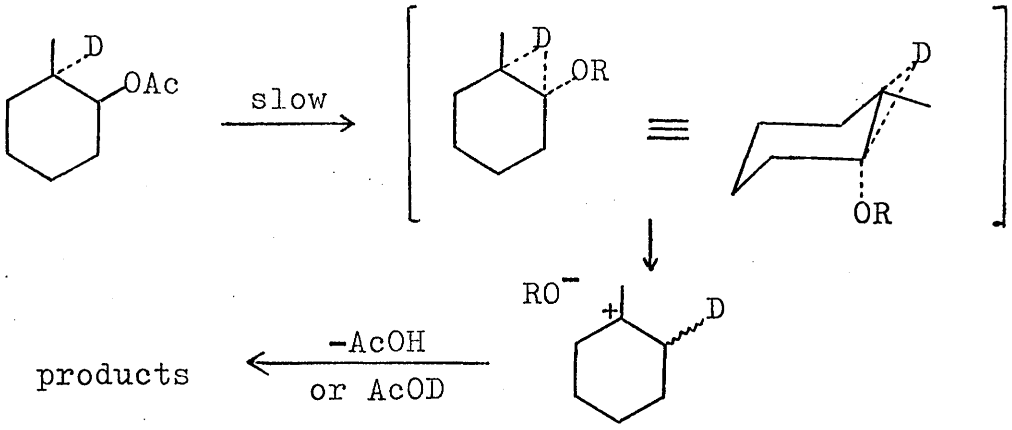
(17)

The observed β-deuterium kinetic isotope effect[26] ruled out a simple ion-pair mechanism. However, the kinetic results are accommodated by proposing[24] a rapid equilibrium between the ground state ester and the ion-pair intermediate followed by a slow transfer of proton to give the acid and the olefin as in Scheme 2; this was supported subsequently by Hanack <u>et al</u>.[27]



Scheme 2

Briggs and Djerassi did not find[28] an isotope effect in <u>trans</u>-elimination but did find one for <u>cis</u>-elimination when they pyrolysed the epimeric 2-$\underline{d}_1$-2-methylcyclohexyl acetates. They suggested in the <u>trans</u>-elimination, a concerted 1,2-deuterium shift involving neighbouring



Scheme 3

deuterium assistance for the loss of the acetate in a slow step, resulting in ion-pair formation as shown in Scheme 3; This operates where <u>cis</u>-elimination cannot occur.

Tinkelenberg <u>et al</u>.[29] did not observe any isomerisation in the thermolysis of pure <u>cis</u>- and <u>trans</u>-2-chlorocyclohexyl acetates, and from the study of a series of substituted cycloalkyl and β-acetylalkyl esters, they described the reaction mechanism as a 'concerted heterolysis' with both C--O and C--H bonds polarised in the transition state as shown in Fig. 3. The 'classical' ion-pair assumption can be seen as one extreme (A), with a whole spectrum of intermediate structures extending to the other extreme of C--H ion-pair formation (B). The authors claim that on this basis, all known subtituent effect can be readily interpreted.

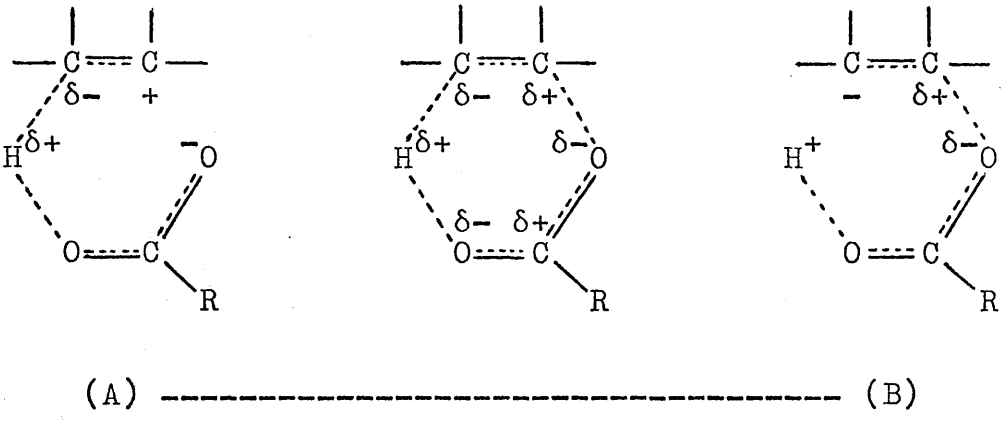
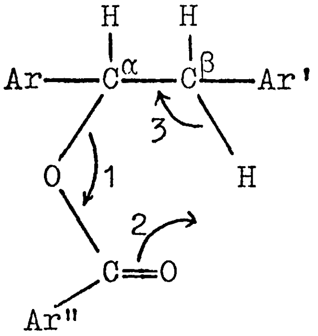


Fig. 3

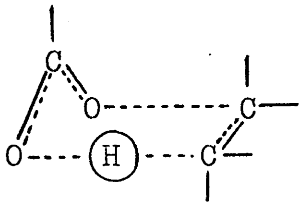
Taylor[30] pyrolysed 1-phenyl- and 1,2-diphenyl-ethyl acetates and their deuterated derivatives and obtained a primary β-kinetic isotope effect $\underline{k}_H/\underline{k}_D$ value of 2.15, ca. 80% of the theoretical maximum and therefore concluded that the β-C--H bond is no more than one third broken in the rate determining step. By interpretation of Hammett ρ values, he estimated that the charge at C_α is only 1.65 times larger than that on C_β in the transition state (18). Thus, if the C_β--H bond is less than one third broken, the C_α--O



(18)

bond will still be far short of completely broken in the transition state. Furthermore, from the rates of the pyrolysis of ethyl benzoate and isopropyl benzoate and the corresponding Hammett ρ-factor, he suggested that the extent of movement of the electron pairs follow the order 1>2>3 in (18).

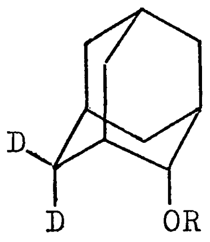
A recent determination[31] by Kwart and Slutsky of the β-deuterium kinetic isotope effect for the pyrolysis of both ethyl and t-butyl carbamate almost corresponds with the theoretical maximum value. This suggests a close parallel between the transition state for ester pyrolysis and that for the pericyclic 'retro-ene' reaction for which k_H/k_D is close to the maximum.[18] The authors generalised the mechanism for ester pyrolysis and suggested a symmetrical non-heterolytic transition state which by analogy[32] with other pericyclic reactions should be non-planar (19).



(19)

The planar transition state suggested by Tinkelenberg[29] (Fig. 3) would be expected to result in a smaller isotope effect[14] in view of the 120° C--H--O angle. The large isotope effect for 1-phenyl- and 1,2-diphenyl-ethyl acetates obtained by Taylor[30] appears to be consistent with that from the carbamate study by Kwart and Slutsky[31] though they present different pictures of the transition states involved.

Against this background of mechanistic studies on β-elimination by ester pyrolysis, it was decided to investigate the γ-*cis*-deuterium kinetic isotope effect in 1,3-eliminations in an attempt to define the mechanism more precisely. This thesis describes the synthesis of (20), (21), and (22) and the analysis of their pyrolysis products.



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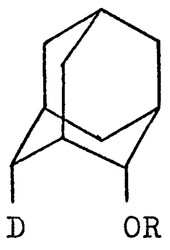
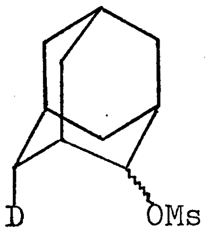


(21)

R = SO_3Me or $COCF_3$

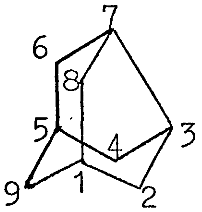


(22)

RESULTS AND DISCUSSION

2-NORADAMANTYL METHANESULPHONATES

The trivial name noradamantane is used for tricyclo-$[3.3.1^{1,5}0^{3,7}]$nonane (23) in line with current practice.[33]



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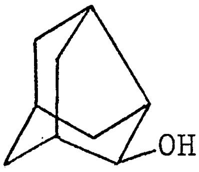

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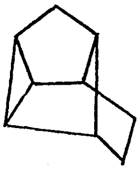
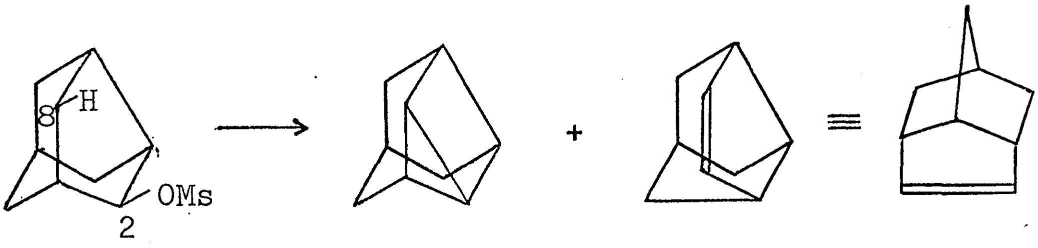


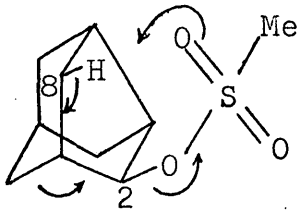
(25)

2-Equatorial-noradamantanol (24) has been previously synthesised in high yield from the reaction of deltacyclane (tetracyclo$[4.3.0.0^{2,4}0^{3,7}]$nonane) (25) with sulphuric acid.[34,35] For the work here described, a sample of (24) was kindly made available to us by Professor P. Schleyer (Princeton).



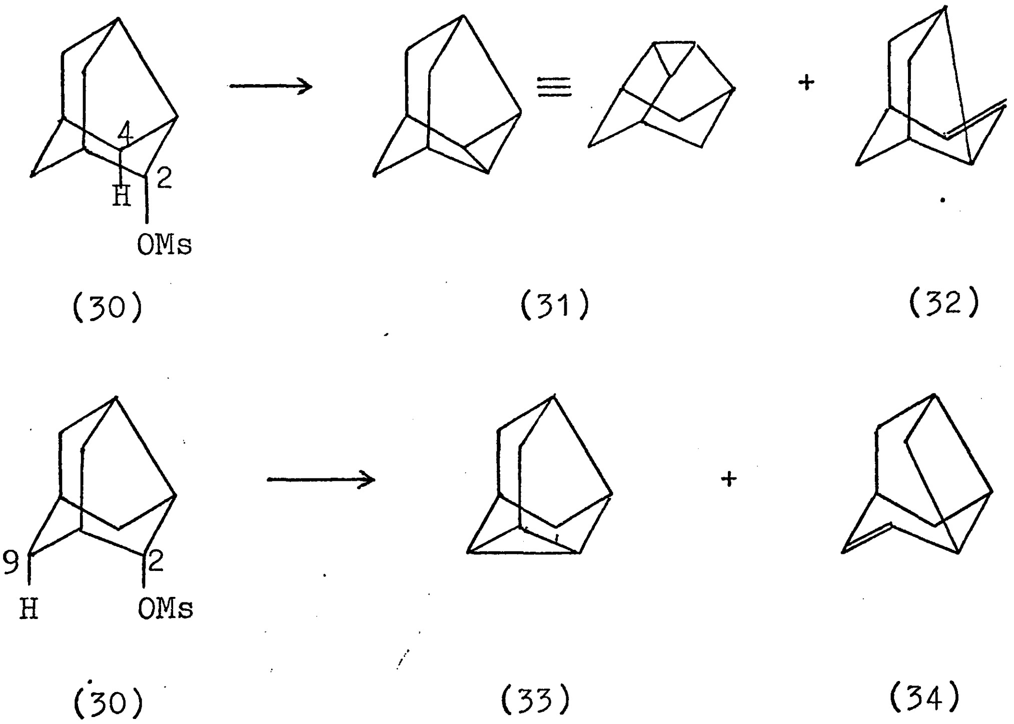
(26) (27) (28)

Scheme 4



(29)

According to the stereochemical requirements of sulphonate ester pyrolysis with rearrangement outlined on page 3, the pyrolysis of 2-equatorial-noradamantyl mesylate (26) should lead to the interesting hydrocarbon (27) and (28) through 1,3-elimination of the C-8 cis hydrogen as shown in Scheme 4. It would give (27) without skeletal rearrangement and (28) via a transition state as in (29).

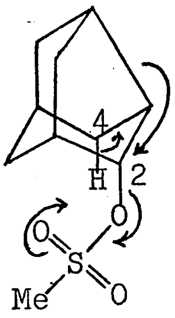


(30) (31) (32)

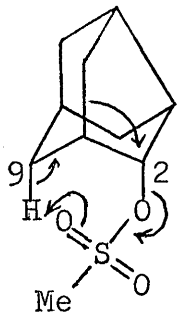
(30) (33) (34)

Scheme 5

Likewise, the expected products from the pyrolysis of the axial-mesylate (30) are shown in Scheme 5. Compounds



(35)



(36)

(32) and (34) would be obtained via the transition states (35) and (36) respectively eliminating either the C-4 *cis*- or C-9 *cis*-hydrogen.

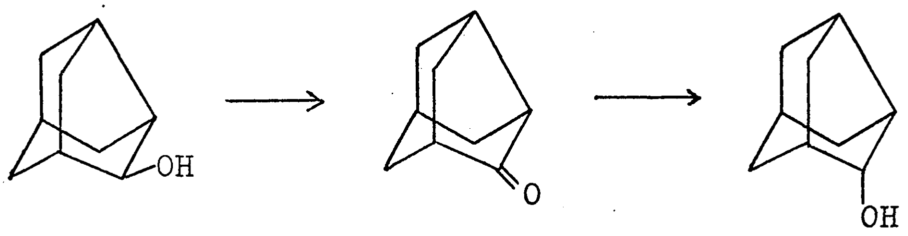
Upon pyrolysis, the mesylate (26) gave three hydrocarbons in the ratio of 67:27:6 as revealed by g.l.c. analysis. G.c.m.s. analysis showed the major hydrocarbons to have $\underline{M}^+$ 120 (loss of $MeSO_3H$) while the minor one had $\underline{M}^+$ 122.

The two major hydrocarbons were successfully separated by preparative g.l.c. The more abundant one (67%), $C_{10}H_{12}$, m.p. 178 - 180°, is a tricyclic olefin [$\nu_{max.}$ 3053, 1603 cm^{-1}, δ 5.92(2H, broad s)]; the ^{13}C n.m.r. spectrum showed resonances at δ 139.74(2C, =C-H), 54.23(1C, CH), 43.19(2C, CH), 42.32(1C, CH_2), and 36.30(2C, CH_2). From this evidence, it was assigned structure (28) of brendene (tricyclo-[4.2.1.$0^{4,8}$]non-2-ene). It was later found to be identical by comparison with spectra of authentic brendene kindly provided by Professor A. Nickon[36] (Baltimore).

The second major component (27%), $C_{10}H_{12}$, m.p. 177 - 178°, is a tetracyclic compound containing a cyclopropane ring ($\underline{M}^+$ 120, $\nu_{max.}$ 3040 cm^{-1}, no double bond resonances in the ^1H and ^{13}C n.m.r. spectra) which is highly symmetrical. There are only four distinct multiplets each of three protons in the ^1H n.m.r. and three signals of similar intensity in the ^{13}C n.m.r. spectrum [δ 47.22(CH_2), 40.37(CH), and 37.18 (CH)]. On this basis the compound was formulated as triaxane (tetracyclo[$3.3.1.0^{2,4}0^{3,7}$]nonane) (31), and found to be identical by i.r. and ^1H n.m.r. comparison with triaxane prepared by a different route[37] by Professor A. Nickon.

The minor hydrocarbon (6%) has not been investigated further because of the small amount available.

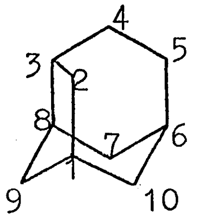
The remainder of the available sample of (24) was converted stereospecifically to its epimer, 2-<u>axial</u>-nor-adamantanol (38) <u>via</u> the ketone (37) by the published method[34] and its mesylate (30) was prepared in the usual way. Its pyrolysis gave a mixture of triaxane (31) and brendene (33) in the ratio of 4:1.



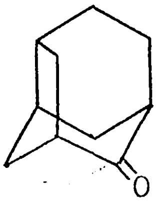
(24) (37) (38)

According to Schemes 4 and 5, pyrolysis of the *equatorial*-mesylate (25) should give brendene (28), while pyrolysis of the *axial*-mesylate (30) should give triaxane (31). Since a mixture of brendene (28) and triaxane (31) was obtained from *either* epimer (their ratios in the two pyrolyses being different), this strongly suggests either (a) the possibility of epimerisation of the sulphonate function during or prior to pyrolysis, or (b) that the pyrolysis goes through an ion-pair intermediate. These two points have bearing on the discussion in section (b) and will be discussed there in detail.

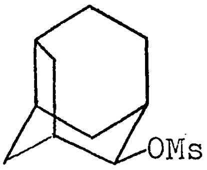
10-PROTOADAMANTYL METHANESULPHONATES



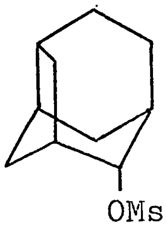
(39)



(40)



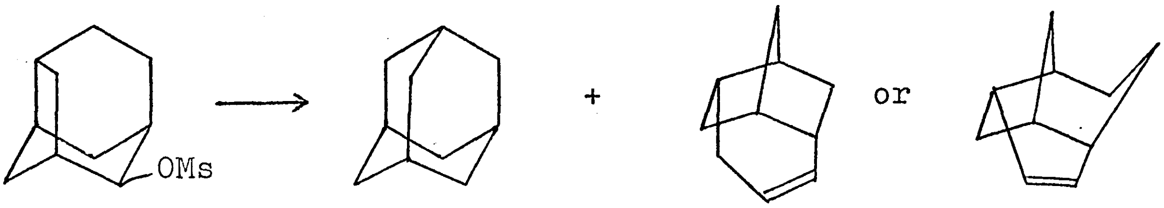
(41)



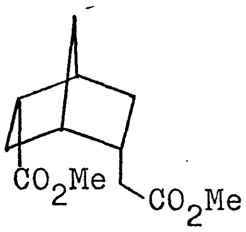
(42)

The trivial name protoadamantane is used for tricyclo-$[4.3.1.0^{3,8}]$decane (39) for brevity.[33] 10-Protoadamantanone (40) has been previously synthesised and through it the epimeric 10-protoadamantyl methanesulphonates (41) and (42).[38] The compounds (41) and (42) used in this study were kindly made available by Professor C. Cupas (Case Western Reserve, Ohio).

The pyrolysis of 10-equatorial-protoadamantyl methanesulphonate (41) was first studied by Boyd in this laboratory,[3] who obtained in addition to adamantane (43) an olefin predicted to be either (44) or (45). A synthesis of the diester (46) was also explored, for comparison with a degradation product of what was thought to be from n.m.r. analysis the more likely olefin (44).

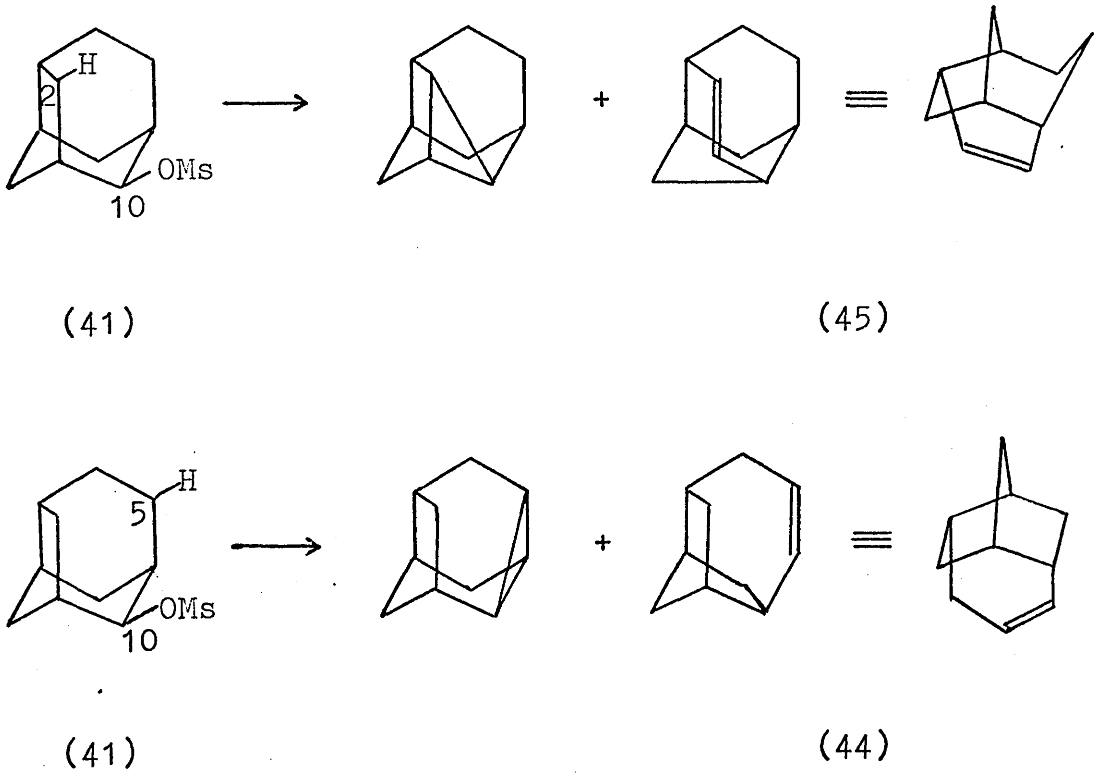


(41) (43) (44) (45)

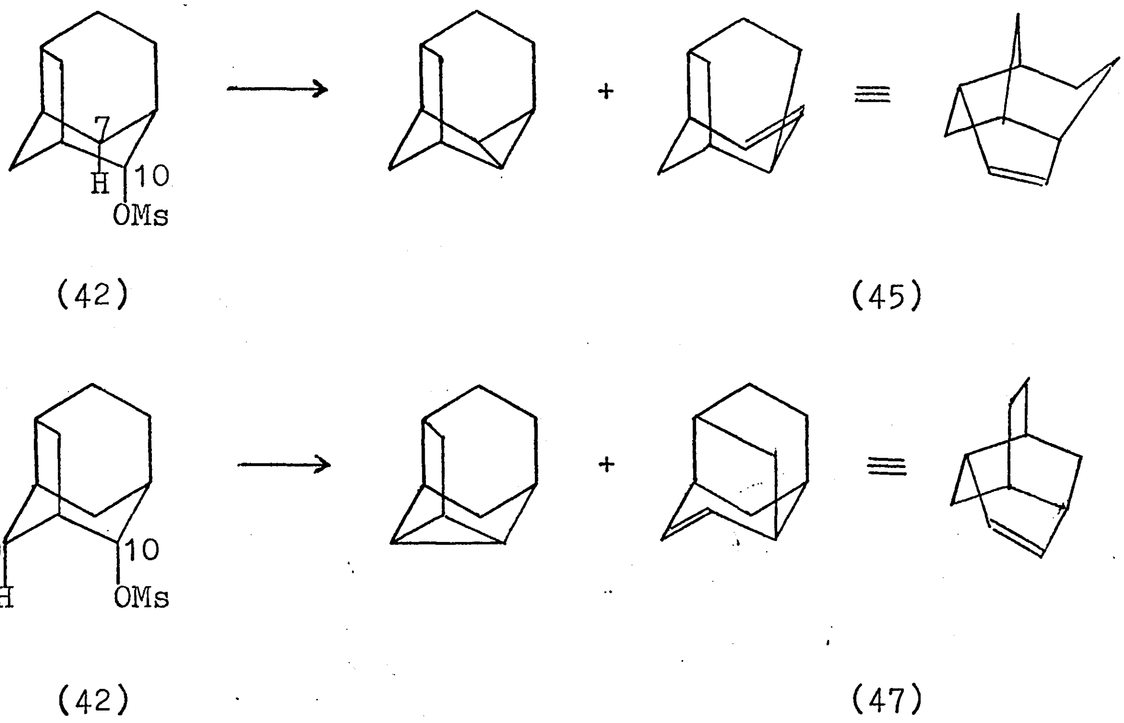


(46)

The pyrolysis of mesylates (41) and (42) was continued in this study, since this would provide further test cases for the steric requirements of the 1,3-elimination as well as affording interesting products. Scheme 6 shows the possible pyrolysis products from the <u>equatorial</u>-epimer (41), Scheme 7 those from the <u>axial</u>-epimer (42).



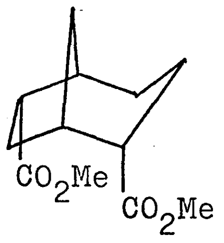
Scheme 6



Scheme 7

The available (41) (0.7 g) was pyrolysed and products identical (g.l.c.) to those previously obtained by Boyd[3] were isolated, namely, adamantane (43) and an olefin in the ratio of 3:2. The olefin, separated from adamantane by chromatography over silver nitrate-alumina, had i.r. absorption at 3020, 1635 cm^{-1} and in the n.m.r. two approximate double doublets at δ 5.89(*J* = 9.5 and 6.5 Hz) and 5.20(*J* = 9.5 and 3.0 Hz) each of one proton. It was not evident from the spectroscopic data whether the olefin was (44) or (45).

The olefin was then cleaved oxidatively by permanganate-periodate in aqueous acetone[39] to give (after methylation with diazomethane) the diester (46) or (48). The diester (an oil) had i.r. absorptions at 1740, 1435 cm^{-1}

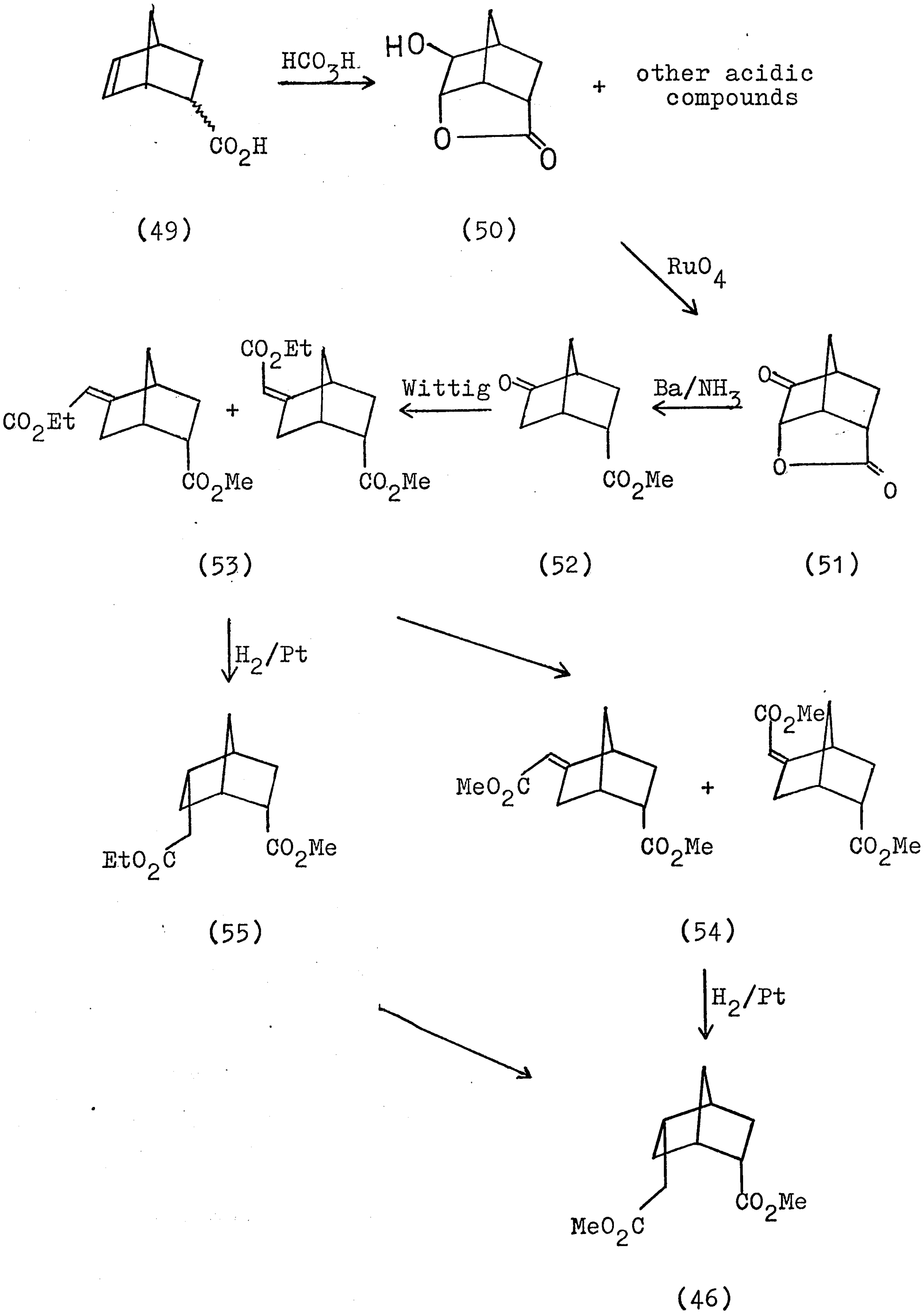


(48)

and n.m.r. signals at 3.68(3H, s) and 3.67(3H, s). It was shown on g.l.c. to be ca. 98% pure using 2m x 1/8in 1% SE30 column at 110°, 2m x 1/8in 1.5% QF1 column at 150°, 2m x 1/8in 1% ApL column at 160°, 2m x 1/8in 8% Carbowax column at 150°, and 2m x 1/8in 8% 1,4-butanediol succinate column at 150°. It was not evident from these data whether the diester was (46) or (48).

To establish the structure of the diester, the synthesis of (46) was carried out as shown in Scheme 8.

The hydroxylactone (50)[40,41] was synthesised by treating a commercial mixture of bicyclo[2.2.1]hept-5-ene-2-carboxylic acids (49) with performic acid according to Henbest and Nicholls.[40] The acidic products derived from the β-acid component of the mixture in (49) were removed by saturating the reaction mixture with bicarbonate prior to extraction and were not further investigated. The hydroxylactone (50) was oxidised to the corresponding ketolactone (51) by ruthenium tetroxide.[42] Reduction of the ketolactone (51) by barium-liquid ammonia[43] and treatment of the products with diazomethane gave a complex mixture whose components showed varying polarities from the relatively non-polar ketoester to polar diols (t.l.c.) whose separation by


HCO3H
HO
O
O
+ other acidic compounds
CO2H
(49)
(50)
RuO4
CO2Et
CO2Et
+
CO2Me
CO2Me
Wittig
O
CO2Me
Ba/NH3
O
O
O
(53)
(52)
(51)
H2/Pt
CO2Me
MeO2C
+
CO2Me
CO2Me
EtO2C
CO2Me
(55)
(54)
H2/Pt
MeO2C
CO2Me
(46)

Scheme 8

preparative t.l.c. proved difficult. The mixture was then oxidised by Jones reagent,[44] and upon treatment with diazomethane, gave the ketoester (52) as an oil. After completion of this work, different synthetic routes[45] to (52) came to our attention.

Treatment of the ketoester (52) by triethyl phosphonoacetate-sodium hydride[46] gave a mixture of geometrical isomers of the unsaturated diester (53). Base hydrolysis of (53) and methylation of the products with diazomethane gave the mixture (54), which, on hydrogenation gave (46). The unsaturated diesters (53) were also hydrogenated to give (55) and converted to (46).

The oily diester (46) was homogeneous by g.l.c. and gave i.r. absorptions at 1739, 1435, and 1417 cm^{-1}, n.m.r. resonances at δ 3.64(3H, s), 3.62(3H, s), 2.75(1H, m), and 2.48(2H, m). It was found to give different g.l.c. retention times and n.m.r. spectrum, on comparison with the diester obtained on oxidative cleavage of the olefin (44) or (45).

This suggested that the pyrolysis of the mesylate (41) gave the olefin (45) and not (44), and that the diester obtained from it was (48). A careful comparison of the i.r. and the mass spectra of the two diesters proved to support this. The synthetic diester (46) gave an i.r. absorption at 1417 cm^{-1} indicating a methylene group α to a carbonyl function,[47] an ion at <u>m/e</u> 152 (relative intensity 31%) in the mass spectrum (Table 1) indicating also a methylene group α to the ester function, and these were not found in the other diester (48).

Table 1

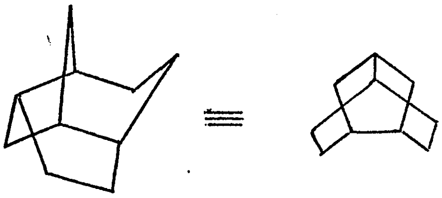
Mass Spectra of (46) and (48)
Numbers in brackets are percentage intensities

Compound	(46)	(48)
$\underline{M}^+$	226(11)	226(19)
$\underline{M}^+ - \mathrm{OMe}$	195(57)	195(38)
$\underline{M}^+ - \mathrm{MeOH}$	194(100)	194(43)
$\underline{M}^+ - \mathrm{MeOH} - \mathrm{H_2O}$	176(12)	
$\underline{M}^+ - \mathrm{MeOH} - \mathrm{CO}$	164(65)	164(95)
$\underline{M}^+ - 2\mathrm{MeOH}$	162(41)	162(15)
$\underline{M}^+ - \mathrm{MeOH} - \mathrm{CH_2CO}$ $(\underline{M}^+ - \mathrm{MeOH} - \mathrm{CO} - \mathrm{CH_2})$	152(31)	
$\underline{M}^+ - 2\mathrm{MeOH} - \mathrm{CO}$	134(38)	134(100)

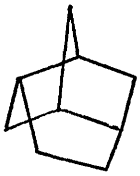
At this stage of the work, a sample (0.2 g) of the epimeric 10-axial-protoadamantyl methanesulphonate (42) was made available to us by Professor C. Cupas. Pyrolysis of a small sample (0.02 g) gave a mixture of four compounds in the ratio of 1:1:4:1 (g.l.c.); while pyrolysing a large sample (0.17 g) under similar conditions gave only adamantane (43) and the olefin previously obtained from the epimeric mesylate (41). This further supports structure (45) for the olefin since this is the predicted common product from pyrolysis of either mesylate (41) or (42).

It is notable that varying the quantity of mesylate pyrolysed alters the ratio of the products formed. The factors that are difficult to reproduce in any two pyrolyses are the amount of sodium carbonate coating in the exit end and the amount of glass wool inside the pyrolysis tube (see Experimental for the details). This suggests the intervention to a variable degree of surface reactions in addition to true vapour phase processes.

The small amount of olefin (45) at hand was hydrogenated to give 90% of the saturated hydrocarbon (56) (distinguished from the olefin by g.l.c.). A ^{13}C n.m.r. spectrum of the sample purified by preparative g.l.c. was measured. This should differentiate (56) and (57) due to the symmetry of the former, but disappointingly this failed to provide convincing information because of the small amount of sample available.



(56)

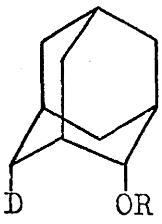


(57)

A STUDY OF THE γ-CIS DEUTERIUM ISOTOPE EFFECT IN THE PYROLYSIS OF 2-ADAMANTYL ESTERS

SYNTHESIS OF DEUTERIUM-LABELLED 2-ADAMANTYL ESTERS

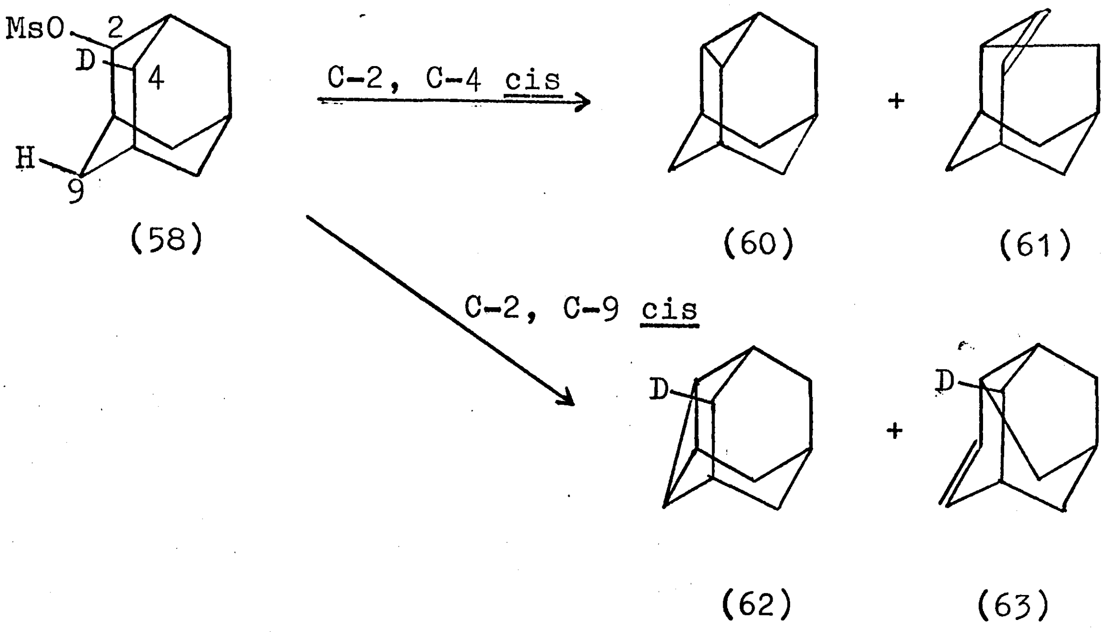
Against the background of mechanistic studies on β-elimination by ester pyrolysis described in the Introduction, it was decided to investigate the γ-*cis* deuterium kinetic isotope effect in 1,3-elimination in an attempt to define the mechanism more precisely.



(58) R = Ms
(59) R = $COCF_3$

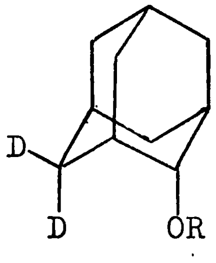
The synthesis of the labelled esters (58) and (59) was first attempted. It was expected that by their pyrolysis, the sample of dehydroadamantane (60) and (62) and of protoadamantene (61) and (63) thus available would give a $\underline{d}_1$:$\underline{d}_0$ ratio from g.c.m.s. analysis, which in effect is the ratio of (62):(60) in the case of dehydroadamantane and (63):(61) in protoadamantene.

The stereochemical environment of the ester (58) is set such that elimination of C-2, C-4 *cis* or C-2, C-9 *cis* groups is possible as shown in Scheme 9. The C-4 *cis* deuterium and the C-9 *cis* hydrogen are stereochemically



Scheme 9

equivalent. Thus, through an intramolecular competition, the ratio of (62):(60) would give $\underline{k}_H/\underline{k}_D$ for 1,3-elimination without rearrangement, and (63):(61) in elimination with rearrangement.



(64) R = Ms
(65) R = $COCF_3$

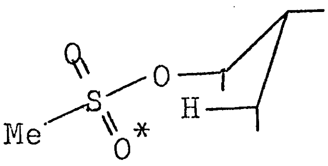
Pyrolysis of the esters (64) and (65), which present a simpler synthetic problem, would serve as an additional check.

In a proton-transfer reaction as in Fig. 4 where A and B are the reactant and the product respectively, the $\underline{k}_H/\underline{k}_D$

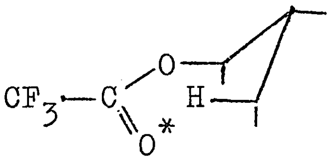
$$AH + B \longrightarrow A{-}{-}{-}H{-}{-}{-}B \longrightarrow A + HB$$

Fig. 4

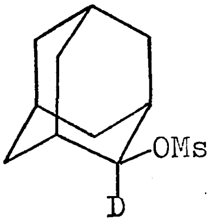
varies according to the basicities of groups A and B[15,16,17] (see page 8). In ester pyrolysis, the sulphonate oxygen O^* in (66) and the trifuoroacetate oxygen O^* in (67) have different basicities. The labelled trifluoroacetates (59) and (65) were also prepared and it was expected that their pyrolysis might give a different $\underline{k}_H/\underline{k}_D$ from that of the corresponding mesylates.



(66)



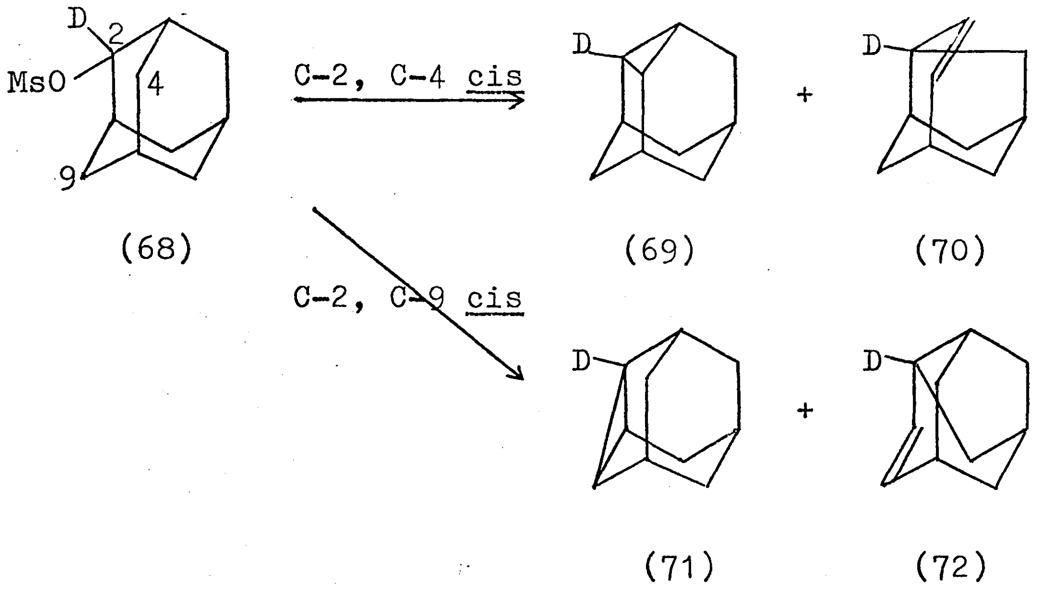
(67)



(68)

Ester (68) could be used as a control to see if there is scrambling of the label during pyrolysis. Scheme 10 shows the possible pyrolysis products of (68).

A C-2, C-4 <u>cis</u>-elimination in (68) would give (69) and (70) whereas C-2, C-9 would give (71) and (72); but (69) and (71) are enantiomeric and so are (70) and (72). ^{13}C N.m.r. analysis would reveal if the deuterium is stereospecifically in one position in the products (see below).



Scheme 10

As a check on the possibility of epimerisation of the sulphonate ester group during or prior to pyrolysis (see following section), a 1:1 mixture of the epimeric $\underline{d}_1$-mesylates (73) and (74) was also synthesised.

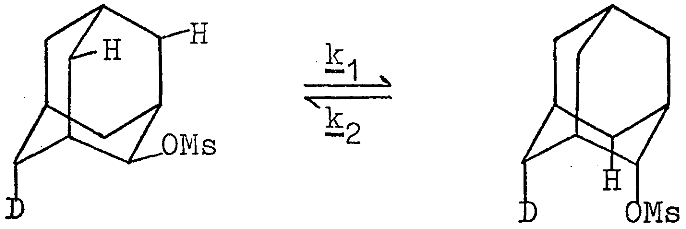
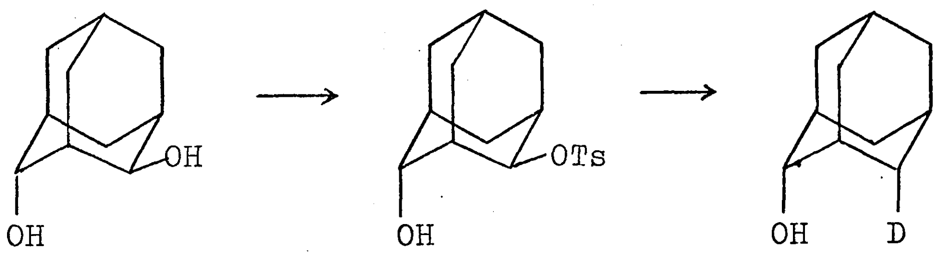


Fig. 5

Assuming there is no deuterium isotope effect in the isomerisation of the sulphonate group in Fig. 5, the rate of isomerisation in (73) and that in (74) should then be equal, that is $\underline{k}_1=\underline{k}_2$. In this way, the mixture always contains equal amount of (73) and (74). Thus, pyrolysis of (73) would give a complete retention of deuterium while that of (74) would give a mixture of $\underline{d}_1$- and $\underline{d}_0$-hydrocarbons in the product whose ratio is a measure of $\underline{k}_H/\underline{d}_D$ in the pyrolysis. In effect, there are in the mixture of (73) and (74) three hydrogens having the right stereochemistry to be eliminated for every one deuterium, the $\underline{d}_1:\underline{d}_0$ ratio in the product would then be three times the true $\underline{k}_H/\underline{k}_D$ for the pyrolysis.

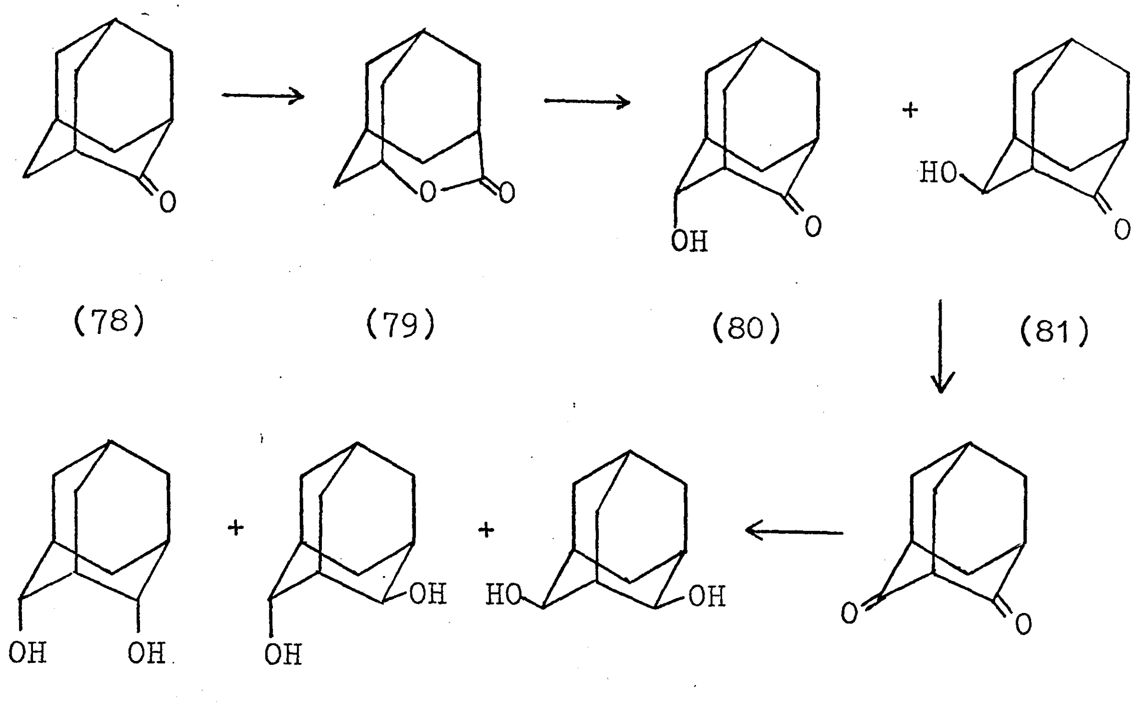
If there is fast epimerisation during or prior to pyrolysis, pyrolysis of the mixture (73) and (74) and pyrolysis of (58) would give products identical in deuterium content, detectable by ^{13}C n.m.r. spectroscopy.



(75) (76) (77)

For the synthesis of (58), it was decided to prepare the diol (75) and from it the tosylate (76); lithium aluminium deuteride reduction should then give the labelled 2-adamantanol (77).

The synthesis of diol (75) began with the commercially available adamantanone (78) as shown in Scheme 11.[48]



(78) (79) (80) (81)

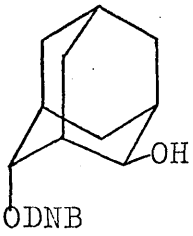
(83) (84) (85) (82)

Scheme 11

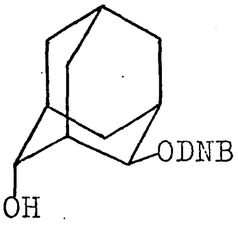
Adamantanone (78) was converted to 4-oxahomoadamantan-5-one (79) through a Baeyer-Villiger reaction with hydrogen peroxide-selenium dioxide. The lactone (79) was rearranged by 50% sulphuric acid at 90^{0} to a mixture of 4-hydroxyadamantan-2-ones (80) and (81) via a π-route process.[48] Jones oxidation[44] gave adamantane-2,4-dione (82), which, on reduction with lithium aluminium hydride, gave a mixture of adamantane-2,4-diols (83) — (85).

Attempts to separate these diols (83) — (85) completely proved difficult. Adamantane-2a,4a-diol (83) was easily separated from the other two either by column chromatography or preparative t.l.c. since the optimal geometry leading to the formation of intramolecular hydrogen bonding effectively lowered its polarity. The other two diols (84) and (85) were found to be inseparable on t.l.c. and attempted separation by column chromatography proved fruitless. However, g.l.c. analysis of their bistrimethylsilyl ethers showed the diol mixture to consist of two compounds in the ratio of 7:3. The bisacetyl- and the bis(3,5-dinitrobenzoyl)-derivatives[49] of the diols were also inseparable on t.l.c.

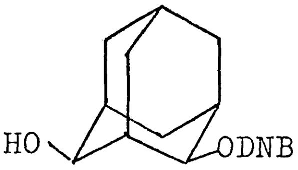
A further attempt to separate the diols (84) and (85) was made by preparing the mono-3,5-dinitrobenzoates modifying the method used by Owen and Robins[50] for the preparation of the monotosylate of cyclohexane-1,4-diol. Only one of the three mono-3,5-dinitrobenzoates (86) — (88) could be isolated pure by preparative t.l.c. Since it was reduced by lithium aluminium hydride to give an unsymmetrical diol (84), the pure mono-3,5-dinitrobenzoate was either (86) or (87).



(86)



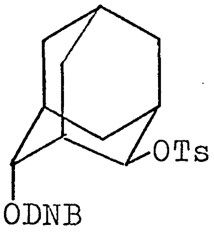
(87)



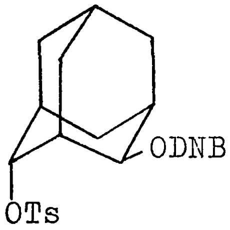
(88)

This synthesis of adamantane-2*e*,4*a*-diol (84) from the diketone (82), with the necessary separation procedures, gave an overall yield of only 9%. Other methods to reduce the diketone (82) and the hydroxyketones (80) and (81) were attempted in the hope of effecting a more stereospecific reduction and thus obtain the diol (84) as major product.

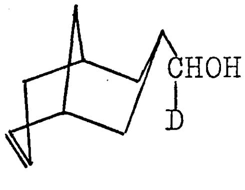
A Meerwein-Ponndorf-Verley[51] reduction of adamantane-2,4-dione (82) gave a diol mixture separated by preparative t.l.c. into (83) (10%) and a mixture of (84) and (85) (50%) in the ratio of 7:3 (g.l.c.). Lithium-ammonia reduction[52] of hydroxylactone (80) afforded diol (83) and (84) in the ratio of 99:1. Lithium aluminium hydride reduction of hydroxyketone (81) gave diol (84) and (85) in the ratio of 3:2. Attempted equilibration of the mixed diol [(83) and (84) or (84) and (85)] with aluminium isopropoxide in isopropanol gave a mixture containing *ca.* 95% of (83). Thus, reduction either of the diketone (82) or the hydroxyketones (81) and (80) by the methods tried gave a diol mixture (83) — (85).



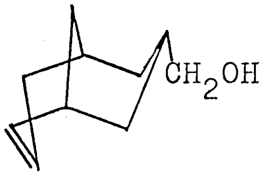
(89)



(90)



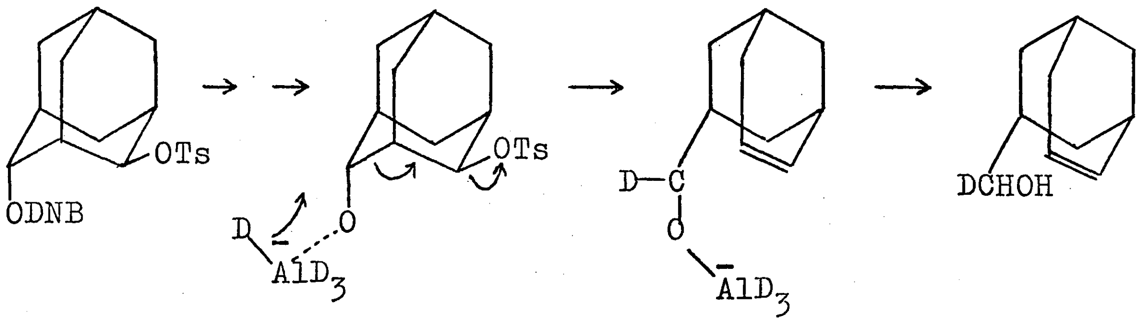
(91)



(92)

The tosylate (89) or (90) was prepared from the mono-3,5-dinitrobenzoate (86) or (87) of diol (84). Reduction by lithium aluminium deuteride gave the alcohol (91) and this suggested the starting diester was (89) and not (90).

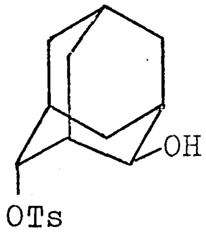
Scheme 12 shows the possible steps involved in this fragmentation.



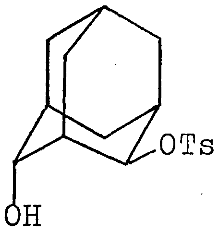
(89) (91)

Scheme 12

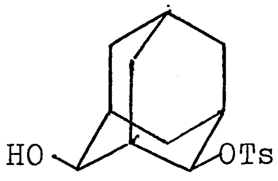
In order to reduce the loss involved in the isolation of (84), the mixture of diols (84) and (85) was converted into monotosylates. The three monotosylates (93), (94), and (95) were successfully separated by preparative t.l.c. from the minor amount of bistosylates (96), (97) and the starting diols (84), (85).



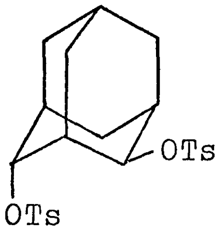
(93)



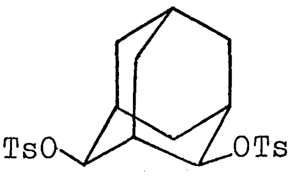
(94)



(95)

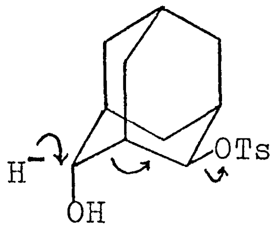


(96)

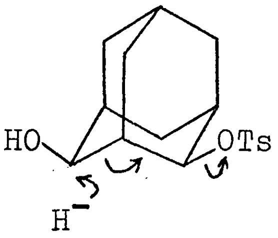


(97)

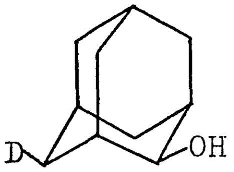
The compound (95) was distinguished from (93) and (94) by further tosylation to give a symmetrical bistosylate (97) while (93) and (94) gave the unsymmetrical bistosylate (96). The compounds (93) and (94) were distinguished by their lithium aluminium hydride reduction products. When treated with lithium aluminium hydride, (94) and (95) gave the alcohol (92) in essentially quantitative yield presumably as in (98) and (99) respectively. Lithium aluminium deuteride reduction of (93) gave the alcohol (91) and the labelled 2-adamantanol (100) in the ratio of 3:7.



(98)



(99)



(100)

The position of the deuterium in (100) was identified by Eu(dpm)$_3$-shifted ^{1}H n.m.r. using a 0.5 mole-ratio of shift reagent. Fig. 6 shows the Eu(dpm)$_3$-shifted n.m.r. spectrum of unlabelled 2-adamantanol (101) while Fig. 7 shows that of (100). The assignment[53] of the signals in Fig. 6 was accomplished by double resonance and from the Eu--H distance and the angle of the Eu--H line with the principal magnetic axis of the complex shown by molecular models.

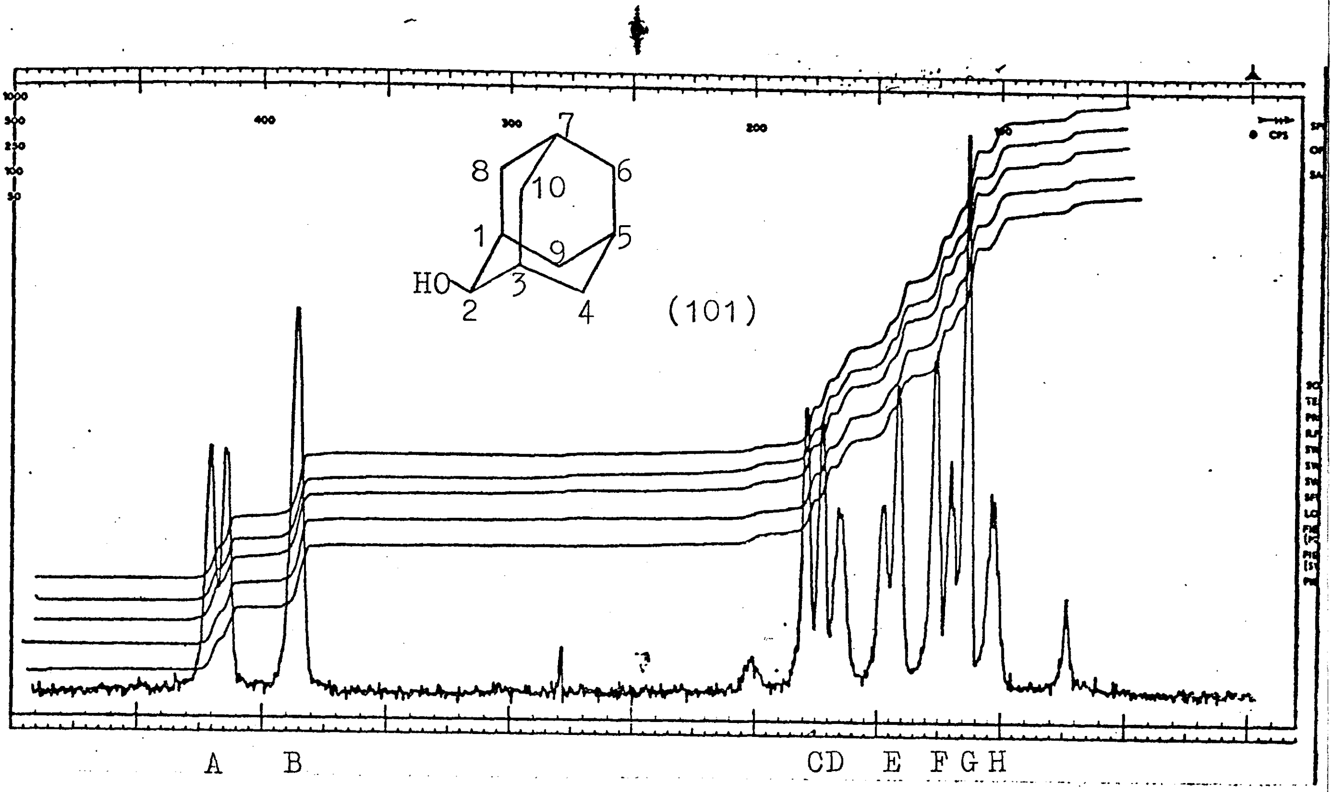


Fig. 6 Eu(dpm)$_3$-shifted 100 MHz N.m.r. Spectrum of (101) {[Eu(dpm)$_3$]:[(101)] = 0.5}

A	C-8, C-10 *cis*	E	C-4, C-9 *cis*
B	C-1, C-3	F	C-4, C-9 *trans*
C	C-8, C-10 *trans*	G	C-6
D	C-7	H	C-5

In Fig. 7, the signal of the 4,9-*cis* protons (E), instead of giving a doublet, is broadened to give a broad singlet with a shoulder but integrated to two protons; that of the 4,9-*trans* protons (F) remains a doublet but integrated to give only one proton. Since the geminal CH_2 and CHD coupling constants are different,[54] the introduction of a 4-*trans* deuterium reduced half of the 4,9-*cis* signal to a broad singlet thus giving the signal shown. Hence, the structure of (100) was defined.

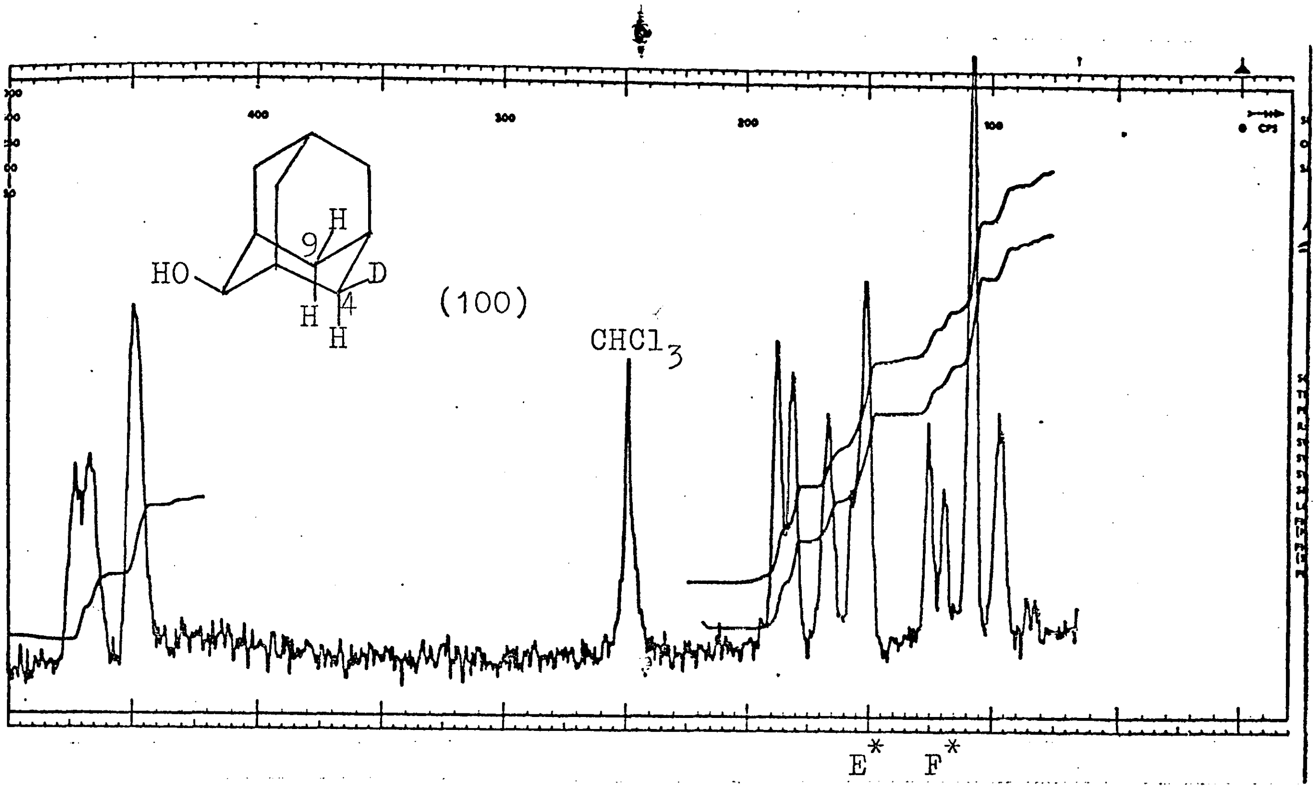
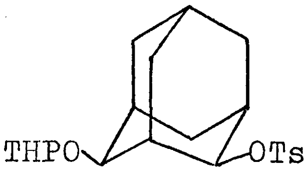


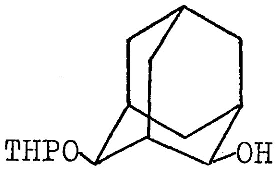
Fig. 7 Eu(dpm)$_3$-shifted 100 MHz N.m.r. Spectrum of (100) $\{[\mathrm{Eu(dpm)_3}]:[(100)] = 0.5\}$

* See Fig. 6

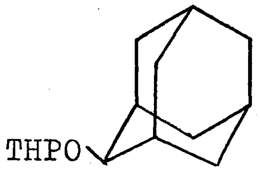
In order to prevent the participation of the hydroxy-group during the lithium aluminium hydride reduction of the hydroxytosylate (94) resulting in the C--C bond cleavage product (92), a tetrahydropyranylether was prepared. The THP-ether (102) of (95) was first prepared^{44} as a model. Upon lithium aluminium hydride reduction in tetrahydrofuran it gave the mono-THP-ether (103) of diol (85), and in ether it gave (102), (103), (104) in the ratio of 17:2:1. The diol (85) was obtained on acid hydrolysis of (103). The compound (104) obtained in this way was identical with a sample prepared from 2-adamantanol (101).



(102)

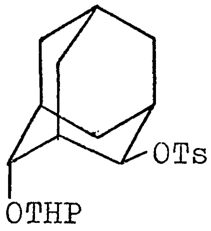


(103)

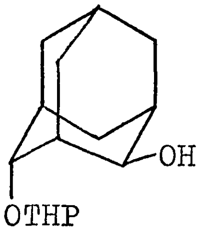


(104)

The THP-ether (105) was likewise prepared from (94) and reduced with a slight excess of lithium aluminium hydride giving (105) and (106) in the ratio of 3:7. With a large excess of lithium aluminium hydride, (105) gave (106) in essentially quantitative yield.



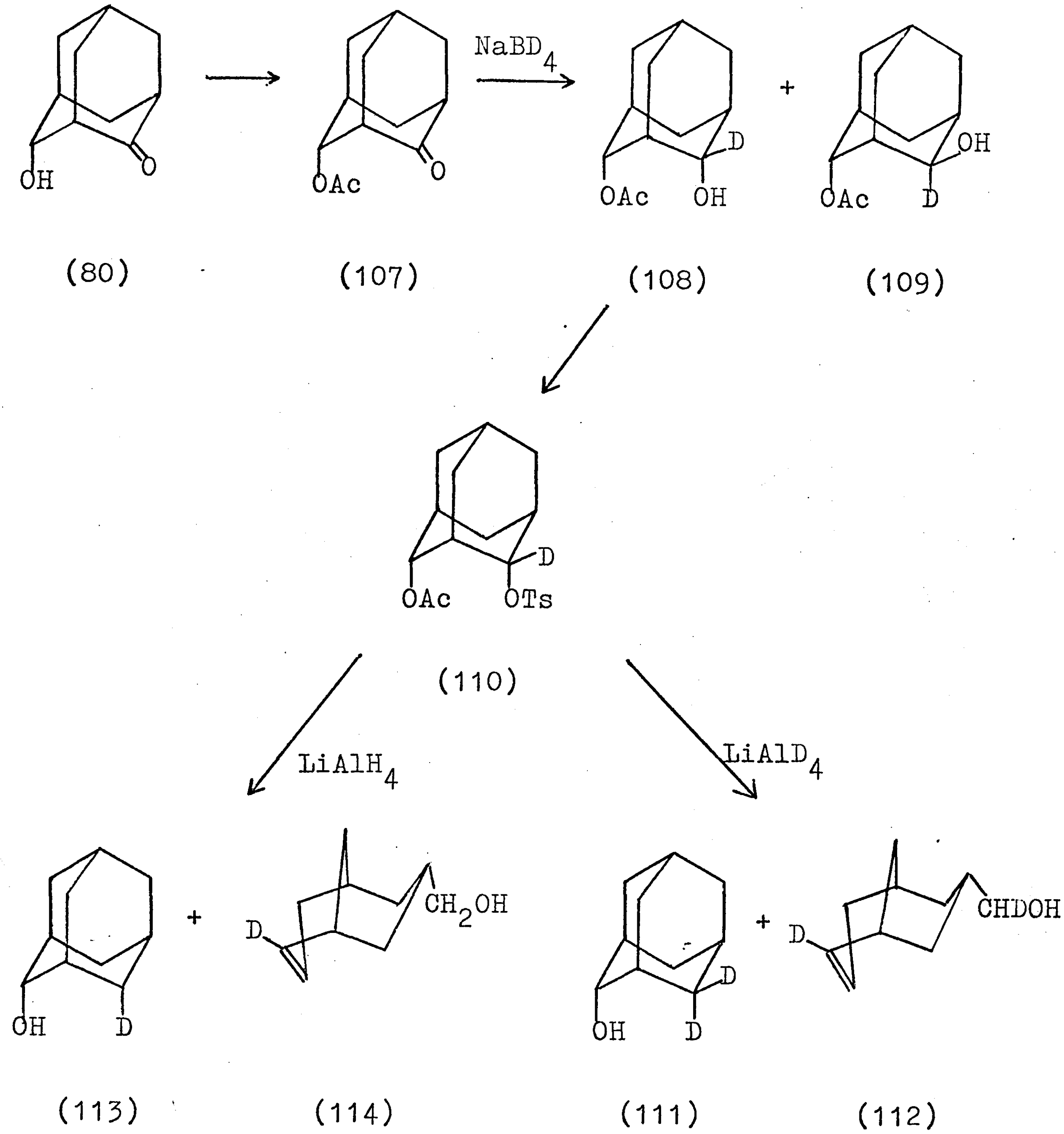
(105)



(106)

The synthesis of the labelled 2-adamantanols (111) and (113) was finally achieved by the route shown in Scheme 13.

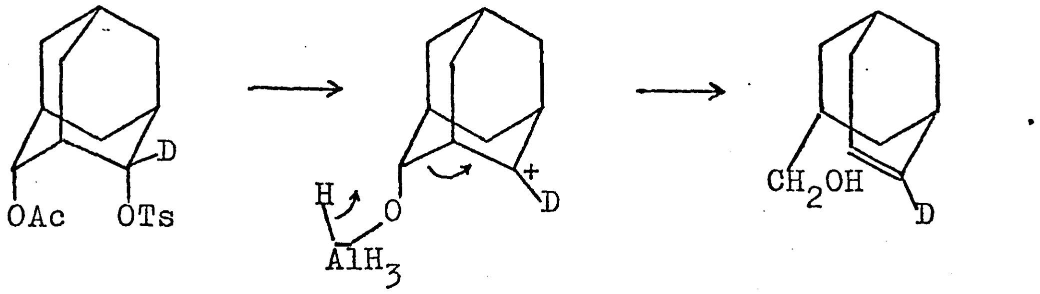
The hydroxyketone (80) was acetylated to give the ketoacetate (107), which, on reduction with sodium borodeuteride, gave labelled hydroxyacetates (108) and (109) in the ratio of 17:3. The compound (108), separated from (109) by preparative t.l.c., was then converted to the tosylate (110) which was reduced by lithium aluminium hydride or lithium aluminium deuteride to give the labelled



Scheme 13

2-adamantanol (113) or (111) respectively.

The success of this synthesis is based on the stereochemical relationship of the acetoxy- and the tosyloxy-groups in (110). Since they are _cis_ to each other, participation of the hydroxy-group (derived from the acetoxy-



(110) (115) (114)

group on treatment with lithium aluminium hydride) similar to Scheme 12 [see also (98) and (99)] cannot operate. However, minor amounts (8%) of the fragmentation products (112) and (114) were still obtained. This suggested that the hydrogenolysis was accompanied by some carbonium ion (115) formation leading to the fragmentation product as shown. The facile rearrangement (115) → (114) in this case prevented racemisation which has sometimes been observed in hydrogenolysis of tosylates.[55]

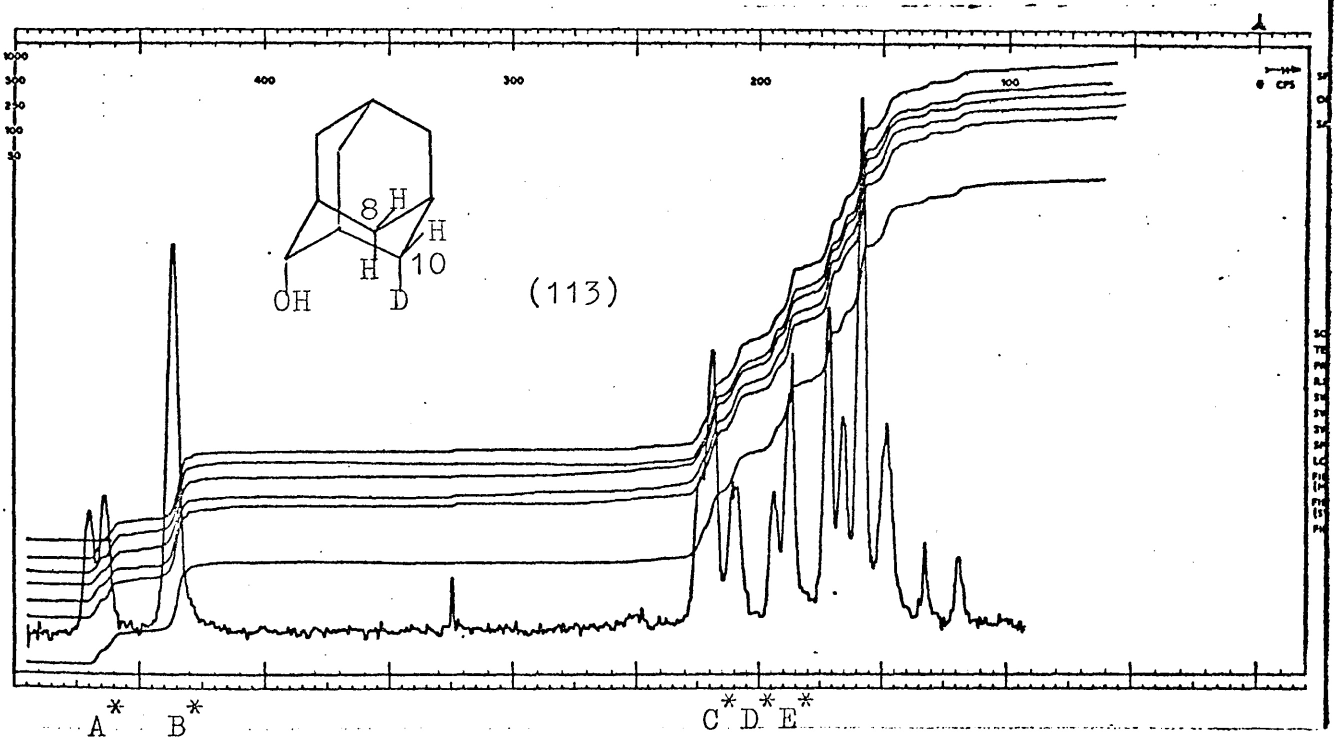


Fig. 8 Eu(dpm)$_3$-shifted 100 MHz N.m.r. Spectrum of (113) $\{[\mathrm{Eu(dpm)_3}]:[(113)] = 0.5\}$

* See Fig. 6

The position of the deuterium in (113) was revealed by the Eu(dpm)$_3$-shifted n.m.r. spectrum as shown in Fig. 8 when compared with that of the unlabelled alcohol (101) in Fig. 6. In the integration of the spectrum shown in Fig. 8 the ratio of the signals for the 8,10 cis protons (A) to that for the 1,3 protons (B) is (1.01 ± 0.08):2 (Table 2), indicating that one of the 8,10 cis protons is substituted by deuterium. The collapse of the 8,10 trans doublet (C) and its correct integration [(C + D):E = 3:2, see Fig. 8] showed the deuterium is stereospecifically at the 8- or 10-cis positions.

Table 2 Ratio of the Integrals of the Eu(dpm)$_3$-shifted N.m.r. of (113)

Repeats / Integral of	A*	B*	(A:B) x 2	(C + D)*	E*	(C + D):E
1	14.0	26.5	1.0566	39.6	26.0	1.5231
2	15.0	26.0	1.1538	39.0	25.2	1.5476
3	13.3	28.0	0.9500	38.0	26.2	1.4504
4	13.0	26.9	0.9665	39.5	26.0	1.5192
5	13.6	27.6	0.9855	39.0	26.0	1.5000
6	12.4	26.8	0.9254	40.0	26.0	1.5385
Mean			(1.01 ± 0.08):2			(3.03 ± 0.06):2

* See spectrum

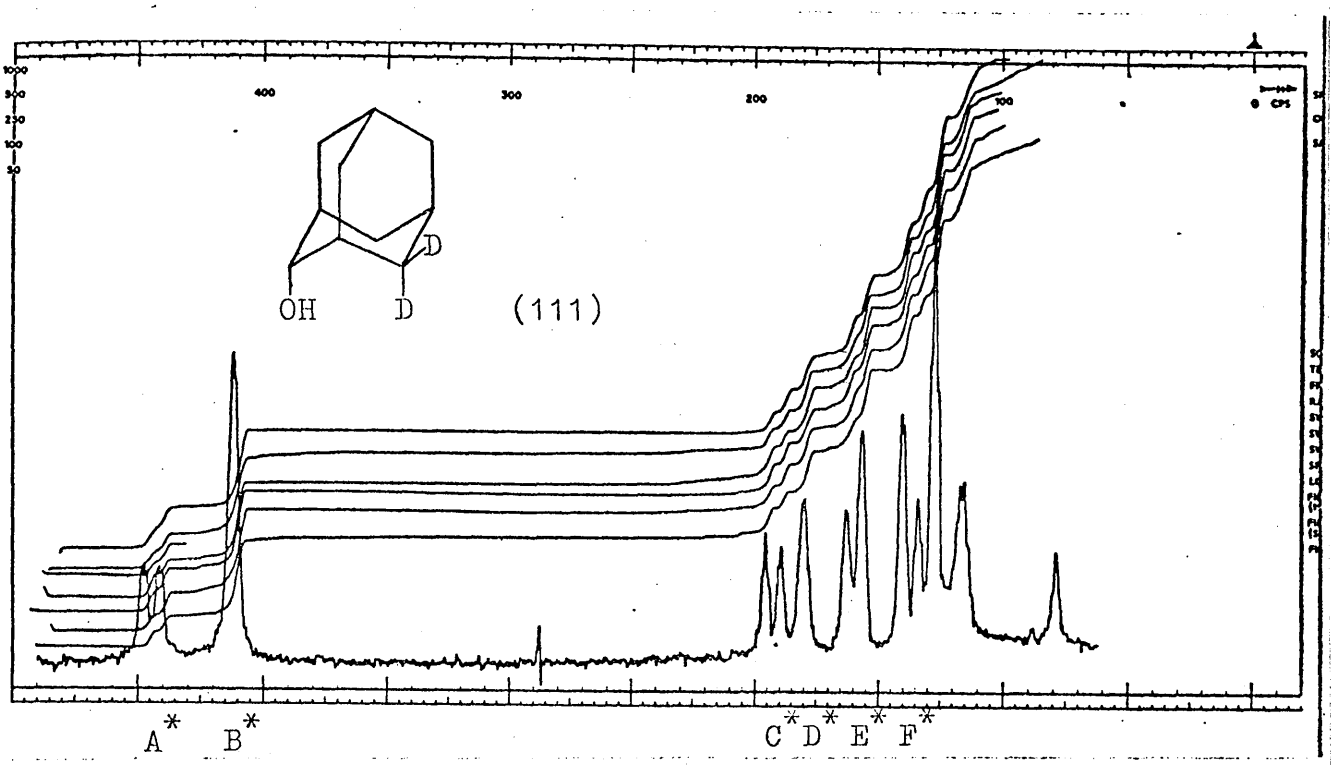


Fig. 9 Eu(dpm)$_3$-shifted 100 MHz N.m.r.
Spectrum of (111) $\{[\mathrm{Eu(dpm)_3}]:[(111)] = 0.5\}$
* See Fig. 6

Fig. 9 shows the Eu(dpm)$_3$-shifted n.m.r. spectrum of (111) in which both the 8,10 <u>cis</u> (A) and 8,10 <u>trans</u> (C) signals integrating for only one proton each (Table 3). They are both doublets showing the two deuterium nuclei are bonded to the same carbon (C-8 or C-10).

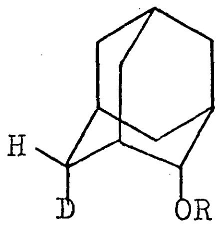
From the alcohols (111) and (113), the esters (116) -- (119) were then prepared by the usual method.

The ester (120) was also synthesised from (78) <u>via</u> the labelled alcohol (121) obtained by lithium aluminium deuteride reduction of (78).

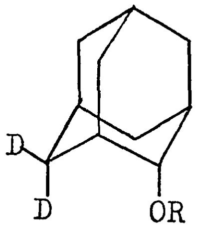
Table 3 Ratio of the Integrals of the $Eu(dpm)_3$-shifted N.m.r. of (111)

Repeats Integral of	A*	B*	(A:B) x 2	C*	D*	C:D	(C + D)*	E*	(C + D):E
1	16.0	30.0	1.0667	17.0	13.0	1.3077	30.0	30.0	1.0000
2	13.5	29.2	0.9247	15.0	15.5	0.9677	30.2	29.2	1.0342
3	14.4	29.0	0.9931	17.8	17.5	1.0171	34.6	30.0	1.1533
4	17.0	29.5	1.1525	11.0	13.4	0.8209	32.0	31.4	1.0191
5	15.0	31.0	0.9677	19.0	14.4	1.3194	31.5	30.3	1.0396
6	12.1	29.0	0.8345	16.0	16.2	0.9877	32.0	30.8	1.0390
Mean			(0.99 ± 0.1):2			(1.07 ± 0.18):1			(1.05 ± 0.05):1

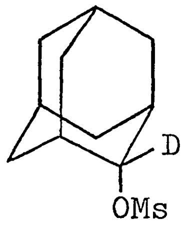
* See spectrum



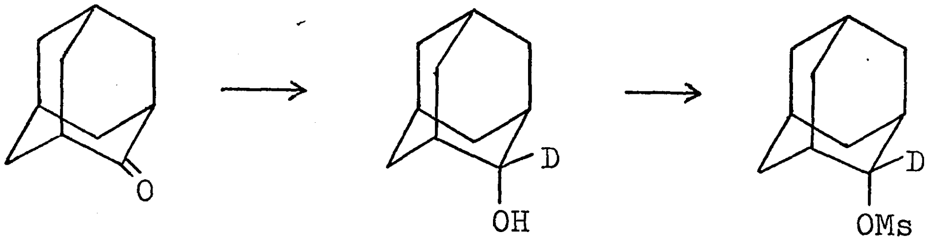
(116) R = Ms
(117) R = $COCF_3$



(118) R = Ms
(119) R = $COCF_3$



(120)



(78) (121) (120)

Assuming the isotopic contents of alcohol (111), (113), and (121) remain the same during esterification, the deuterium in the labelled esters should be >95% stereospecifically in the assigned position (this is limited by the sensitivity of the measurement of the integrals in the n.m.r. spectra). Further checks on the isotopic purities of esters (116), (118), and (120) were made by repeatedly scanning the M^+ region in their mass spectra and measuring the ratio of $(M^+ - 1):M^+$. After correcting for the same ratio in the spectrum of the unlabelled mesylate, under similar conditions of operating the mass spectrometer, this gives the ratio of d_0-ester:d_1-ester. Such determinations showed ester (116) to contain $97.3 \pm 0.7\%$ d_1-ester (Table 4); (118) is isotopically pure (Table 5); and (121) contains $98.9 \pm 0.4\%$ d_1-ester (Table 6).

Table 4 M.S. Data for the Determination of the Isotopic Purity of (116)

2-Adamantyl Methanesulphonate			Compound (116)		
$M^+ - 1$	M^+	ratio*	$M^+ - 1$	M^+	ratio*
1.20	37.0	0.03243	2.55	37.0	0.06892
1.12	34.5	0.03246	2.20	36.0	0.06111
1.05	35.2	0.02983	1.70	28.2	0.06028
1.20	36.2	0.03315	2.45	40.5	0.06049
1.25	38.0	0.03289	1.55	27.0	0.05741
1.55	40.0	0.03875	2.40	37.0	0.06486
1.15	35.5	0.03239	2.50	37.0	0.06757
1.15	32.5	0.03538	2.40	37.0	0.06486
1.10	31.5	0.03492	2.20	36.5	0.06027
1.10	30.2	0.03642	2.20	36.0	0.06111
0.95	28.0	0.03393	2.20	36.0	0.06111
1.10	27.0	0.04074	2.40	35.0	0.06857
1.05	25.0	0.04200	2.20	35.5	0.06197
0.90	25.0	0.03600	2.05	34.0	0.06029
1.00	24.0	0.04167	2.05	34.5	0.05942
Mean	0.036 ± 0.004		Mean	0.063 ± 0.003	

d_0-Ester : d_1-Ester in (116) = (0.063 − 0.036) ± (0.004 + 0.003)
= 0.027 ± 0.007

* The ratio is on the relative intensities of repeated scans in the range *m/e* 225–240

Table 5 M.S. Data for the Determination of the Isotopic Purity of (118)

2-Adamantyl Methanesulphonate			Compound (118)		
$\underline{M}^+ - 1$	$\underline{M}^+$	ratio*	$\underline{M}^+ - 1$	$\underline{M}^+$	ratio*
1.25	35.0	0.03571	1.50	40.5	0.03704
1.80	33.5	0.05373	1.30	37.0	0.03514
1.60	32.5	0.04923	1.10	27.2	0.04044
1.55	32.0	0.04844	1.40	38.0	0.03684
1.45	35.0	0.04143	1.50	37.5	0.04000
1.65	32.5	0.05077	1.70	37.0	0.04595
1.80	32.0	0.05625	1.75	36.0	0.04861
1.50	33.0	0.04545	1.35	36.0	0.03750
1.50	32.0	0.04688	1.25	36.0	0.03472
1.40	30.0	0.04667	1.30	34.0	0.03824
1.70	31.0	0.05484	1.55	33.0	0.04697
1.40	30.0	0.04667	1.50	31.0	0.04839
1.50	31.0	0.04839	1.35	31.0	0.04355
1.60	30.0	0.05333	1.35	32.0	0.04219
1.50	29.5	0.05085	1.20	29.5	0.04068
1.70	27.0	0.06295	1.40	30.5	0.04590
Mean	0.049 ± 0.006		Mean	0.041 ± 0.004	

* The ratio is on the relative intensities of repeated scans in the range m/e 225-240

Table 6 M.S. Data for the Determination of the Isotopic Purity of (120)

2-Adamantyl Methanesulphonate			Compound (120)		
$M^+ - 1$	M^+	ratio*	$M^+ - 1$	M^+	ratio*
0.24	15.1	0.01589	0.45	16.8	0.02679
0.40	16.1	0.02484	0.50	17.1	0.02924
0.36	16.2	0.02222	0.49	17.2	0.02849
0.40	16.6	0.02410	0.55	17.3	0.03179
0.30	16.0	0.01875	0.57	17.5	0.03257
0.30	16.0	0.01875	0.52	18.1	0.02873
0.30	16.0	0.01875	0.52	18.0	0.02889
0.30	16.2	0.01852	0.50	17.5	0.02857
0.30	16.0	0.01875	0.55	17.2	0.03198
0.33	16.8	0.01964	0.55	17.0	0.03235
0.30	16.0	0.01875	0.51	16.5	0.03091
0.30	16.5	0.01818	0.51	16.0	0.03188
0.30	16.5	0.01818	0.51	15.0	0.03400
0.32	16.2	0.01975	0.48	15.0	0.03200
0.32	16.2	0.01975	0.41	14.0	0.02929
Mean	0.020 ± 0.002		Mean	0.031 ± 0.002	

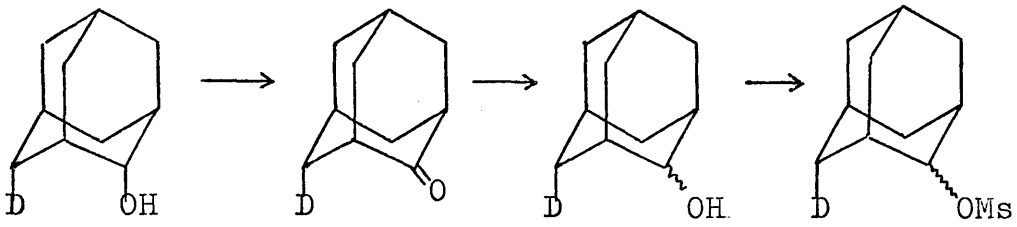
d_0-Ester : d_1-Ester in (120) $= (0.031 - 0.020) \pm (0.002 + 0.002)$

$= 0.011 \pm 0.004$

---

* The ratio is on the relative intensities of repeated scans in the range *m/e* 225–240.

The synthesis of the ester mixture (124) began with the alcohol (113). Jones oxidation[44] of (113) gave the ketone (122) which on lithium aluminium hydride reduction afforded the 1:1 epimeric alcohol mixture (123). The mixture of esters (124) was then synthesised in the usual way.



(113) (122) (123) (124)

The position of the deuterium in the ketone (122) was revealed by Eu(fod)$_3$-shifted ^{1}H n.m.r. using a 0.6 mole-ratio of shift reagent. Fig. 10 shows the Eu(fod)$_3$-shifted n.m.r. spectrum of unlabelled adamantanone (125) while Fig. 11 shows that of (122). In the integration of the spectrum shown in Fig. 11, the ratio of the signals for the 4,8,9,10 *cis* protons (B) to that for the 4,8,9,10 *trans* protons (C) is (3.16±0.06):4 (Table 7) indicating that one of the equivalent 4,8,9,10 *cis* protons is substituted by deuterium.

Fig. 12 shows the Eu(dpm)$_3$-shifted n.m.r. spectrum of (123) in which both the 8,10 *cis* (A) and 4,9 *cis* (E) signals integrating for only one and a half protons each (Table 8). This indicates that half a deuterium is at the 8,10 *cis* position and another half at 4,9 *cis* position as in (126).

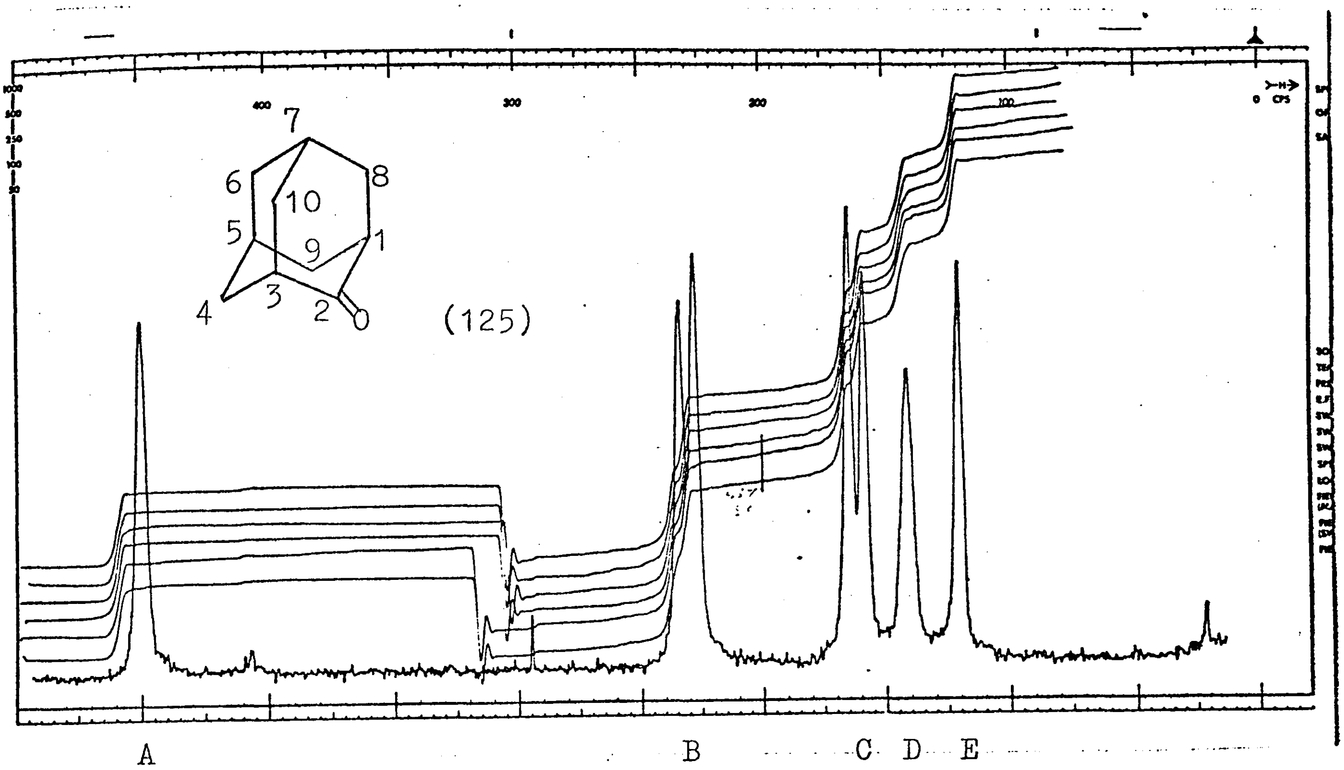


Fig. 10 Eu(fod)$_3$-shifted 100 MHz N.m.r. Spectrum of (125) $\{[Eu(fod)_3]:[(125)] = 0.6\}$

A	C-1, C-3
B	C-4, C-8, C-9, C-10 <u>cis</u>
C	C-4, C-8, C-9, C-10 <u>trans</u>
D	C-7, C-5
E	C-6

Structure (126) is equivalent to a 1:1 mixture of (73) and (74), thus structure (123).

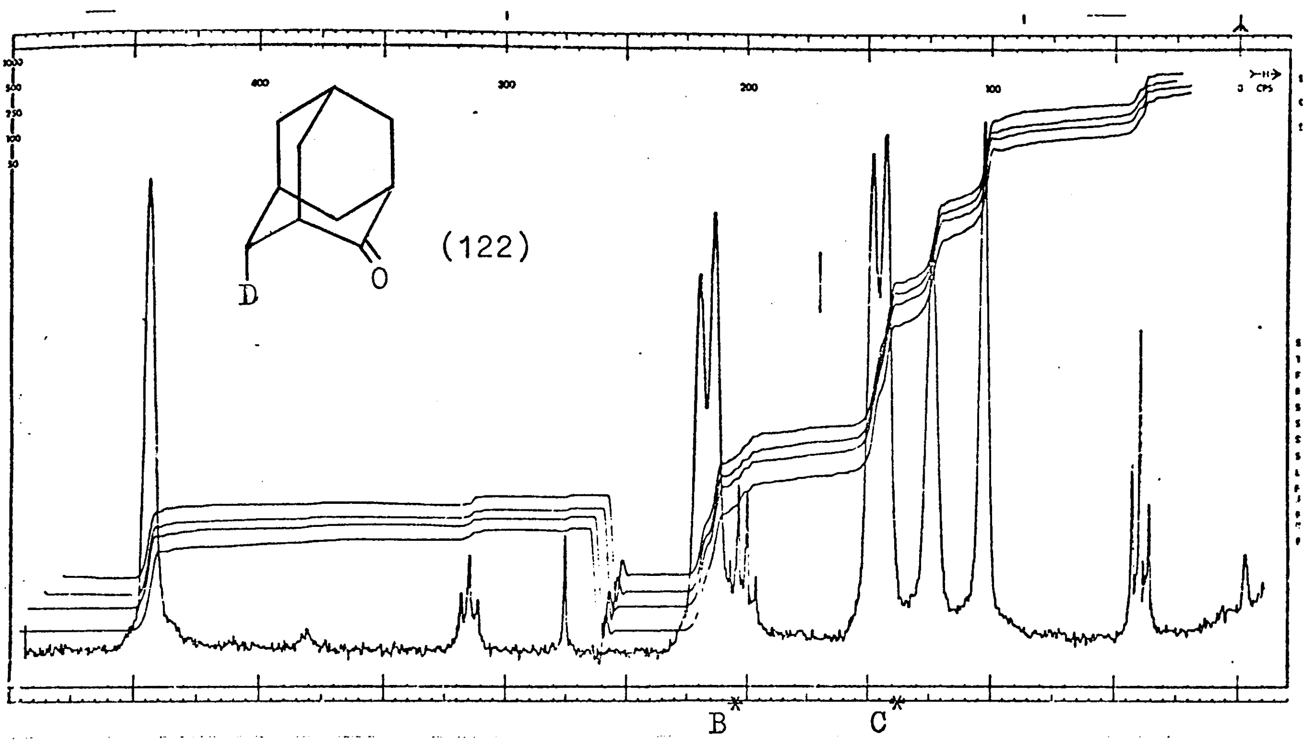


Fig.11 Eu(fod)$_3$-shifted 100 MHz N.m.r. Spectrum of (122) {[Eu(fod)$_3$]:[(122)] = 0.6}

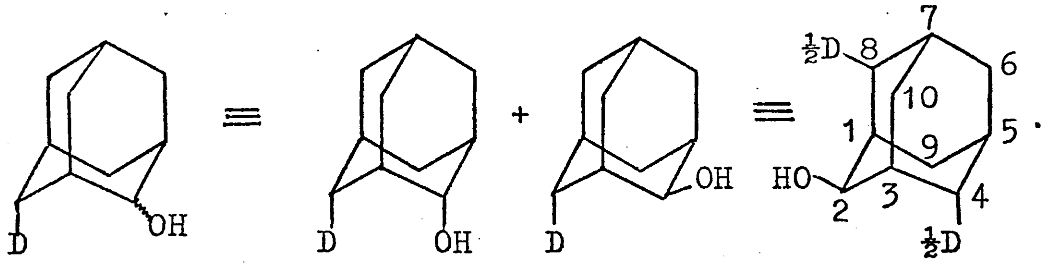
* See Fig.10

Table 7 Ratio of the Integrals of the Eu(fod)$_3$-shifted N.m.r. of (122)

Repeats	Integral of B^*	C^*	(B:C) x 4
1	46.0	58.5	3.1453
2	47.5	58.5	3.2479
3	46.0	58.5	3.1453
4	44.0	57.0	3.0877

Mean (3.16 ± 0.06):4

* See spectrum



1 : 1

(123) (74) (73) (126)

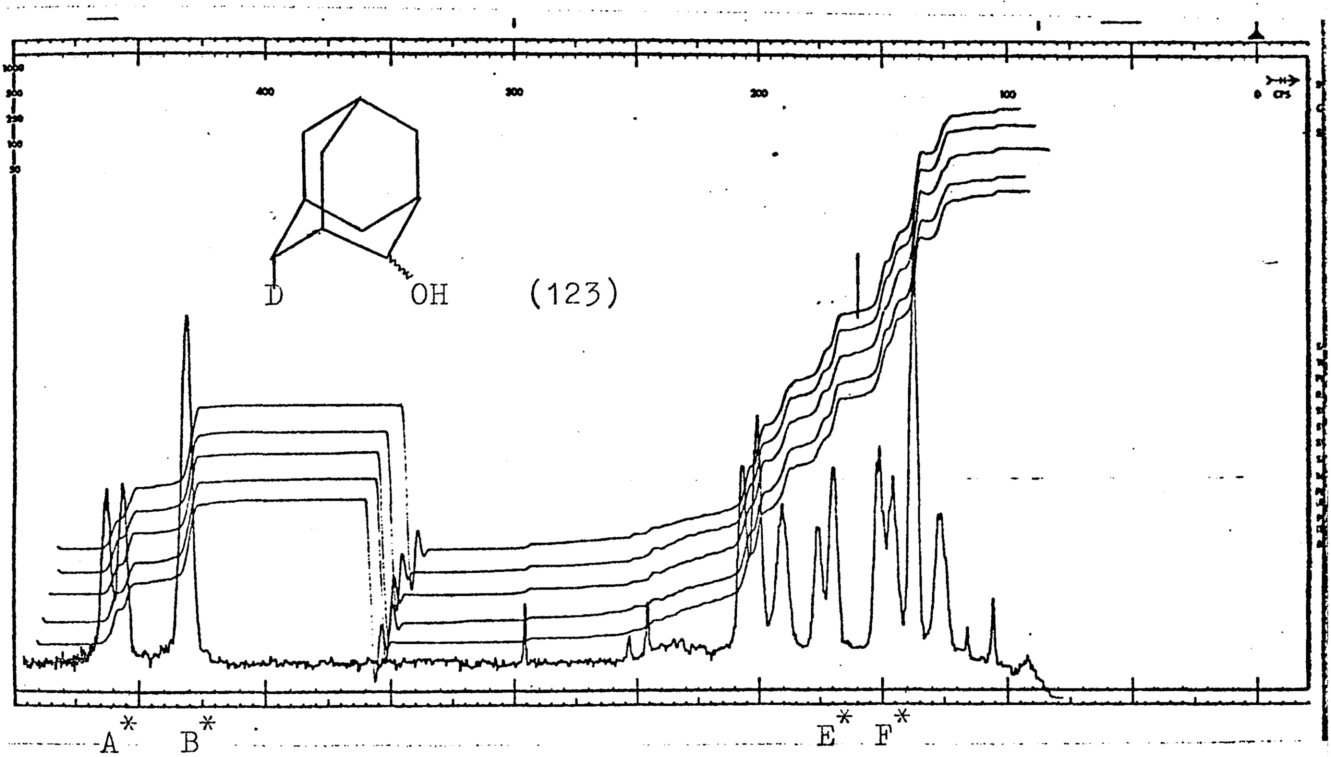


Fig. 12 Eu(dpm)$_3$-shifted 100 MHz N.m.r. Spectrum of (123) {[Eu(dpm)$_3$]:[(123)] = 0.5}

* See Fig. 6

Table 8 Ratio of the Integrals of the $Eu(dpm)_3$-shifted N.m.r. of (123)

Repeats / Integral of	A*	B*	(A:B) x 2	E*	F*	(E:F) x 2
1	24.0	32.0	1.5000	25.0	31.8	1.5723
2	23.3	31.2	1.4936	23.6	31.2	1.5128
3	24.0	32.0	1.5000	24.0	32.0	1.5000
4	24.0	31.0	1.5484	25.0	32.7	1.5291
5	24.0	32.0	1.5000	24.5	32.0	1.5313
Mean			(1.51 ± 0.02):2			(1.53 ± 0.02):2

* See spectrum

ISOTOPE EFFECT IN ADAMANTYL ESTER PYROLYSIS

Before discussing the results from the pyrolyses of the labelled esters whose preparations are described in the previous section, it is appropiate to discuss the two methods available for analysing the partially labelled protoadamantene and dehydroadamantane products obtained from the pyrolyses, namely, g.c.m.s. and ^{13}C n.m.r. spectroscopy analyses.

G.c.m.s. analysis can be used to determine the relative ratio of $\underline{d}_2$-, $\underline{d}_1$-, and $\underline{d}_0$-hydrocarbons in a mixture containing different amounts of isotopically labelled species by measuring the ratio of the molecular ions. However, it should be remembered that this does not indicate specifically the position of label in the product, and can give rise to misleading results if there is scrambling of the isotopic label.

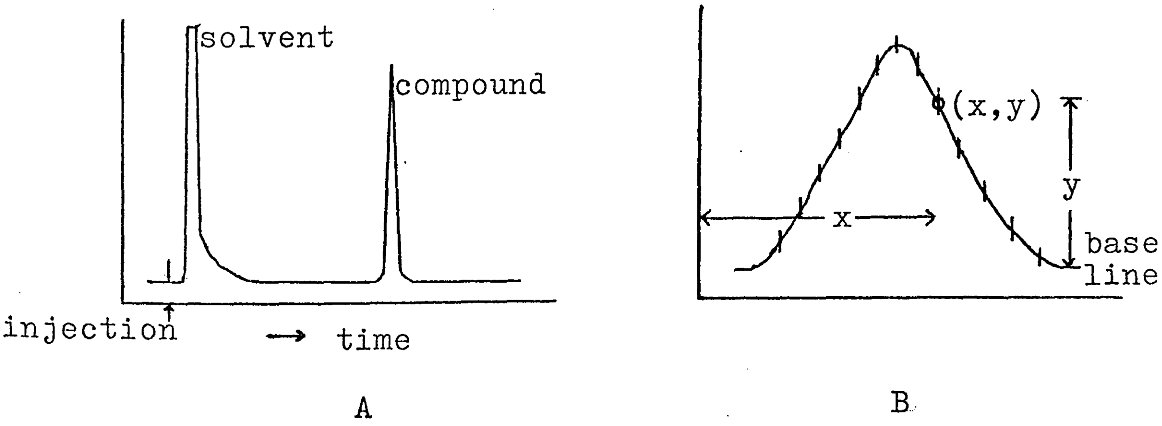


Fig. 13 G.c. Trace in the G.c.m.s. Analysis of Labelled Hydrocarbons. A. The Complete Trace. B. Enlarged Signal of the Compound to Show M.s. Scans.

Fig. 13A shows the g.c. trace of the g.c.m.s. analysis; Fig. 13B shows the trace produced by the compound and positions where mass spectrometric scans are made. Mass scans of m/e 125 - 140 were made about 15 to 20 times uniformly over the peak and the coordinates of each scan were recorded. Each mass scan gave a different $\underline{d}_1$:$\underline{d}_0$ ratio since the $\underline{d}_1$- and $\underline{d}_0$-hydrocarbons have slightly different retention times. The $\underline{d}_1$:$\underline{d}_0$ ratio, after correction for ^{13}C and ^{2}H natural abundance, was used to partition the y-coordinate [(y) in Fig. 13B] to give y($\underline{d}_1$) and y($\underline{d}_0$). A plot of x against y($\underline{d}_1$) and y($\underline{d}_0$) then gave the g.c. peak corresponding to the $\underline{d}_1$- and $\underline{d}_0$-hydrocarbon respectively as shown in Fig. 14. Thus, from the ratio of the two areas (by

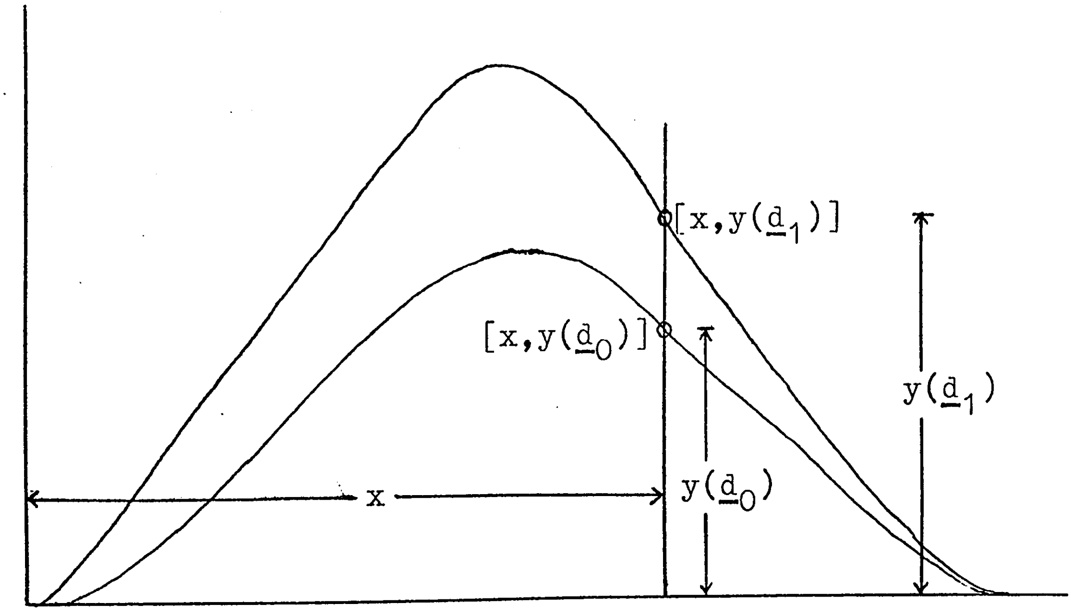
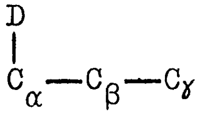


Fig. 14

the cut-and-weigh and counting-squares methods), the ratio of d_1- to d_0-hydrocarbon can be determined and hence the k_H/k_D value for that particular pyrolysis.

The second method used to analyse the deuterium-labelled hydrocarbons is based on ^{13}C n.m.r. spectroscopy. With Fourier-transform operation and wide-band proton noise-decoupling, the effects of a single deuterium atom are readily detected at near carbons[56,57,58] as set out in Table 9.



$$\overset{\displaystyle D}{\overset{|}{C_\alpha}}—C_\beta—C_\gamma$$

$\Delta\delta_{C_\alpha}$	*ca.* 0.3 ppm upfield
$J_{C_\alpha D}$	23 - 25 Hz
$\Delta\delta_{C_\beta}$	*ca.* 0.1 ppm upfield
$J_{C_\beta D}$	0.1 Hz
$\Delta\delta_{C_\gamma}$	*ca.* 0.001 ppm
$J_{C_\gamma D}$	0 - 2 Hz

Table 9 ^{13}C--D Couplings and Isotope Shifts

^{13}C N.m.r. can thus be used quantitatively and qualitatively to locate the deuterium in a deuterium labelled compound. For a ^{13}C--H carbon which is partially deuterated, the ^{13}C--D induced triplet does not overlap with the residual ^{13}C--H absorption because of the isotope shift and coupling. Fig. 15A shows the ^{13}C resonance of unlabelled ^{13}C--H carbon while Fig. 15B shows that of a partially deuterated carbon. In the latter, the ^{13}C--H resonance consists of a sharp singlet though of reduced

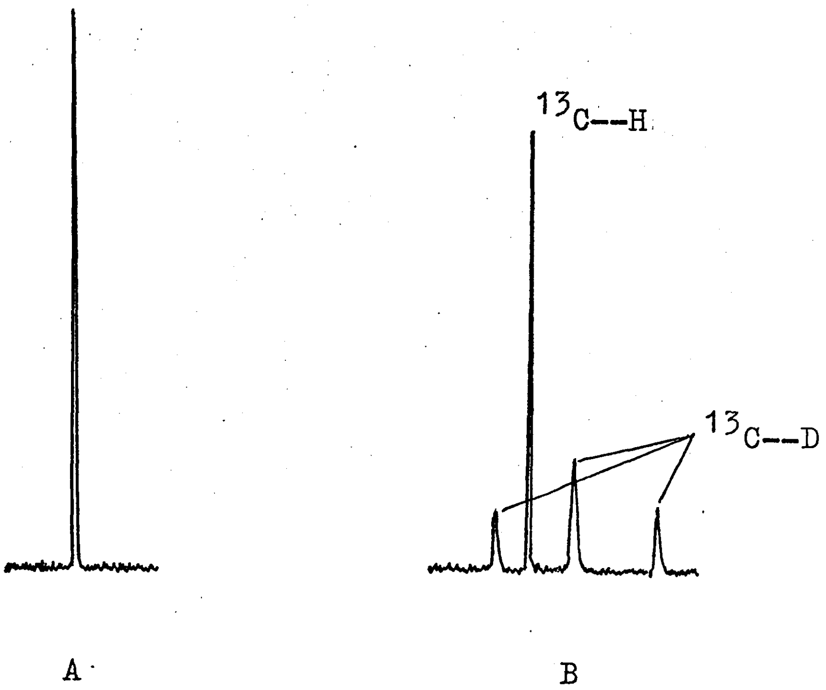
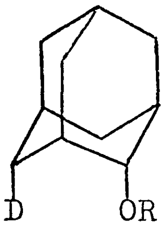


Fig. 15 ^{13}C N.m.r. Resonances of an Unlabelled ^{13}C--H Carbon (A) and a Partially Deuterium-labelled One (B).

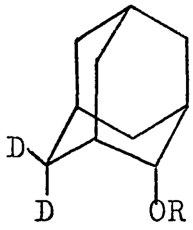
intensity compared with that in Fig. 15A, while the ^{13}C--D resonance consists of a triplet shifted upfield. The amount of shift as well as the ^{13}C--D coupling constant depends on whether the ^{13}C--D carbon forms a methyl, methylene, or a methine group.[56] Although geminal and vicinal ^{13}C--D couplings are small and usually difficult to identify, the isotope shifts are readily observable.

The careful selection of operating parameters leads to total integrated intensities of partially deuterated methyl and/or methylene carbons equal to those for non-labelled material since the Overhauser enhancement from proton decoupling is independent of the number of hydrogens.[59] The decrease in intensity for the residual ^{13}C--H absorption of a partially deuterated methine carbon gives a direct measure of the extent of deuteration. Thus, the D/H ratio at individual carbons can be measured and compared with mass spectrometric data as a check.

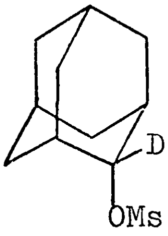
For the purposes of this study, the ^{13}C n.m.r. method to assay deuterium content of a partially labelled compound is superior to that using mass spectrometry because it gives the location as well as the percentage of the deuterium in that position, while mass spectrometry can only give the overall percentage of label in the compound.



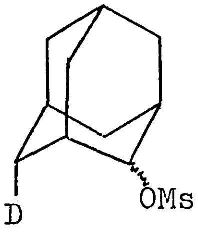
(116) R = Ms
(117) R = $COCF_3$



(118) R = Ms
(119) R = $COCF_3$



(120)



(124)

The esters (116) - (120) and (124) were pyrolysed by the method discussed in the Experimental section. The pyrolysate collected in the liquid-nitrogen trap was extracted with isopentane, which was then filtered through a column of basic alumina to remove any acidic material formed. The dehydroadamantane and protoadamantene products were separated by column chromatography over silver nitrate-alumina and then analysed by the two methods already referred to, namely, g.c.m.s. and ^{13}C n.m.r. spectroscopy.

The pyrolyses of esters (116) - (119) at different temperatures using the commercial furnace (see Experimental page 106) were first studied. The analyses of the samples of dehydroadamantane and protoadamantene obtained in this case were by the g.c.m.s. method. The results are shown in Table 11. Since this is a novel method for obtaining the $\underline{d}_1:\underline{d}_0$ or $\underline{d}_2:\underline{d}_1$ ratio in a partially labelled compound, the calculations leading to the $\underline{d}_1:\underline{d}_0$ ratio in protoadamantene obtained from pyrolysis of (116) at 510° are shown as example.

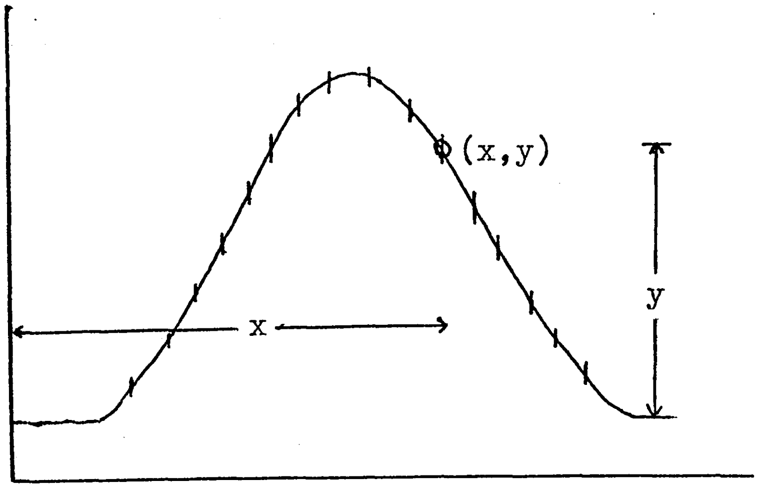


Fig. 16

Fig. 16 shows the g.c. trace in the g.c.m.s. analysis produced by the compound and positions (with known coordinates) where m.s. scans were made. The coordinates of these scan-points were tabulated against the uncorrected $\underline{d}_1:\underline{d}_0$ ($M^+_{\underline{d}_1}:M^+_{\underline{d}_0}$) ratio as shown in Table 10. This ratio,

Table 10

Scan no.	x-coord.*	y-coord.*	$\underline{d}_1:\underline{d}_0$	$\underline{d}_1:\underline{d}_0$ (corrected)	$y(\underline{d}_1)$	$y(\underline{d}_0)$
3	12.0	8.0	3.60	3.47	6.21	1.79
4	15.0	13.0	3.65	3.53	10.13	2.87
5	17.0	22.5	3.70	3.57	17.58	4.92
6	19.0	37.0	3.40	3.28	28.35	8.65
7	21.0	51.0	3.05	2.92	38.00	13.00
8	25.0	76.0	2.77	2.65	55.17	20.83
9	27.0	92.0	2.66	2.53	65.96	26.04
10	29.0	91.0	2.54	2.42	64.35	26.65
11	33.5	57.0	2.22	2.10	38.60	18.40
12	36.0	38.0	2.26	2.14	25.89	12.11
13	40.0	20.0	2.22	2.10	13.54	6.46
14	43.5	12.0	2.32	2.19	8.24	3.76
15	46.0	9.0	2.60	2.47	6.41	2.59

* See Fig. 16

after correction for ^{13}C and ^{2}H natural abundance, was used to partition the y-coordinate in Fig. 16 to give $y(\underline{d}_1)$ and $y(\underline{d}_0)$. A plot of x against $y(\underline{d}_1)$ and $y(\underline{d}_0)$ as shown in Fig. 17 then gave the g.c. peak corresponding to the $\underline{d}_1$- and $\underline{d}_0$-hydrocarbon respectively. The ratio of the two areas (by cut-and-weigh method of three identical plots as well as counting squares method) then gave the $\underline{d}_1:\underline{d}_0$ figure in Table 11.

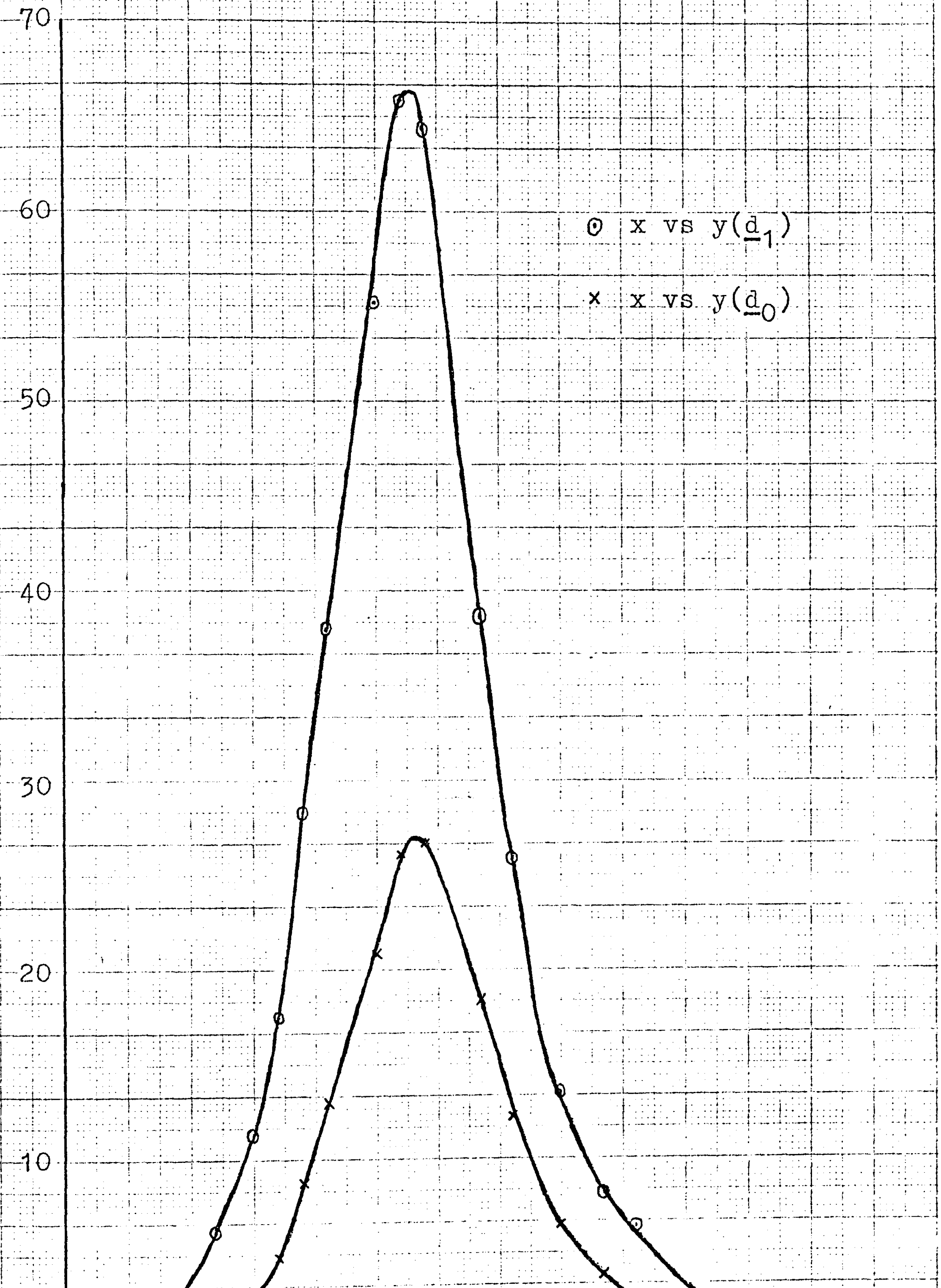

70
60
50
40
30
20
10
0
10
20
30
40
50
60
ʘ x vs y($\underline{d}_1$)
× x vs y($\underline{d}_0$)

Fig. 17

Table 11 Pyrolyses of the Labelled Esters (116) - (119)

Compound	Scale (g)	Temp. (°C)[a]	Pressure (torr)	Products			
				Protoadamantene		Dehydroadamantane	
				% Comp[b]	d_2- : d_1- or d_1- : d_0-	% Comp[b]	d_2- : d_1- or d_1- : d_0-
(116)	0.02	510±20	0.05±0.03	16	2.51±0.02[c]	83	5.24±0.13[c]
(116)	0.02	450±20	0.05±0.02	45	2.63±0.06[c]	45	5.44±0.03[c]
(116)	0.02	410±20	0.07±0.03	40	2.31±0.03[c]	30	5.26±0.06[c]
(117)	0.02	510±20	0.10±0.02	10	1.95±0.02[c]	88	3.16±0.03[c]
(117)	0.02	420±20	0.07±0.02	32	2.21±0.01[c]	40	4.95±0.03[c]
(117)	0.02	350±20	0.09±0.02	2	3.34±0.08[c]	48	9.73±0.10[c]
(118)	0.03	500±20	0.04±0.02	16	1.82±0.01[d]	83	1.95±0.01[d]
(118)	0.03	410±20	0.04±0.02	25	2.75±0.02[d]	25	3.02±0.05[d]
(118)	0.03	360±20	0.04±0.02	20	2.89±0.02[d]	20	3.42±0.05[d]
(119)	0.03	480±20	0.04±0.01	20	1.38±0.005[d]	70	1.79±0.005[d]
(119)	0.03	410±20	0.04±0.01	20	1.68±0.01[d]	30	3.56±0.03[d]
(119)	0.03	320±20	0.05±0.01	5	2.13±0.005[d]	55	6.62±0.10[d]

[a] It was noticed after the work had been completed that the furnace gave a much larger temperature gradient. [b] Estimated from g.l.c. trace. [c] d_1-:d_0- [d] d_2-:d_1-

Table 12 Pyrolyses of Labelled Esters Using the Improved Furnace[a]

				Products			
				Protoadamantene		Dehydroadamantane	
Compound	Scale (g)	Temp. (°C)	Pressure (torr)	% Comp[b]	or $\underline{d}_2$- : $\underline{d}_1$- / $\underline{d}_1$- : $\underline{d}_0$-	% Comp[b]	or $\underline{d}_2$- : $\underline{d}_1$- / $\underline{d}_1$- : $\underline{d}_0$-
(116)	0.03	562± 7	0.03±0.01	30	2.55±0.002[d]	70	5.10±0.09[d]
(116)	0.03	467±13	0.03±0.01	60	4.33±0.06[d]	40	7.34±0.08[d]
(116)	0.05	371±18	0.03±0.01	20	4.13±0.02[d]	18	8.42±0.11[d]
(117)	0.04	560±12	0.05±0.01	45	1.97±0.003[d]	50	3.20±0.02[d]
(117)	0.04	465±12	0.06±0.01	40	2.64±0.03[d]	40	5.78±0.13[d]
(117)	0.04	362±16	0.05±0.01	20	3.30±0.04[d]	10	9.54±0.18[d]
(118)	0.03	569± 9	0.01±0.005	40	2.93±0.01[c]	60	2.91±0.02[c]
(118)	0.03	466±15	0.03±0.01	60	3.01±0.03[c]	40	3.10±0.04[c]
(118)	0.03	363±16	0.04±0.01	20	3.03±0.03[c]	18	3.45±0.02[c]
(119)	0.03	558± 8	0.06±0.02	45	1.89±0.02[c]	50	2.14±0.004[c]
(119)	0.03	464±12	0.06±0.02	40	1.92±0.04[c]	30	2.73±0.01[c]
(119)	0.03	362±14	0.04±0.01	20	2.57±0.03[c]	10	4.46±0.06[c]

[a] See Experimental, page 109. [b] Estimated from g.l.c. trace. [c] $\underline{d}_2$-:$\underline{d}_1$-

[d] $\underline{d}_1$-:$\underline{d}_0$-

The results obtained in the pyrolysis of (116) indicated a reversed temperature effect and it subsequently transpired that a relative large temperature gradient existed in the commercial furnace (see Fig. 32 in Experimental, page 108). In order to eliminate this uncertainty, an improved furnace that could be regulated to within $\pm 10^{\circ}$ was constructed (see Experimental, page 109) and the pyrolyses were repeated. A similar analysis of the products gave the results shown in Table 12.

The discrepancies between the results in Tables 11 and 12 can be explained by the superior temperature control possible with the improved furnace. This clearly indicates that the improved furnace, having a smaller temperature gradient, produced a more reliable result.

However, most of the results gave a $\underline{d}_1:\underline{d}_0$ or $\underline{d}_2:\underline{d}_1$ value greater than the theoretical maximum isotope effect calculated for the three temperatures by the method of Wiberg,[5] which is shown in Fig. 18. This clearly showed that the simple derivation of $\underline{k}_H/\underline{k}_D$ as discussed earlier on page 30 is not applicable.

The results can, however, be rationalised by assuming a fast isomerisation of the ester function during or prior to pyrolysis. An analogous isomerisation, though not found in acetate[29,59] and carbamate[61] pyrolyses, was observed in the pyrolysis of 2-adamantyl xanthate (127) during which the thiolocarbonate (128) was obtained.[2,3]

Temp. (°C)	100	300	500
$(\underline{k}_H/\underline{k}_D)_{max.}$	3.4	2.7	2.1
$1/T \times 10^3$	2.114	1.745	1.294
$\log[(\underline{k}_H/\underline{k}_D)_{max.}]$	0.521	0.431	0.322

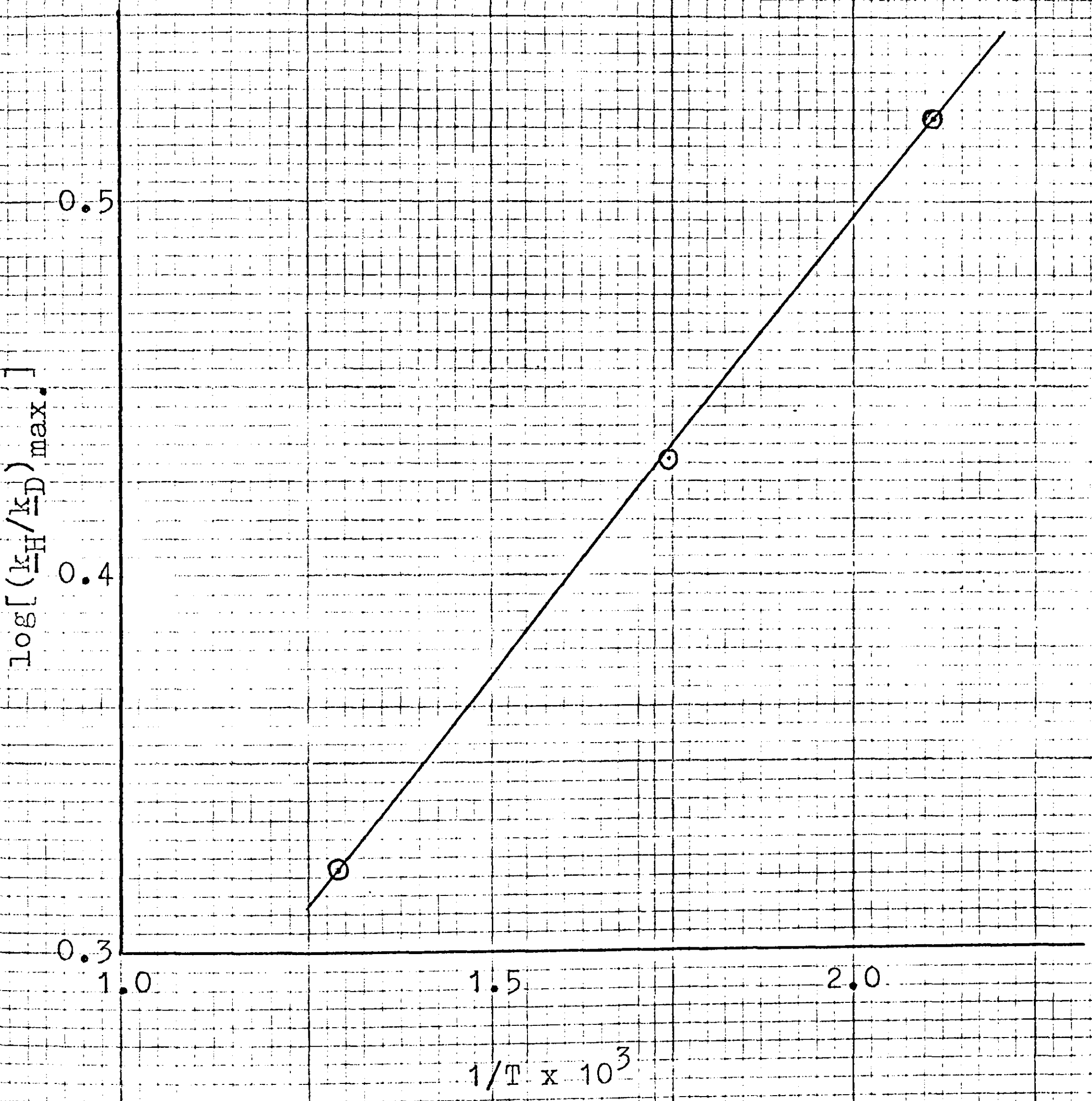
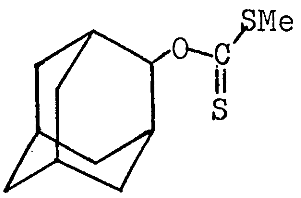
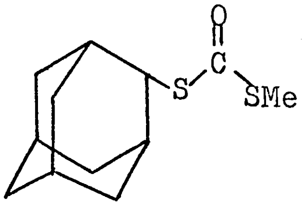


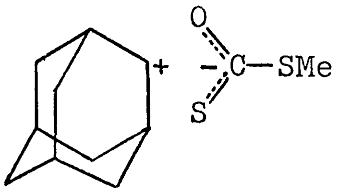
Fig. 18 Plot of the Logarithm of the $(\underline{k}_H/\underline{k}_D)_{max.}$ for C--H Stretching as a Function of Reciprocal Temperature



(127)



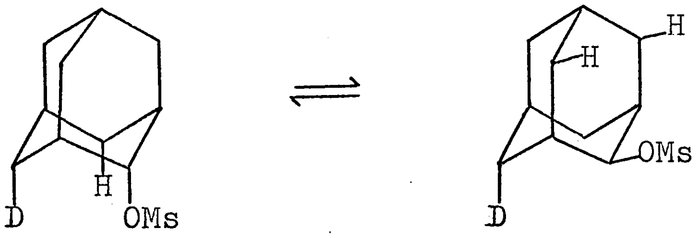
(128)



(129)

The process could be going through a four-membered transition state or simply an ion-pair intermediate as shown in (129).

The completion of the work in part (a) (Pyrolysis of 2-noradamantyl methanesulphonate) also indicated that the sulphonate ester epimerised to a certain extent during or prior to pyrolysis (see page 20). This also bears on the production of adamantane during the pyrolysis of some adamantyl and protoadamantyl esters [see section (a), page 21 and section (c), page 100].



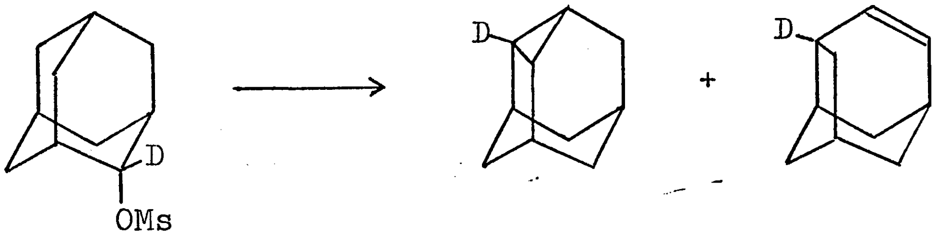
(116)

(130)

If the epimerisation of the ester function is fast, the ester (116) would effectively become a 1:1 mixture of (116) and (130). There will be three hydrogen atoms of the required stereochemistry for elimination available for every deuterium atom. And if there is no deuterium isotope effect, the $\underline{d}_1:\underline{d}_0$ or $\underline{d}_2:\underline{d}_1$ ratio would then be 3. The results obtained in pyrolysing (118) (Table 12) appear to be in agreement with this. However, if the epimerisation is not so fast, the ratio of (116):(130) during pyrolysis varies; and if there is a deuterium isotope effect, the $\underline{d}_1:\underline{d}_0$ or $\underline{d}_2:\underline{d}_1$ ratio would then be greater than 3.

Irrespective of the rate of isomerisation, the composition of a 1:1 mixture of (116) and (130) [equivalent to (124), see also page 32] would remain unchanged. This should still give a measure of the $\underline{k}_H/\underline{k}_D$ ratio if the location and amount of deuterium in the products can be ascertained.

At this stage of the work, it became clear that ^{13}C n.m.r. spectroscopy, by revealing quantitatively the location of deuterium at each carbon atom in the product, would give a closer insight into the mechanism of these 1,3-eliminations. The ^{13}C n.m.r. spectra discussed in this section were measured in the laboratory of Professor J.B. Stothers, University of Westers Ontario, London, Canada, to whom we are greatly indebted.



(120) (131) (132)

The pyrolysis of (120) was first studied which served as a control to detect any deuterium scambling other than that caused by the epimerisation of the ester function. Because of the symmetry of the adamantane molecule, epimerisation of the ester function in (120) will give only one labelled dehydroadamantane (131) and one protoadamantene (132) (see Scheme 10, page 31).

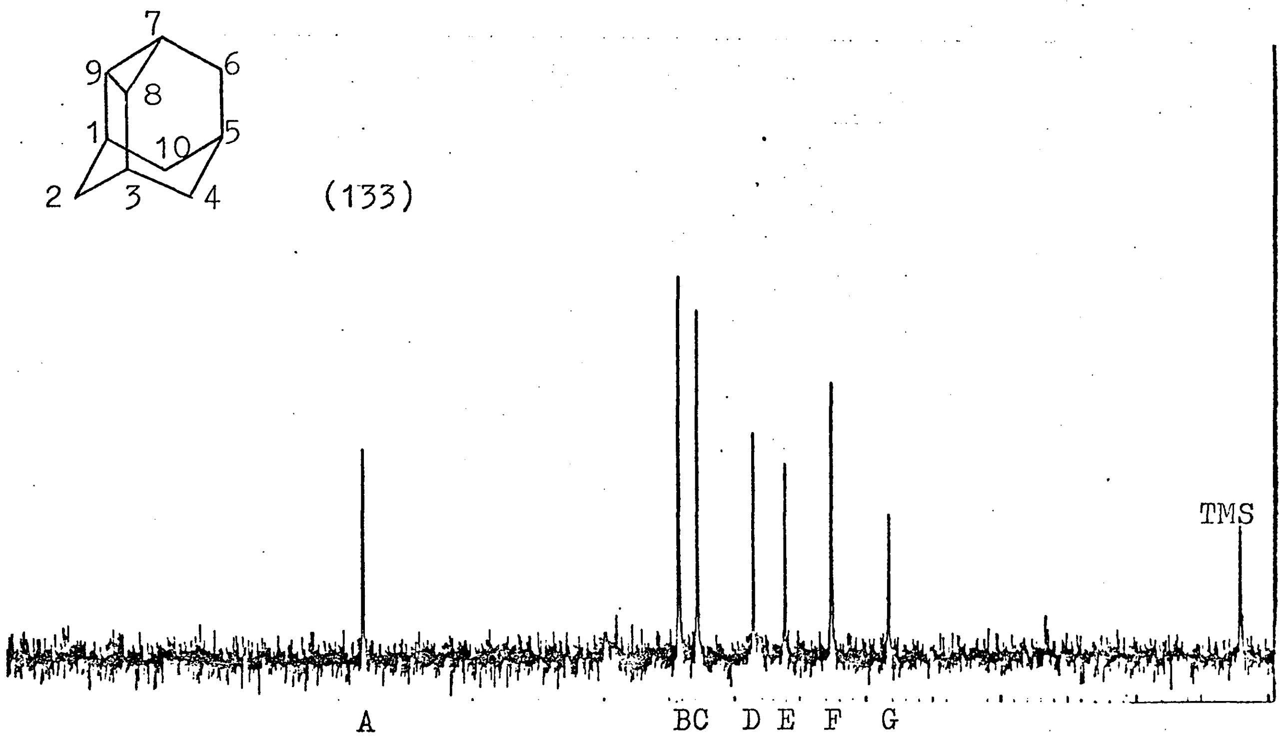


Fig. 19 ^{13}C N.m.r. Spectrum of (133).

The ^{13}C n.m.r spectra of (133) and (131) are shown in Fig. 19 and Fig. 20 respectively and their integrals in Table 13. The assignments of the signals B, C, and F are evident when the two spectra are compared. Signal B, being the only two equivalent methylene carbons, arises from C-4 and C-10. Signal F is of much reduced intensity in (131) and shows the structure of ^{13}C--D coupling as in

Table 13

The Integrals of the ^{13}C N.m.r. Spectra of (131) and (133)

Signal	A	B	C	D	E	F	G
δ	52.5	33.4	32.3	28.9	26.9	24.2	20.7
CH_2 or CH	CH_2	CH_2(2C)	CH(2C)	CH_2	CH	CH(2C)	CH
Assignment	C-2/C-6	C-4,C-10	C-1,C-3	C-6/C-2	C-5	C-8,C-9	C-7
Integral[1] of (133)	0.501	1.313	1.000	0.661	0.494	1.028	0.494
Integral[1] of (131)	0.511	1.282	1.000	0.622	0.511	0.596	0.489
$\frac{\text{Integral of (131)}}{\text{Integral of (133)}}$	-	0.976	1.000	0.941	-	0.580	0.990
% deuterium[2] in (131)		2.4		5.9		42.0	1.0

[1] Average of atleast two separate runs under identical conditions and parameter adjustment.[58]

[2] This was calculated by normalising signal C. Normalisation of other signals has been attempted and found not as satisfactory.

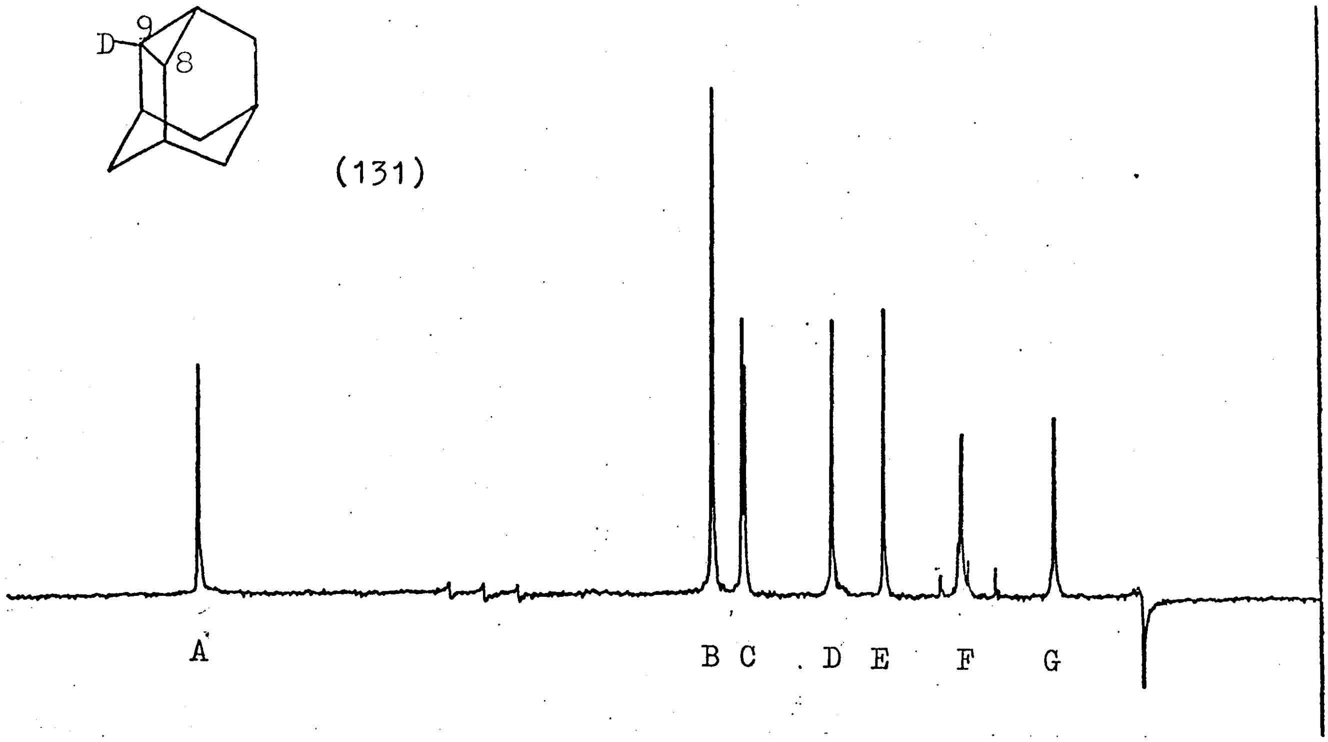


Fig. 20 ^{13}C N.m.r. Spectrum of (131)

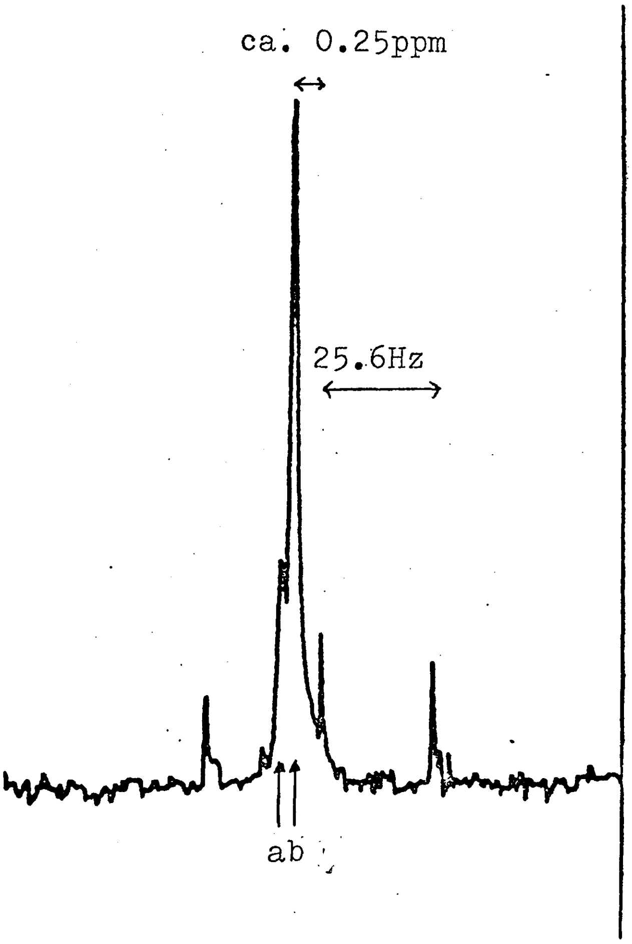
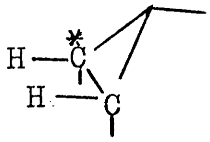
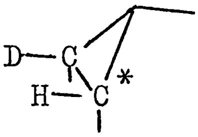


Fig. 21 Signal F in the ^{13}C N.m.r. Spectrum of (131)

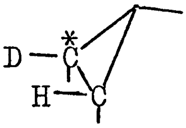
Fig. 21. The ^{13}C--D triplet (J = 25.6 Hz) is shifted upfield by ca. 0.25 ppm. It is therefore assigned the equivalent C-8 and C-9 carbons. The ^{13}C resonances of these partially deuterated equivalent carbons can be assigned to (134), (135), and (136) having different chemical shifts according to Table 9. In (134), the two carbons are equivalent, and being a minor component in the mixture, give rise to signal a in Fig. 21. The carbon in (135) gives the signal b which is shifted upfield by about 0.1 ppm, while (136) gives the familiar ^{13}C--D triplet. Signal C (Table 13) is then assigned to the remaining two equivalent methine carbons, namely, C-1 and C-3, which also show a geminal isotopic shift as shown in Fig. 20.



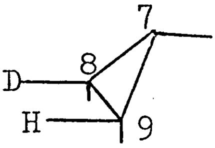
(134)



(135)



(136)

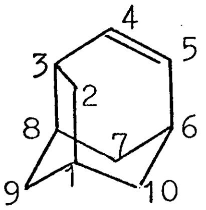


(137)

The signal G is just resolvable into two peaks of ca. 0.1 ppm apart; the major one is upfield similar to that of F. In (137) where C-8 is 84% deuterated (see following paragraph), the signal of C-7 would show the same 84% geminal upfield shift in the order of ca. 0.1 ppm

(Table 9). The remaining 16% of the signal would be unshifted. Therefore, the signal G is assigned to C-7, the remaining methine signal E to C-5. This is confirmed by other labelled dehydroadamantanes studied later.

From the integrals in Table 13, the signal F in (131) has only 42.0% deuterium label. Since the signal arises from two equivalent carbons and we cannot have the deuterium atom in <u>both</u> carbons, the label at the equivalent C-8 or C-9 carbon is thus 84%. The rest of the deuterium label is distributed among the C-2 or C-6, C-4(C-10), and C-7 positions.



(138)

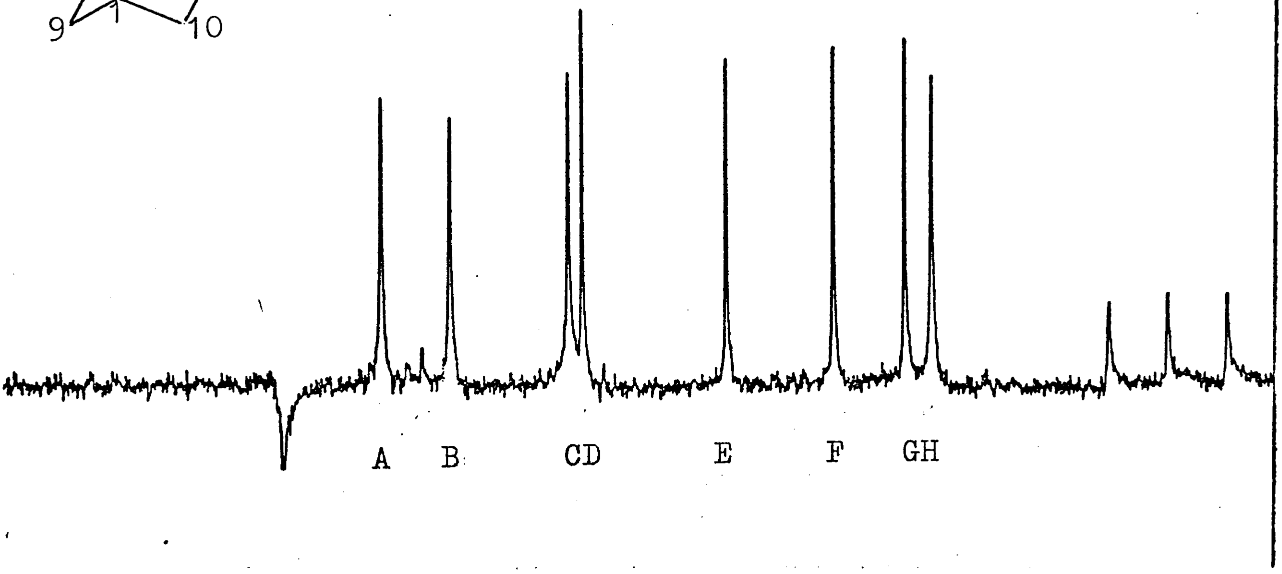


Fig. 22 ^{13}C N.m.r. Spectrum of (138)

The assignment of the signals in the ^{13}C n.m.r. spectrum of protoadamantene is more difficult than that in dehydro-

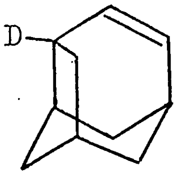
Table 14

The Integrals of the ^{13}C N.m.r. Spectra of (132) and (138)

Signal	A	B	C	D	E	F	G	H
CH δ	43.9	42.4	39.9	39.6	36.4	34.1	32.6	32.0
CH_2 or CH	CH_2	CH_2	CH_2	CH	CH	CH	CH	CH_2
Assignment	C-9	C-2	C-7	C-1	C-3	C-8	C-6	C-10
Integral[1] of (138)	1.103	1.083	1.351	0.969	0.876	0.979	0.928	1.000
Integral[1] of (132)	1.042	0.908	1.092	0.891	0.378	0.807	0.832	1.000
$\frac{\text{Integral of (132)}}{\text{Integral of (138)}}$	0.945	0.838	0.809	0.919	0.432	0.824	0.897	-
% deuterium[2] in (138)	5.5	16.2	19.1	8.1	56.8	17.6	10.3	-

[1] Average of at least two separate runs under identical conditions and parameter adjustment.[58]

[2] This was calculated by normalising H. Normalisation of other signals has been attempted and found not satisfactory.



(132)

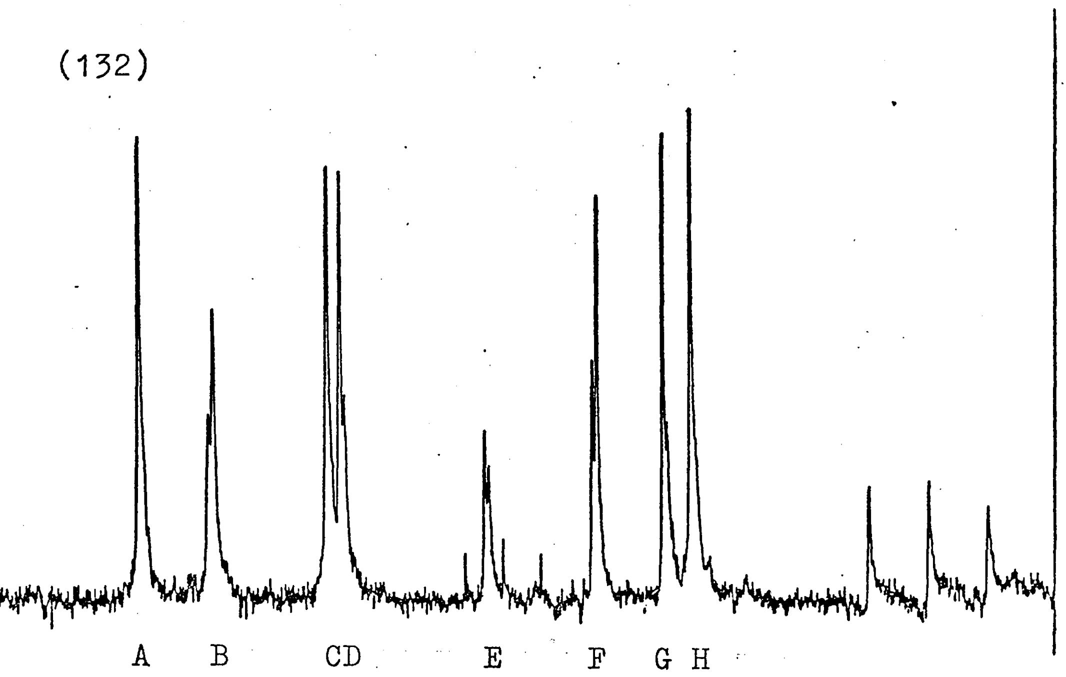


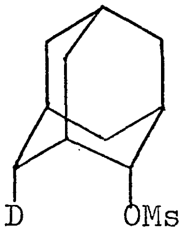
Fig. 23 ^{13}C N.m.r. Spectrum of (132)

adamantane because there is no symmetry element and also more deuterium scrambling is observed.

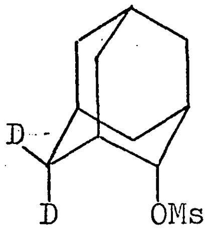
In Fig. 23, signal E arises from the C-3 carbon where the deuterium is expected. Table 14 shows that the deuterium consists of 56.8%. Signals B(CH_2) and F(CH) show the corresponding geminal isotope shift and therefore are assigned to C-2 and C-8 respectively. Signals D and E show qualitatively a similar degree of geminal isotope shift, presumably by the same deuterium in the molecule. The only saturated methine carbons unassigned in the molecule are those of C-1 and C-6. If there is some deuterium lable in C-2, it would shift C-1 and C-3 upfield to the same degree. Therefore, signal D is assigned to C-1. The remaining methine carbon C-6 must then give rise to the signal G.

The assignment of signals A, C, and H is not very clear at this stage. Studies of other labelled protoadamantene described later show that the assignment of C-9, C-7, and C-10 to signal A, C, and H respectively is in agreement with all the data obtained.

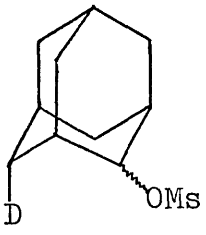
The available results so far show that there is a certain degree of deuterium scrambling in the 2-adamantyl mesylate pyrolysis leading to both dehydroadamantane and protoadamantene. However, this would still give valuable information towards the distribution of the deuterium in the product and hence the mechanism of the pyrolysis.



(116)



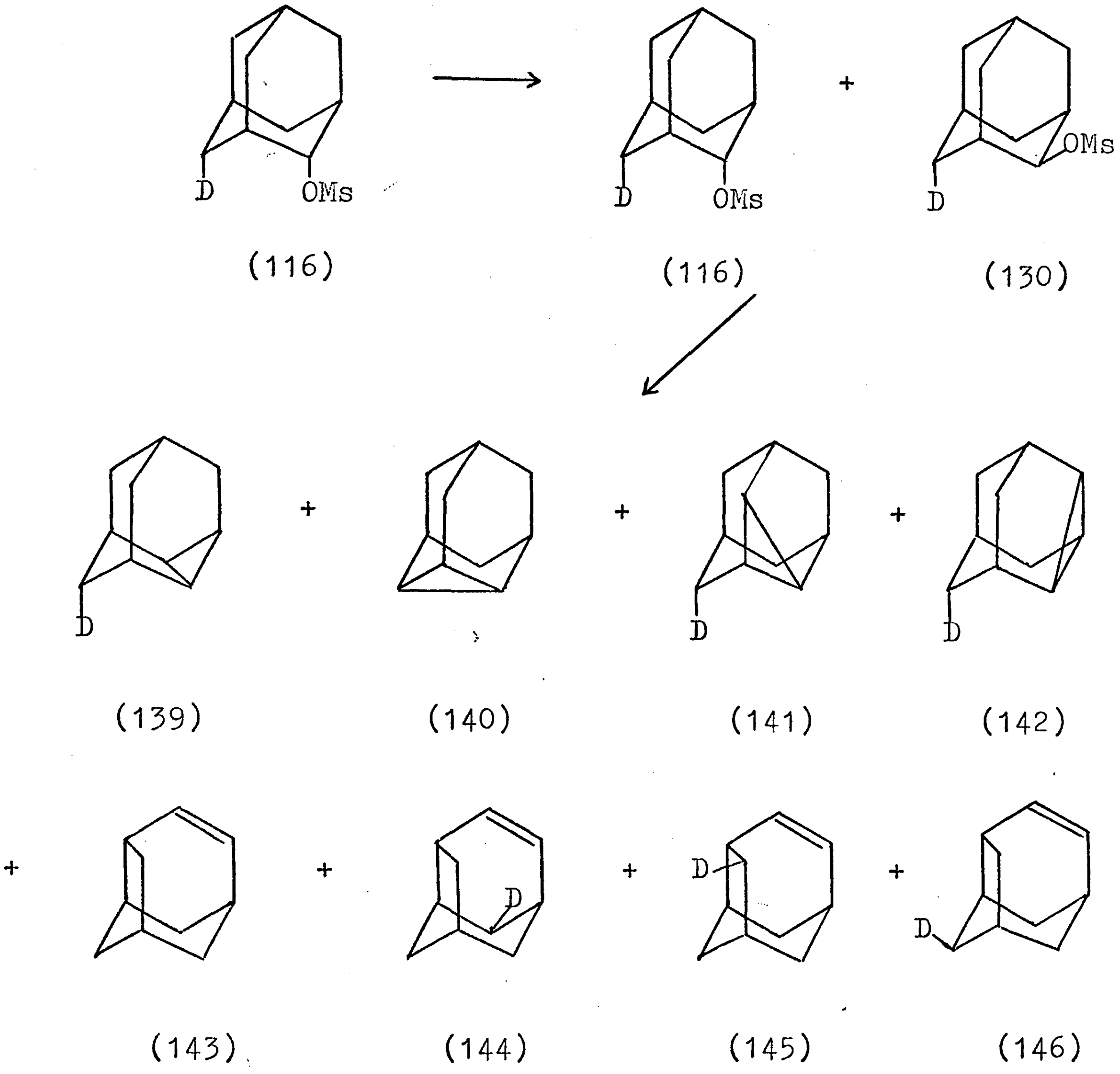
(118)



(124)

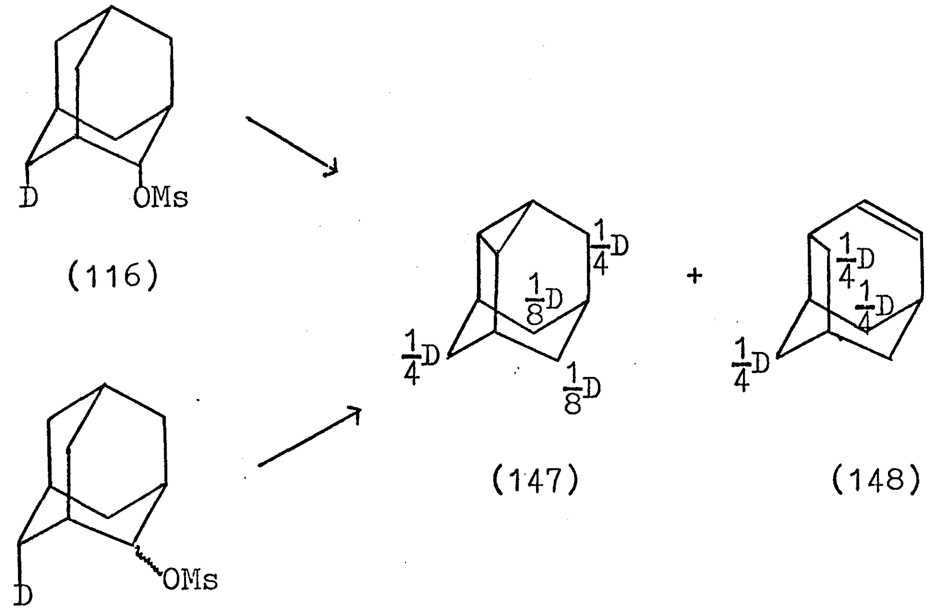
The pyrolyses of esters (116), (118), and (124) were carried out and the products were separated by column chromatography over silver nitrate-alumina and analysed by the ^{13}C n.m.r. method described.

In the pyrolysis of esters (116) and (118) at different temperatures, the results from g.c.m.s. analysis could be rationalised by assuming a very fast isomerisation of the ester function during a prior to pyrolysis (see page 66).



Scheme 14

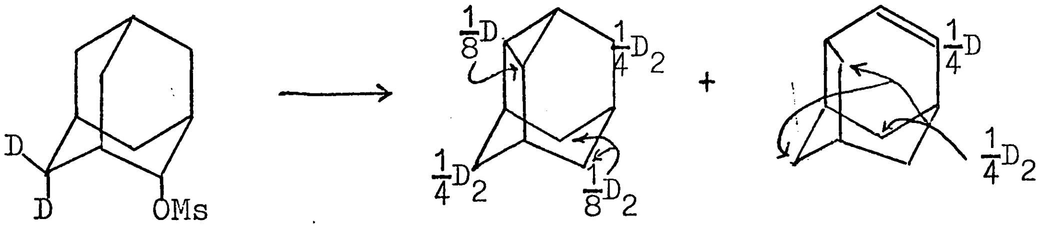
If the epimerisation of the ester function is fast, the ester (116) would effectively become a 1:1 mixture of (116) and (130) and give, upon pyrolysis, dehydroadamantane products (139) - (142) and protoadamantene products (143) - (146) as shown in Scheme 14. If there is no kinetic isotope effect, the compounds (139) - (142) will be formed in equal proportions, as will compounds (143) - (146). The pyrolysis of (124) would then give identical products to that of (116), namely (147) and (148).



(116)

(124)

(147) (148)



(118) (149) (150)

Likewise, on the basis of epimerisation of the ester function prior to or during pyrolysis, the ester (118) would give a dehydroadamantane mixture (149) and a protoadamantene mixture (150).

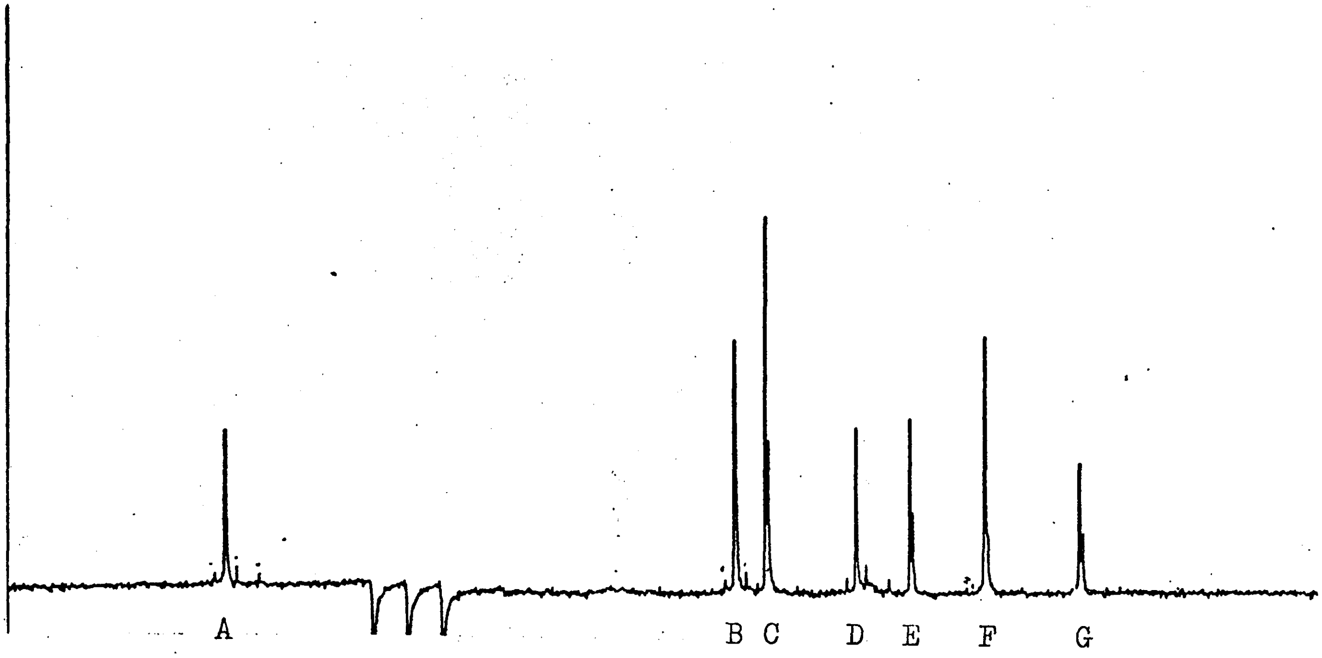


Fig. 24 ^{13}C N.m.r. Spectrum of Dehydroadamantane Mixture from (116)

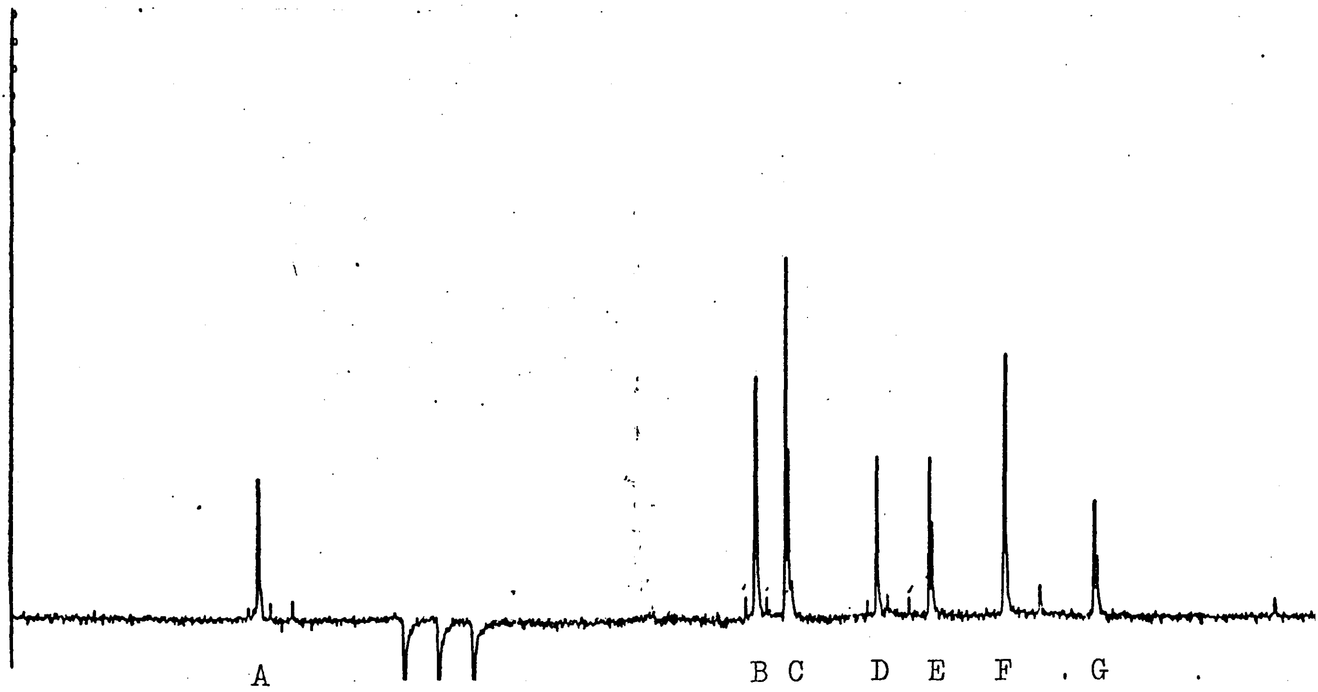


Fig. 25 ^{13}C N.m.r. Spectrum of Dehydroadamantane Mixture from (124)

Table 15 The Integrals of the ^{13}C N.m.r. Spectra of Dehydroadamantane from (116), (124), and (118)

Integral[1] of compound \ Signals	A C-2/C-6	B C-4,C-10	C C-1,C-3	D C-2/C-6	E C-5	F C-8,C-9	G C-7
(133) unlabelled	0.569	1.182	1.000	0.562	0.460	0.971	0.448
from (116)	0.459	0.966	1.000	0.478	0.478	0.859	0.424
Ratio[2]	0.807	0.817	1.000	0.851	-	0.885	0.968
% deuterium	19.3	18.3		14.9		11.5	3.2
from (124)	0.469	0.994	1.000	0.469	0.514	0.870	0.429
Ratio[2]	0.824	0.841	1.000	0.836	-	0.896	0.979
% deuterium	17.6	15.9		16.5		10.4	2.1
from (118)	0.410	0.974	1.000	0.405	0.487	0.836	0.405
Ratio[2]	0.721	0.824	1.000	0.721	-	0.861	0.925
% deuterium	27.9	17.6		27.9		13.9	7.5

[1] Average of at least two separate runs under identical conditions and parameter adjustment.[58]

[2] The ratio of the normalised integral (at signal C) to the corresponding integral of (133).

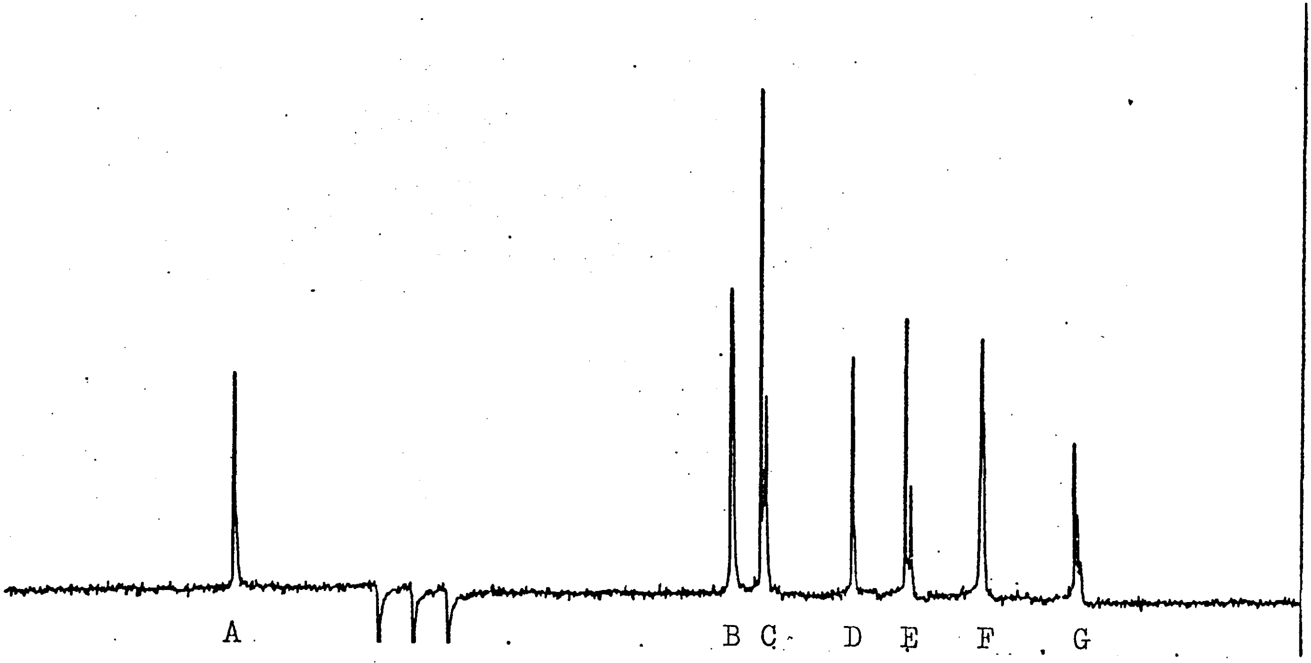


Fig. 26 ^{13}C N.m.r. Spectrum of Dehydroadamantane Mixture from (118)

The ^{13}C n.m.r. spectra of the dehydroadamantane samples obtained from pyrolysing (116), (124), and (118) are shown in Fig. 24, 25, and 26 respectively and their integrals in Table 15.

Qualitatively, the ^{13}C n.m.r. spectra of the dehydroadamantane samples obtained in (116) and (124) are identical (Fig. 24 and 25), while quantitatively (Table 15), the distribution of the deuterium in the two samples differ only slightly, probably within the experimental error.[57,58]

In Fig. 24 and 25, the usual ^{13}C--D triplet (_J_ = 21 Hz) is observed in signals A, B, and D showing the presence of deuterium atoms attached to C-2, C-4(C-10), and C-6 where expected [see (147)]. There are geminal ^{13}C--D upfield shifts in signals C, E, and G, i.e., C-3, C-5, and C-7, the only carbons β to the deuterium atom. The spectra are then in agreement with a mixture as represented by (147).

In Fig. 26, there are larger upfield shifts in signals C, E, and G due to the presence of an additional deuterium atom at C-2, C-4(C-10), and C-6 in (149) compared to (147).

All these data indicate that the deuterium atom is located at C-2, C-4(C-10), and C-6 as expected, and to a small extent in C-8(C-9), though in a slightly different ratio from that expected in the pyrolysis of esters (116) and (124), but in excellent agreement with that from (118).

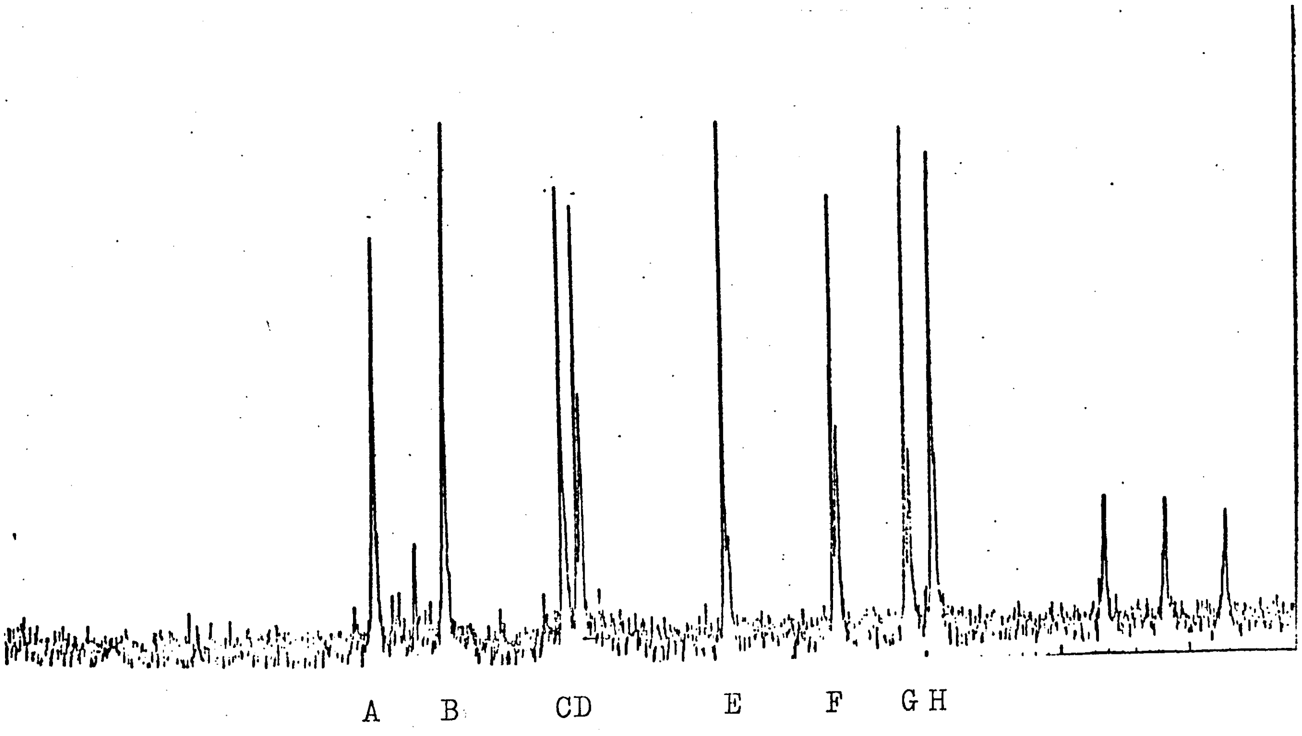


Fig. 27 ^{13}C N.m.r. Spectrum of Protoadamantene Mixture from (116)

Table 16 The Integral of the ^{13}C N.m.r. Spectra of Protoadamantene from (116) and (118)

Integral[1] of Compound / Signal	A C-9	B C-2	C C-7	D C-1	E C-3	F C-8	G C-6	H C-10
138 unlabelled	1.021	1.052	1.103	0.928	0.794	0.835	0.825	1.000
from (118)	0.806	0.827	0.816	0.911	0.684	0.765	0.786	1.000
Ratio[2]	0.790	0.786	0.740	0.982	0.861	0.917	0.953	1.000
% deuterium	21.0	21.4	26.0	1.8	13.9	8.3	4.7	
from (116)	0.904	0.981	0.962	1.000	0.788	0.865	0.875	1.000
Ratio[2]	0.886	0.933	0.872	1.078	0.993	1.036	1.061	1.000
% deuterium	11.4	6.7	12.8	-	0.7	-	-	

[1] Average of at least two separate runs under identical conditions and parameter adjustment.[58]

[2] The ratio of the normalised integral (at signal H) to the corresponding integral of (138).

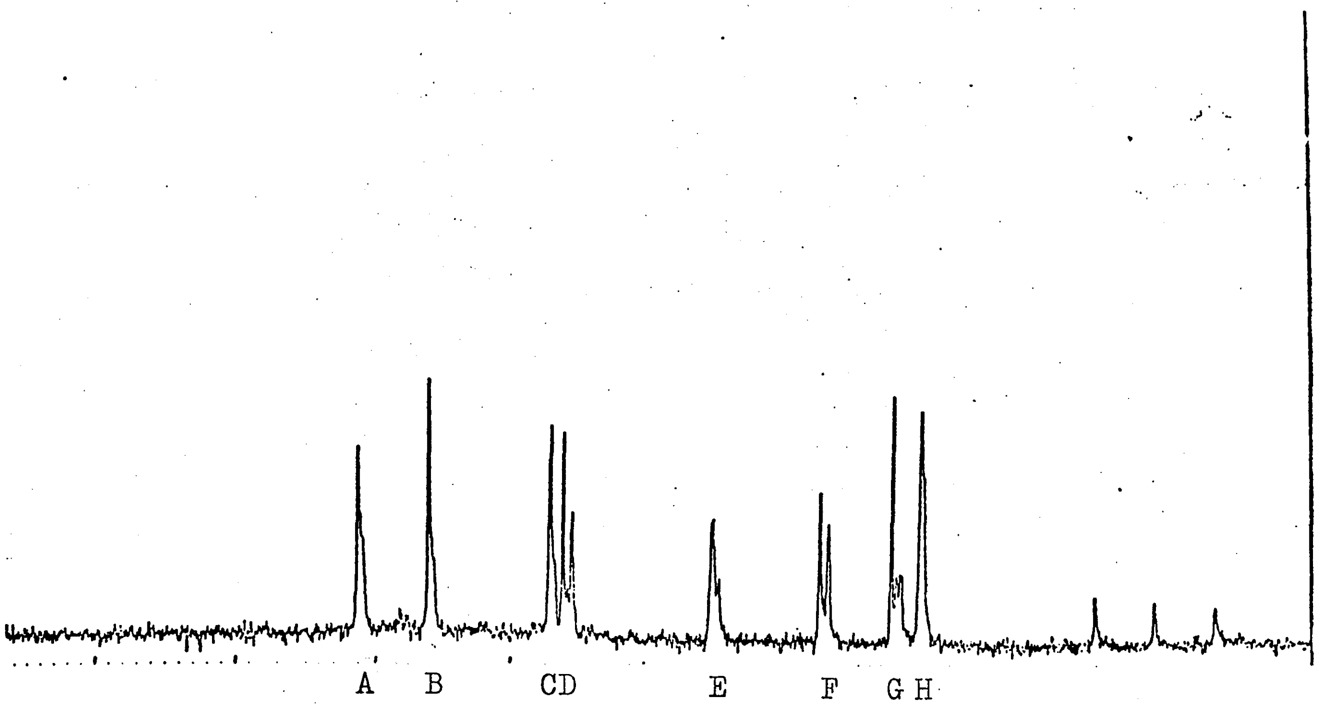


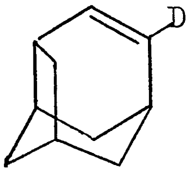
Fig. 28 ^{13}C N.m.r. Spectrum of Protoadamantene Mixture from (118)

The ^{13}C n.m.r. spectra of the protoadamantene samples obtained from pyrolysing (116) and (118) are shown in Fig. 27 and 28 respectively and their integrals in Table 16.

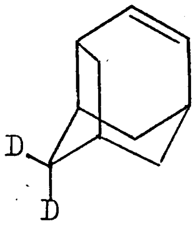
In the protoadamantene sample obtained from (116), the deuterium atom is located at C-2, C-7, and C-9 as shown in Table 16. This is in agreement with the expected product (148) shown in page 79. In addition, the deuterium label at C-2, C-7, and C-9 causes geminal isotope shifts at C-1 and C-3 (signals D and E), C-6 and C-8 (signal G and F), and C-1 and C-8 (signals D and F) respectively as observed in Fig.27.

The data obtained from the protoadamantene sample from

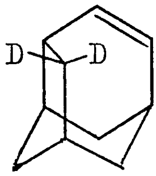
(118) show excellent agreement with the expected result. From Table 16, it is seen that the distribution of the label in C-2, C-7, and C-9 as 21, 21, and 26% respectively while the expected product mixture (150) (see page 79) requires a 25% deuterium label in each of these positions. Since these are $>CD_2$ carbons, the $^{13}C{-}{-}D_2$ quintet arise from a carbon without other protons directly bonded and the Overhauser effect would be very much smaller. Besides, the intensity of the $^{13}C{-}{-}D_2$ carbon is distributed over five lines and therefore very weak and the signal can disappear into the noise. Hence, no $^{13}C{-}{-}D_2$ quintet is observed in Fig. 28. However, the geminal and vicinal $^{13}C{-}{-}D$ couplings and isotope shifts (Table 9) produce a very complex spectrum. Assuming a mixture of (151) - (154), represented by (150), the spectrum can still be interpreted.



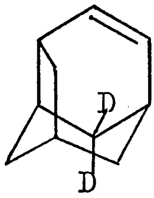
(151)



(152)



(153)

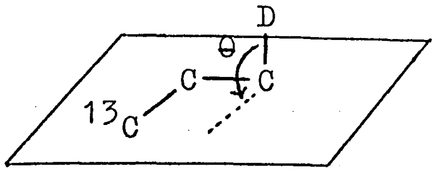


(154)

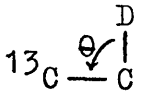
Considering each of the signals A -- H alone as arising from each of the compounds (151) - (154), Table 17 shows all the possible ^{13}C n.m.r. lines due to the mixture. The vicinal and geminal coupling constants also depend[58] on the angle θ in (155) and (156) respectively. Since these coupling constants and isotope shifts are small, many of the lines shown in Table 17 either overlap or are not

Table 17 The Possible ^{13}C N.m.r. Lines of (150)

Signal	Arising from	^{13}C--D Isotope shift	^{13}C--D Coupling
A (C-9)	(151)	unshifted	
	(152)	directly coupled (signal lost)	
	(153)	vicinal	*J* = 0 - 2 Hz
	(154)	vicinal	*J* = 0 - 2 Hz
B (C-2)	(151)	unshifted	
	(152)	vicinal	*J* = 0 - 2 Hz
	(153)	directly coupled (signal lost)	
	(154)	unshifted	
C (C-7)	(151)	vicinal	*J* = 0 - 2 Hz
	(152)	vicinal	*J* = 0 - 2 Hz
	(153)	unshifted	
	(154)	directly coupled (signal lost)	
D (C-1)	(151)	unshifted	
	(152)	geminal	*J* = 0.1 Hz
	(153)	geminal	*J* = 0.1 Hz
	(154)	unshifted	
E (C-3)	(151)	vicinal	*J* = 0 - 2 Hz
	(152)	vicinal	*J* = 0 - 2 Hz
	(153)	geminal	*J* = 0.1 Hz
	(154)	vicinal	*J* = 0 - 2 Hz
F (C-8)	(151)	unshifted	
	(152)	geminal	*J* = 0.1 Hz
	(153)	vicinal	*J* = 0 - 2 Hz
	(154)	geminal	*J* = 0.1 Hz
G (C-6)	(151)	geminal	*J* = 0.1 Hz
	(152)	unshifted	
	(153)	unshifted	
	(154)	geminal	*J* = 0.1 Hz
H (C-10)	(151)	vicinal	*J* = 0 - 2 Hz
	(152)	vicinal	*J* = 0 - 2 Hz
	(153)	vicinal	*J* = 0 - 2 Hz
	(154)	vicinal	*J* = 0 - 2 Hz



(155)



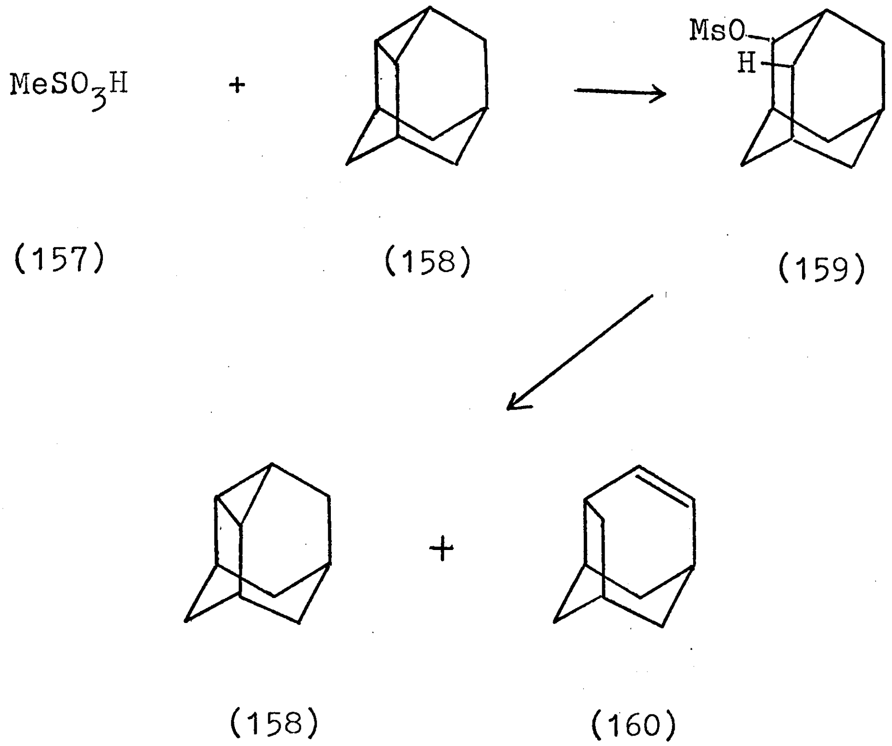
(156)

resolved and appear as broadened lines or shoulders as revealed in Fig. 28. However, this qualitative analysis together with the quantitative data obtained from the integration of the spectrum (Table 16) shows convincingly that the deuterium atoms in (150) are located at C-2, C-7, and C-9 to the extent of 21,21, and 26% respectively.

There are a number of secondary processes which might be responsible for the observed results in the g.c.m.s. analysis as well as the deuterium scrambling revealed in the ^{13}C n.m.r. analysis.

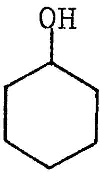
During the pyrolysis of s-butyl thiocyanate, Barroeta <u>et al</u>.[62] showed that there was some 'back addition' of the eliminated acid to the butene formed giving a small amount of s-butyl isothiocyanate. Baldwin and Grayston[63] showed quite convincingly that dehydroadamantane could be converted thermally to protoadamantene. Both processes could occur during the pyrolysis of the labelled sulphonate esters causing a deuterium scrambling.

Control experiments were then devised to investigate the possibility of 'back addition' of methanesulphonic acid

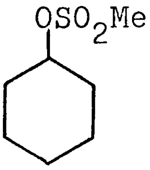


Scheme 15

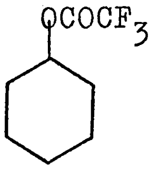
(157) to dehydroadamantane (158) giving the ester (159) which might then be pyrolysed to (158) and (160) as shown in Scheme 15. At the same time, the possibility of the thermal conversion of (158) to (160) similar to that observed by Baldwin and Grayston^{63} was also investigated. The role of trifluoroacetic acid in causing any conversion of this kind was likewise investigated.



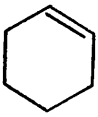
(161)



(162)



(163)



(164)

The ester (162) and (163) were prepared from commercial cyclohexanol (161). Equimolar amounts of (162) and (158) in ether were then co-injected into the pyrolysis tube by a modified inlet system[3] (see Experimental, page 107). The products, obtained by the usual work-up, was analysed by g.l.c. Any conversion of (158) to (160), either directly or through 'back addition', should be detected in this way. This was repeated with different combinations of esters (162), (163) and hydrocarbons (158), (160). The products obtained, other than cyclohexene (164), are shown in Table 18. This shows convincingly that there could not be more than 5% interconversion of (158) and (160) in the sulphonate ester pyrolysis at temperatures above 500°, and none at all at lower temperatures.

The involvement of surface reactions at high temperatures and low pressure is considered not to be very likely. At 0.02 torr, the molecule has a relatively short residence time in the pyrolysis tube. Heterogeneous reactions are usually slow reactions. They require a molecule or radical to reside on a surface or active site and then undergo chemical rearrangement. Re-evaporation of the adsorbed molecule, having a much higher Arrhenius A-factor and lower activation energy at high temperature and low pressure, would be preferred to chemical rearrangement.

Another possible secondary process giving rise to the deuterium scrambling is the intramolecular 1,3-hydride shift.

Table 18 Pyrolysis of Mixtures[a] of Cyclohexyl Esters and the Hydrocarbons in Ether

Method[b]	Oven Temp. (°C)	Pressure (torr)	Vol. of Solu. used (ml)	Products (162):(164)
I	Mesylate (162) and dehydroadamantane (158)			
B	500±20	0.02±0.02	0.2	99:1
B	390±20	0.03±0.02	0.2	100:0
A	500±20	0.03±0.02	0.2	100:0
A	350±20	0.05±0.02	0.2	100:0
II	Mesylate (162) and protoadamantene (160)			
B	530±20	0.03±0.02	0.2	3: 97
B	360±20	0.03±0.02	0.2	0:100
A	500±20	0.05±0.03	0.2	0:100
A	410±20	0.05±0.03	0.1	0:100
III	Trifluoroacetate (163) and dehydroadamantane (158)			
B	510±20	0.02±0.01	0.2	100:0
B	340±20	0.03±0.02	0.2	100:0
A	510±20	0.10±0.05	0.2	100:0
A	350±20	0.10±0.05	0.2	100:0
IV	Trifluoroacetate (163) and protoadamantene (160)			
B	520±20	0.02±0.02	0.2	0:100
B	390±20	0.03±0.02	0.2	0:100
A	510±20	0.05±0.03	0.2	0:100

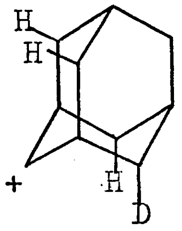
---

[a] The solution is made up of the ester (0.2 g) and the hydrocarbon (0.2 g) in ether (2 ml).

[b] A with Helium flow; B without helium flow (see Experimental).

1,2-Hydride shift in the 1- or 2-adamantyl cation has a high activation energy and this process is considered unlikely; instead, intermolecular hydride shifts take place.[66]

If there were intramolecular 1,3-hydride shift,[64] (165) → (166) → (167), which has been observed in the adamantane nucleus,[65] the deuterium could be scrambled to other positions, depending on which hydrogen atom is transferred and how many intramolecular hydride tranfers are involved.



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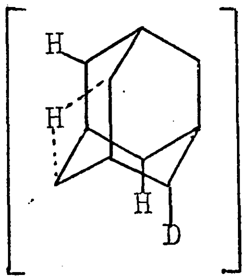

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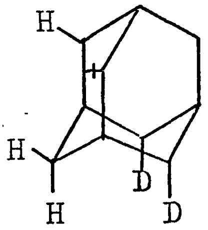
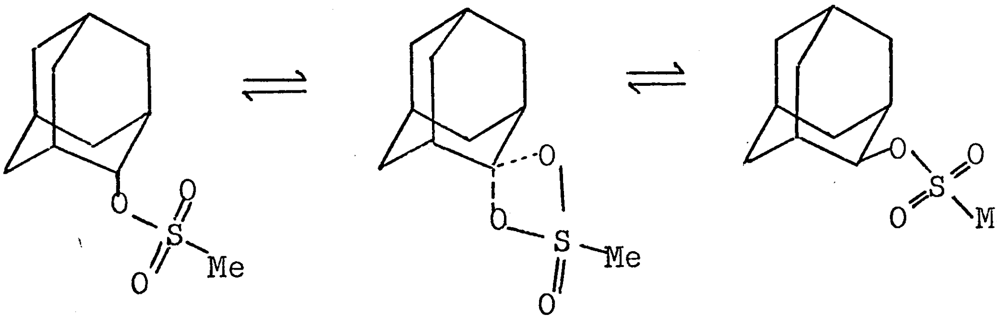


(167)

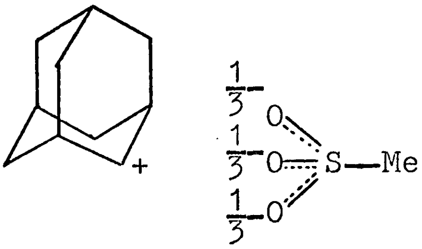
CONCLUSION

All the data in the previous section, obtained both by g.c.m.s. and ^{13}C n.m.r. analysis, indicate that sulphonate ester pyrolyses leading to 1,3-elimination do not go through a simple concerted seven-membered transition state similar to that of the 'retro-ene' reaction[18] mentioned in page 3.

From the data obtained by g.c.m.s. and ^{13}C n.m.r. analysis, the pyrolysis of 2-adamantyl mesylate is observed to proceed through fast prior epimerisation, presumably either _via_ a four-membered transition state (Scheme 16) or simply an ion-pair intermediate (168). There is no direct evidence which of these is involved. However, in the pyrolysis of 10-protoadamantyl mesylate (page 21) and



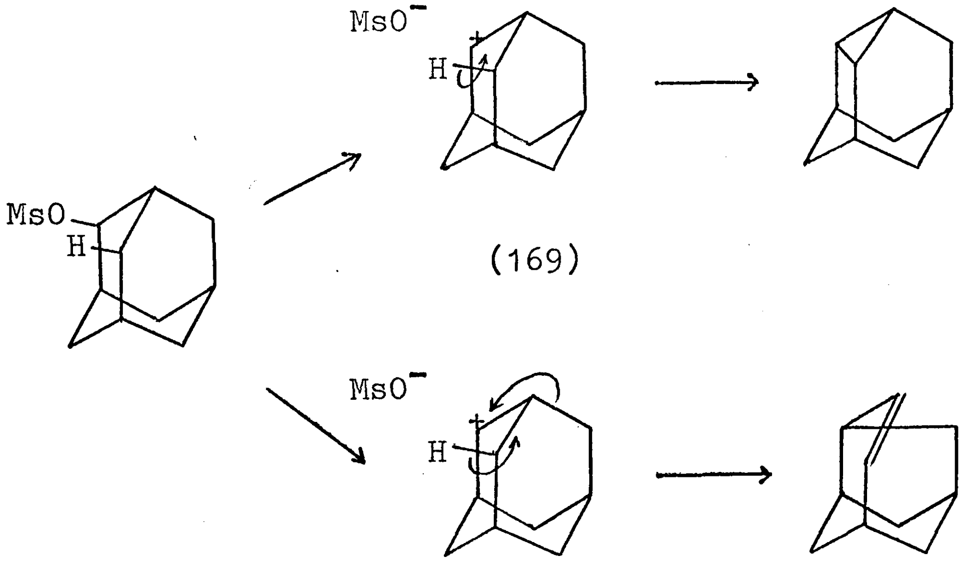
Scheme 16



(168)

2,6-adamantyl bismesylate (page 100), adamantane was obtained as a major product indicating the formation of adamantyl cation followed by an intermolecular hydride shift,[66] although the hydride source has not yet been ascertained. This suggests convincingly that an ion-pair intermediate [such as (168)] is involved in these pyrolyses. Furthermore, the fact that the pyrolyses of (116) and (124) gave products with the same deuterium content indicates that there is a loss of configuration in the ion-pair giving rise to a complete epimerisation of the ester function, and thus implies a reasonable separation of the ion-pair involved.[67]

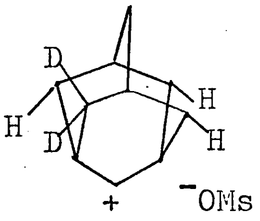
The subsequent elimination with or without rearrangement proceeds stepwise as shown in (169) and (170) respectively. A deuterium isotope effect is not observed for fission of the γ-C--H bond, so that this process presumably plays no part in the rate determining step.



(169)

(170)

The pyrolysis of (118) gives results in excellent agreement with the stepwise mechanism. The ^{13}C n.m.r. analysis of the products from its pyrolysis (Table 15, page 81; Table 16, page 84) shows that the deuterium label is at the expected positions, which are arrived at by considering the loss of a proton (deuterium atom) from (171) (see also page 79). In this case, there will be three hydrogen atoms of the right stereochemistry available for elimination for every deuterium atom. The g.c.m.s. analysis (Table 12, page 65) gives a $\underline{d}_2$:$\underline{d}_1$ ratio of 3.0±0.1 at three different temperatures indicating the absence of a deuterium isotope effect.

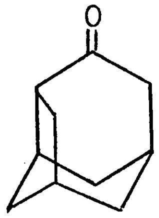


(171)

The results obtained in the ^{13}C n.m.r. analysis from the pyrolyses of other labelled esters show very good qualitative agreement with the above proposed mechanism while those obtained in g.c.m.s. analysis show some irregularities which might be caused by one of the secondary processes discussed in the previous section.

SYNTHESIS OF PROTOADAMANTAN-5-EXO-OL

The synthesis of protoadamantan-5-exo-ol (176) was first attempted by Boyd in this laboratory.[3] He obtained protoadamantan-4-exo- and 4-endo-ol (174) and (175) from the reduction of protoadamantan-4-one (172) by lithium aluminium hydride. However, a similar reduction of protoadamantan-5-one (173) gave mostly protoadamantan-5-endo-ol (177) (95%). Attempted equilibration of (177) also failed to give any significant amount of (176).



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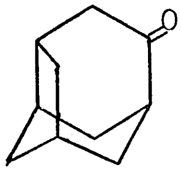

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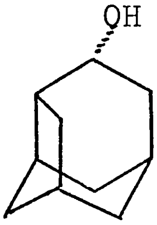

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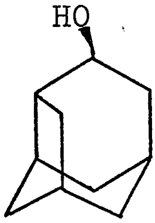
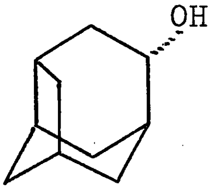
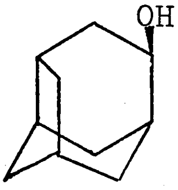


(175)

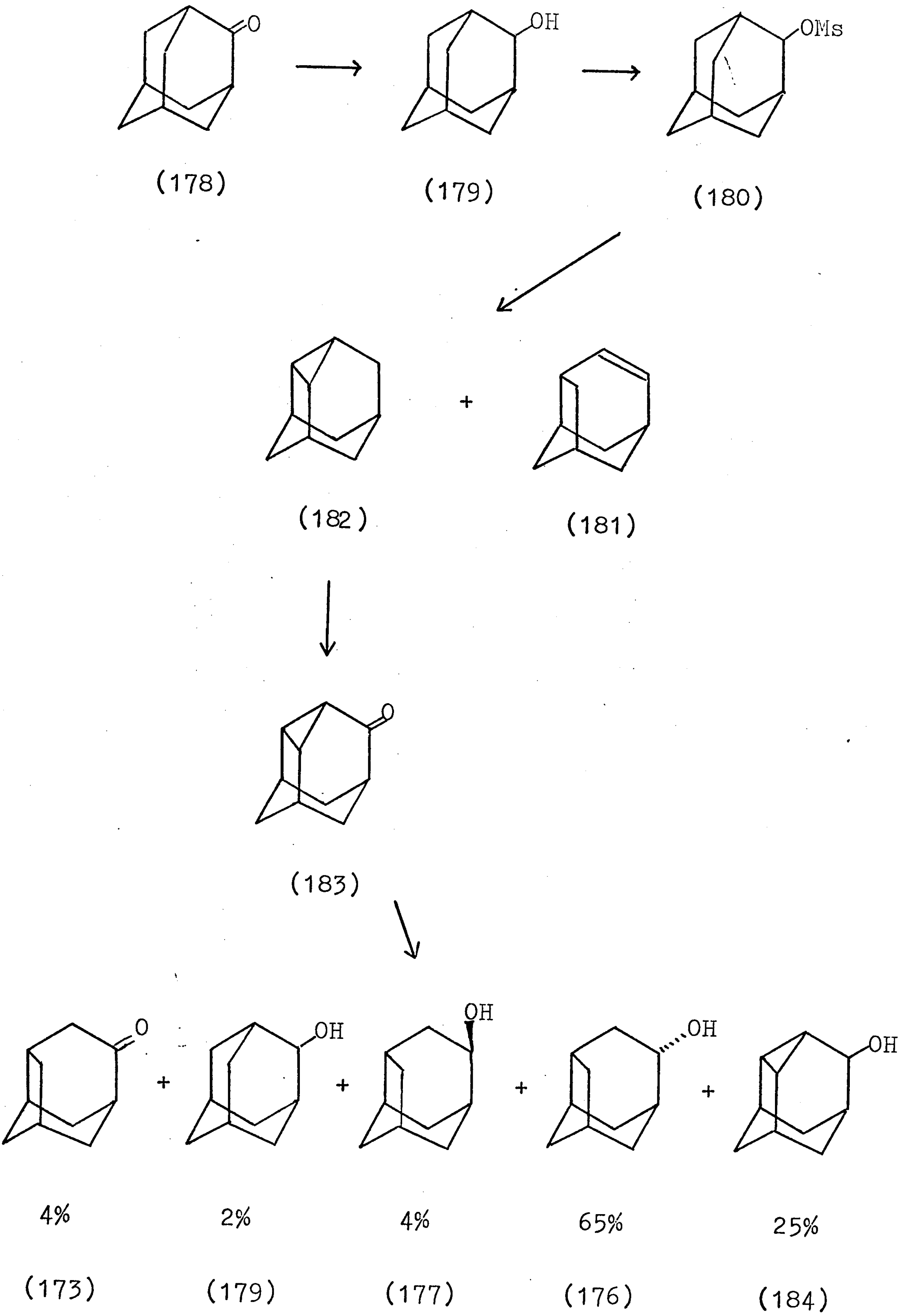


(176)



(177)

The compound (176) is interesting in the study of $Eu(dpm)_3$-shifted n.m.r. spectroscopy. The molecule is relatively simple which enables the chemical shifts of all


O
OH
OMs
(178)
(179)
(180)
+
(182)
(181)
O
(183)
O
+
OH
+
OH
+
OH
+
OH
4%
2%
4%
65%
25%
(173)
(179)
(177)
(176)
(184)

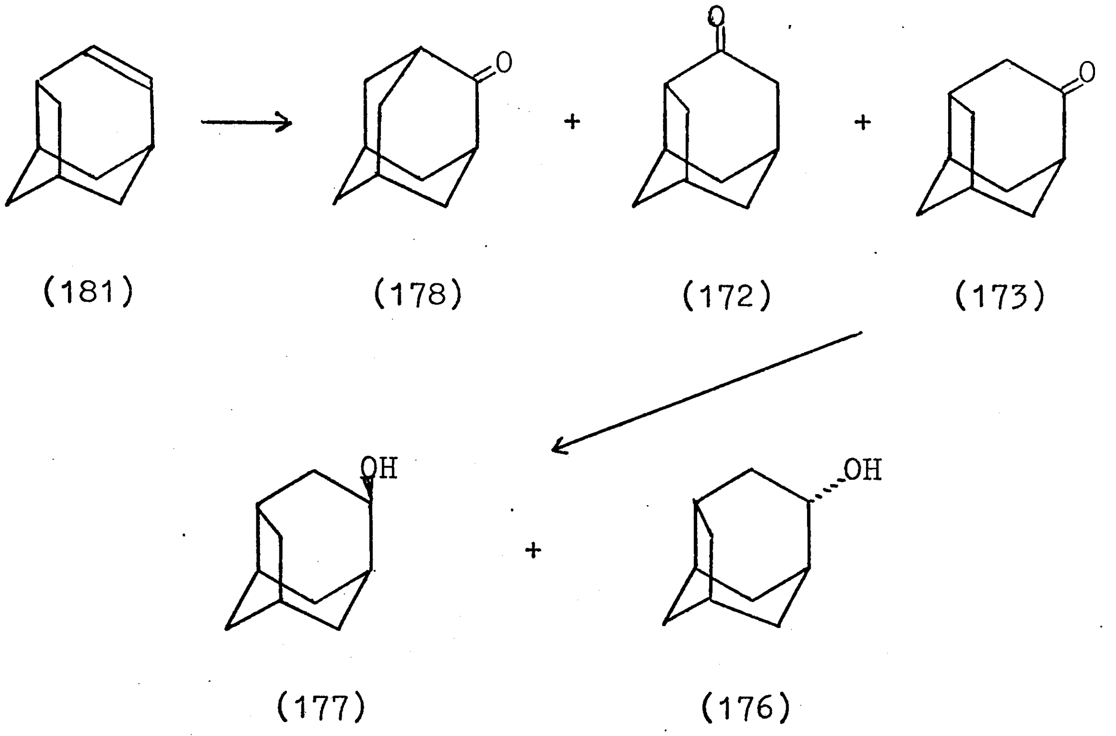
Scheme 17

the protons in the Eu(dpm)$_3$-complex to be calculated and compared with the experimental value. Since (174), (175), and (177) were synthesised and the Eu(dpm)$_3$-shifted n.m.r. spectra measured,[3] the Eu(dpm)$_3$-shifted n.m.r. of (176) would furnish the remaining compound of this study.

The first attempted synthesis began with adamantanone (178) as shown in Scheme 17.

Reduction of (178) with lithium aluminium hydride gave (179), which, on mesylation in the usual way gave (180). Pyrolysis of (180) gave a mixture of (181) and (182) which were separated by column chromatography over silver nitrate-alumina. Oxidation of (182) with ozone at -30° in methylene chloride-pyridine[3] or pyridine chromate in refluxing methylene chloride[68] gave the ketone (183). Reduction of (183) with lithium-ammonia[69] gave a mixture containing (173), (179), (177), (176), and (184) in the ratio of 4:2:4:65:25 (g.l.c.). The mixture was purified by column chromatography over alumina and a sample of (176) contaminated with (184) (25%) was obtained. Further attempts to obtain a pure sample of (176) by preparative t.l.c. proved difficult.

The second attempt to synthesise (176) began with the olefin (181) as shown in Scheme 18. Hydroboration-oxidation[70] of (181) gave the ketone mixture (178), (172), and (173) which was separated by column chromatography over silica gel. Lithium aluminium hydride reduction of (173) gave (177) which remained mostly unchanged upon equilibration with

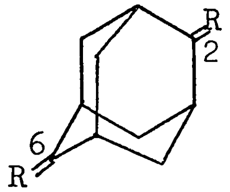


Scheme 18

sodium-methanol. Finally, reduction of (173) with lithium-ammonia gave the starting material (173), (177), and (176) in the ratio of 3:27:70 which were separated by preparative t.l.c.

The Eu(dpm)$_3$-shifted n.m.r. spectrum of (176) has been discussed by Boyd.[3]

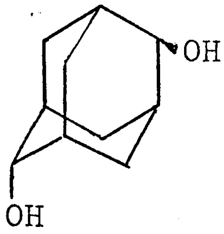
SYNTHESIS AND PYROLYSIS OF THE ESTERS OF ADAMANTANE-2,6-DIOL



(185) R = O

(186) R = $<^{H}_{OH}$

The 2,6-adamantyl derivatives (185) and (186) are highly symmetrical. Thus, the four stereoisomers of adamantane-2,6-diols (187) - (190) form two enantiomeric pairs (187), (190) and (188), (189).



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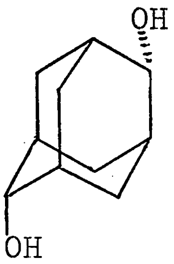

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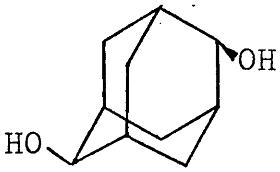

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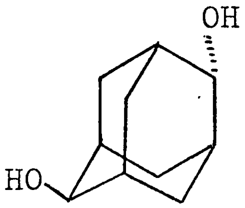
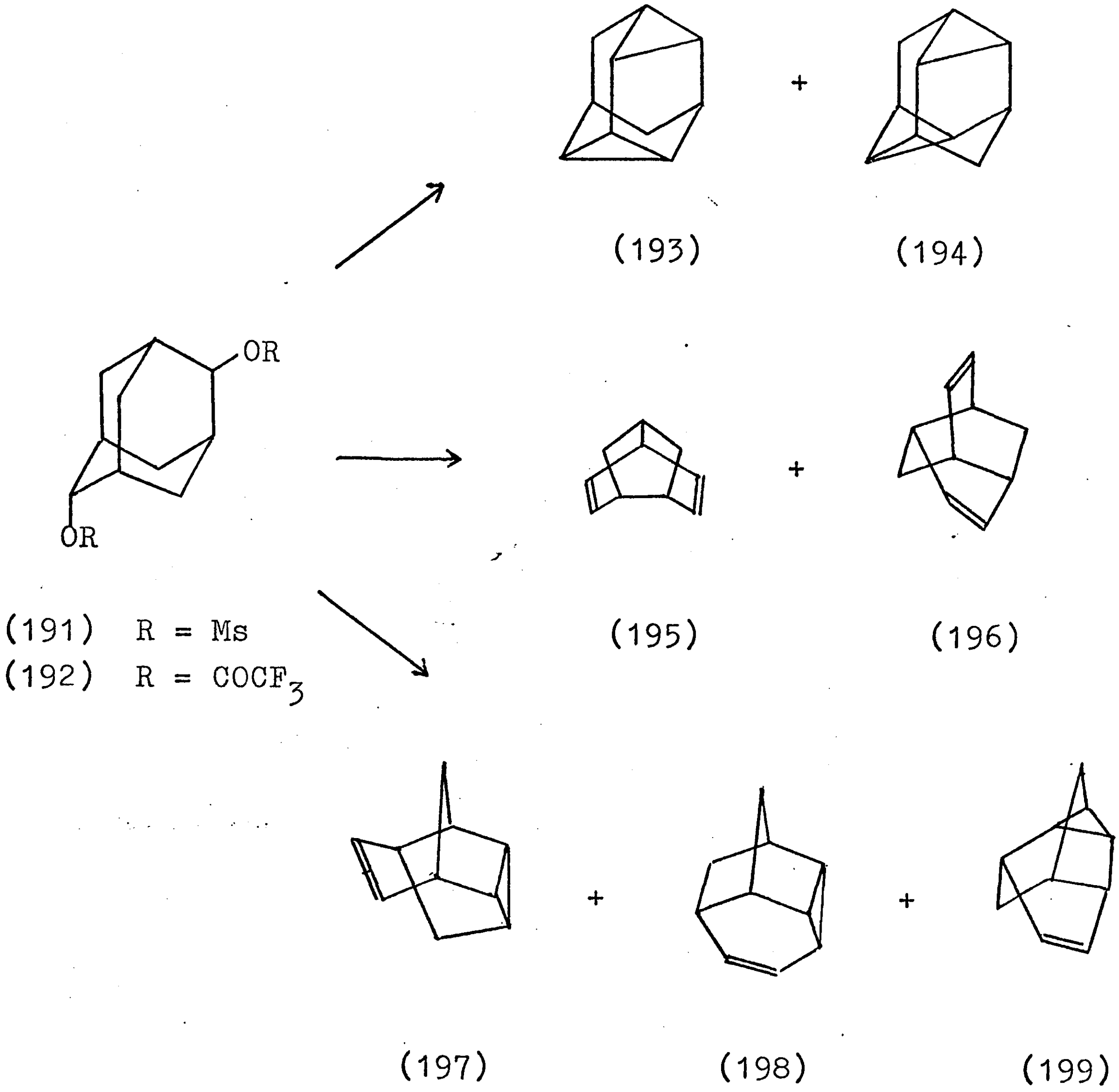


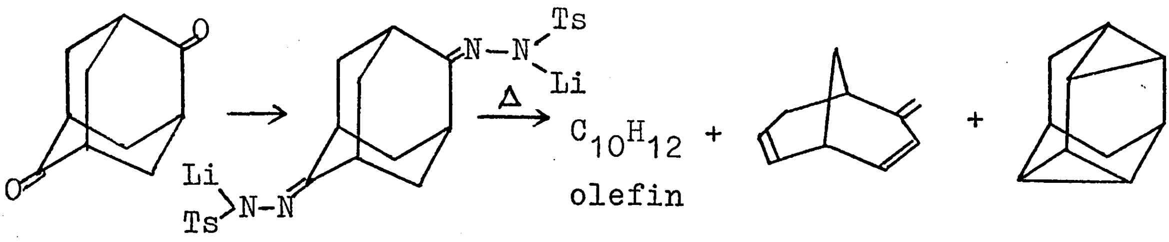
(190)

The pyrolysis of the corresponding bismesylate (191) and bistrifluoroacetate (192) would give, by the 1,3-elimination route, products as shown in Scheme 19. The compounds (193) and (194) would be obtained by two 1,3-eliminations without rearrangement, (195) and (196) by two 1,3-eliminations with rearrangement, while (197), (198), and (199) would result from one elimination without rearrangement and a second with rearrangement.



Scheme 19

2,4,6,9-Tetradehydroadamantane[71] (193) has been previously obtained together with other olefins by intramolecular carbene insertion through the thermolysis of the lithium salt of adamantane-2,6-dione bistosylhydrazone (200) as shown in Fig. 29. It was hoped that the pyrolysis of bismesylate (191) and bistrifluoroacetate (192) would give some of the strained molecules in Scheme 19 and also act



(185) (200) (193)

Fig. 29

as a test model for the predictabiblity of product formation in 1,3-elimination reactions of this kind.

The compound (185) was prepared by the action of fuming sulphuric acid on adamantane.[72] The diol (186) was obtained from the lithium aluminium hydride reduction of the diketone (185). The diesters (191) and (192) were prepared by the standard method.[44]

A pyrolysis of the bismesylate (191) on a small scale (0.2 g) gave only a 10% yield of a hydrocarbon mixture containing 95% of one compound and two minor products of <u>ca</u>. 2% (g.l.c.). The hydrocarbon, purified by preparative g.l.c., gave a molecular formula of $C_{10}H_{12}$ (high resolution m.s.) and a n.m.r. resonance at δ 5.81. A second pyrolysis gave a mixture (<u>ca</u>. 30% yield) of adamantane and the same olefin in the ratio of 6:1 (g.l.c.). Further investigation was not possible due to the small quantity of the material available as well as the low yield of the reaction.

Pyrolysis of the bistrifluoroacetate (192) gave a very complex mixture of hydrocarbons in ca. 10% yield in addition to some starting material (192) (t.l.c.).

EXPERIMENTAL

The following instruments were used: i.r., Perkin-Elmer 225 and 257; ^{1}H n.m.r., 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; g.l.c., Perkin-Elmer F11. Unless otherwise stated, solvents for spectroscopy were: i.r., CCl_4; n.m.r., $CDCl_3$ with internal tetramethylsilane standard. Merck Kieselgel HF_{254} was used for t.l.c. and Woelm alumina or Kock-Light silica gel 200-300 mesh, deactivated to the appropiate Brockmann grade, for column chromatography. All melting points recorded are uncorrected.

^{13}C N.m.r. spectra were measured at the Universities of Edingburgh and Western Ontario, London, Canada on Varian XL100 n.m.r. spectrometers.

Silver nitrate-alumina for column chromatography was prepared as follows: alumina (200 g) was added gradually with stirring to a solution of silver nitrate (40 g) in water (300 ml). The water was then evaporated under reduced pressure and the silver nitrate impregnated alumina was then activated at 120^{o} overnight.

The preparative scale pyrolyses were done with the apparatus shown in Fig. 30. The outlet end of the silica pyrolysis tube is coated with sodium carbonate. The tube is conditioned in the furnace at the pyrolysis temperature for at least 4 h prior to the experiment. The material pyrolysed is placed in the pyrex boat and the inlet part

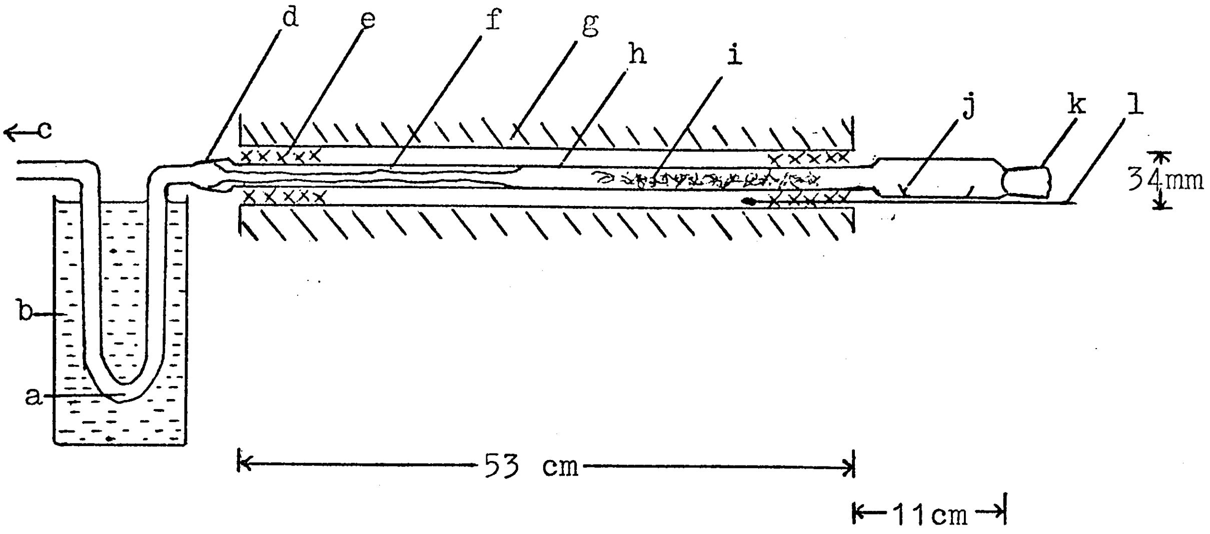


Fig. 30 a pyrolysate, b liquid nitrogen, c to pump, d quick-fit joint, e ceramic wool, f sodium carbonate coating, g commercial furnace, h silica tube, i glass wool, j pyrex boat, k quick-fit stopper, l thermometer.

is heated slowly with a heating tape adjustable by a variable transformer until it reaches 220^{o} and is kept at that temperature. The sublimed material then passes through the hot zone of the tube and the pyrolysate is trapped with liquid nitrogen.

Pyrolysis tubes of different internal diameters were used for different sample sizes as follows: 1.0 - 2.2 g sample, 18 mm diameter; 0.1 - 1.0 g, 13mm; less than 0.1 g, 10 mm.

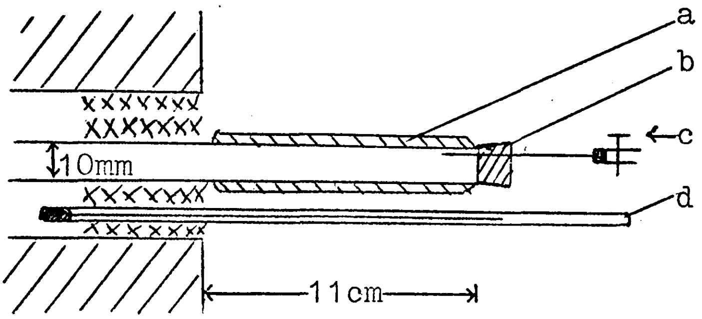


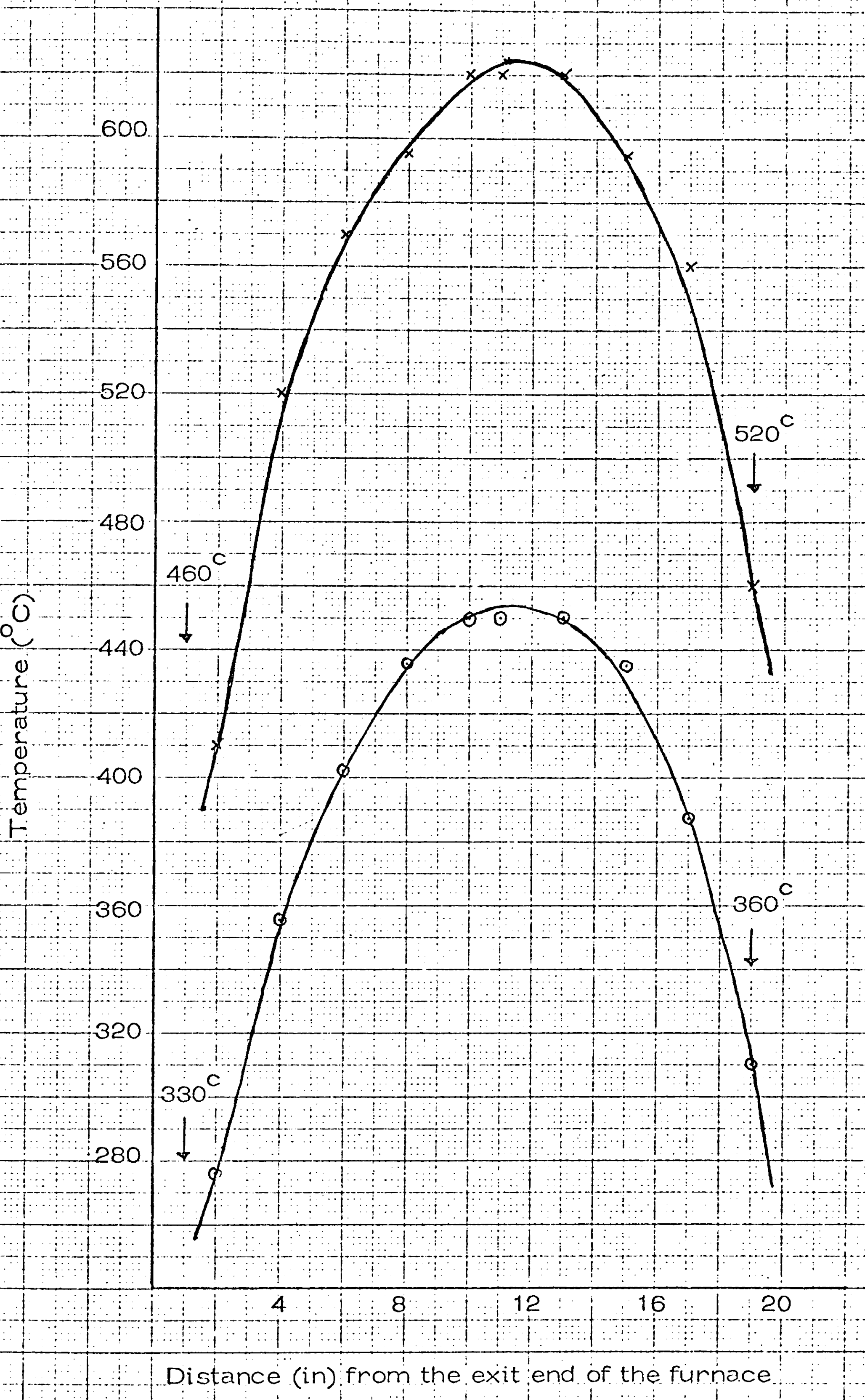
Fig. 31 a heating tape, b silicon rubber,
c helium flow, d thermometer.

The inlet part of the apparatus in Fig. 30 was modified as shown in Fig. 31 for pyrolysing very small or mixed samples. Samples (0.1 g) in ether solution were injected from a glass syringe through a 6 inch needle directly into the hot zone of the pyrolysis tube.

Fig. 32 shows the temperature gradient of the furnace at two different settings. It was later decided that the temperature gradient in the commercial furnace (Fig. 30) was inadequate for quantitative work and an improved furnace was constructed as shown in Fig. 33.

The improved furnace was made up of two 21 in concentric cylindrical ceramic tubes. Nichrom heating tape (0.100in x 0.004in) was wound uniformly around the inner tube (o.d.

Fig. 32 Temperature Gradient[a] of the Furnace[b] in Fig. 30



[a] Measured with a chromel-alumel thermocouple.
[b] Length of furnace 21 in.
[c] Measured with a borosilicate glass thermometer with 76mm immersion.

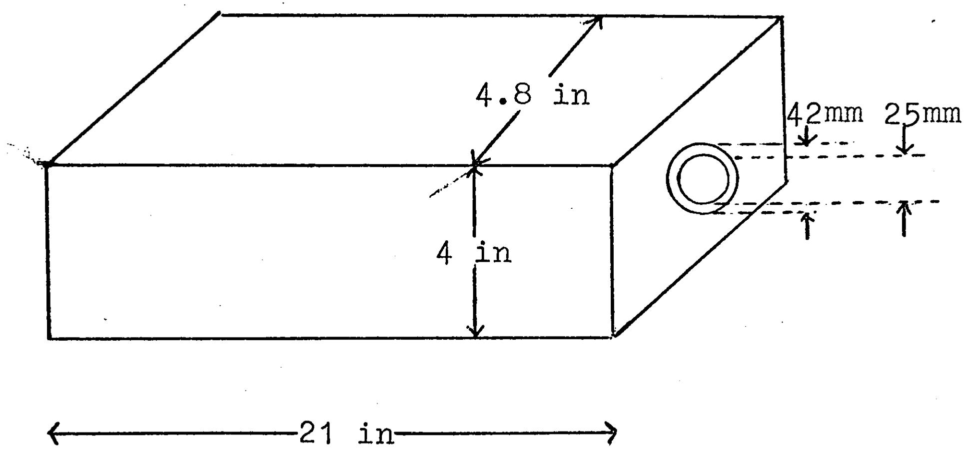


Fig. 33

30 mm, i.d. 25 mm) at 5.5 turns per inch for 20.5 in, while nichrom heating wire (0.020 in) was wound around the outer tube (o.d. 49 mm, i.d. 42 mm) at 24 turns per inch for the first two inches and 22 turns for the next inch from either end of the tube. The space between the two tubes contained air and the space outside the outer tube was filled with powdered magnesium oxide. The inner and outer tube heating wires were controlled by temperature controllers whose thermocouples were placed in the centre and 3 in from one end of the furnace respectively.

The new furnace gives a constant temperature to within ±10° except for the first two inches from either end.

Pyrolysis of 2-Noradamantyl Methanesulphonates

2-Equatorial-noradamantyl Methanesulphonate (26). -- Methane sulphonylchloride (3 ml) was added to a solution of 2-equatorial-noradamantanol (24) (0.5 g, m.p. 222 - 224°, from Professor P.v.R. Schleyer, Princeton) in pyridine (10 ml) and the mixture was stirred at room temperature for 72 h. The reaction mixture was then poured into ice-water (20 ml) which was extracted with ether (3 x 20 ml). The ether extract was washed with 15% hydrochloric acid, saturated sodium carbonate, water, dried, and filtered. Decolourising charcoal (0.1 g) was added to the filtrate and the mixture was filtered through celite after 1 h. Evaporation of the solvent afforded a gum-like solid (0.65 g), which, on crystallisation a few times in pentane-ether at -78° gave (26) (0.42 g), homogeneous on t.l.c., m.p. 65 - 66°, $\nu_{max.}$ 1360, 1340, 1176, and 930 cm^{-1}, δ 4.77 (1H, m), 2.97(3H, s), and 1.40 - 2.77(12H, m), m/e (relative intensity) 216(1, M^+), 120(46), 105(18), 91(35), and 79 (100) (Found: C, 55.6; H, 7.25%. $C_{10}H_{16}O_3S$ requires C, 55.55; H, 7.45%).

Pyrolysis of 2-Equatorial-noradamantyl Methanesulphonate (26). -- The compound (26) (0.5 g) was sublimed slowly during 20 min at 220° into the pyrolysis tube (530±20°) at 0.02±0.03 torr. The pyrolysate, collected at -196°, was extracted with isopentane (3 x 10 ml), which, after being filtered through a column of basic alumina (grade II, 10 g), was analysed by g.l.c. (2m x 1/8in 1%

ApL, 60°). It consisted of three compounds ($\underline{M}^+$ by g.c.m.s.) in the ratio of 67($\underline{M}^+$ 120):27($\underline{M}^+$ 120):6($\underline{M}^+$ 122) having a retention time of 3.6, 4.6, and 5.3 min respectively. The mixture was separated by preparative g.l.c. (14ft x 1/4in 20% ApL, 130°) to give brendene (28) (0.12 g), m.p. 178 - 180°, $\nu_{max.}$ 3053, 2946, 2860, and 1603 cm^{-1}, δ($CFCl_3$) 5.92 (2H, broad s), 2.94(1H, m), 2.36(3H, m), and 1.08 - 1.70 (6H, m), δ_C($CFCl_3$/$CDCl_3$) 139.74(C-2, C-3), 54.23(C-8), 43.19(C-1, C-4), 42.32(C-6), 39.49(C-7), and 36.30(C-5, C-9) (Found: $\underline{M}^+$ 120.0939. C_9H_{12} requires $\underline{M}^+$ 120.0939); and triaxane (31) (0.055 g), m.p. 177 - 178°, $\nu_{max.}$ 3040, 2942, and 2855 cm^{-1}; δ($CFCl_3$) 2.48(3H, m), 2.04(3H, m), 1.69(3H, m), and 1.31(3H, m), δ_C($CFCl_3$/$CDCl_3$) 47.22(CH_2), 40.37(CH), and 37.18(CH) (Found: $\underline{M}^+$ 120.0938. C_9H_{12} requires $\underline{M}^+$ 120.0939).

Noradamantan-2-one (37). — To a stirred solution of (24) (1.5 g) in ether (10 ml), a chromic acid solution prepared from sodium dichromate dihydrate (1 g), water (4.5 ml), and 96% sulphuric acid (1 ml) was added. After the mixture was kept at room temperature for 2 h, water (5 ml) was added and the ether layer was separated. The aqueous layer was extracted twice with ether and the combined ethereal solution was dried and evaporated to give (37) (1.4 g), m.p. 214 - 215° (sublimation), $\nu_{max.}$ 1750 cm^{-1}, δ 1.40 - 2.80(m), $\underline{m/e}$ (relative intensity) 136(51, $\underline{M}^+$), 118(9), 107(17), 92(24), 79(100), and 66(67) (Found: $\underline{M}^+$ 136.0883. $C_9H_{12}O$ requires $\underline{M}^+$ 136.0888).

2-Axial-noradamantanol (38). — To a stirred solution of (37) (1.3 g) in ether (100 ml), a slurry of lithium aluminium hydride (0.4 g) in ether (25 ml) was added. The mixture was boiled under reflux overnight. The usual work-up afforded (38) (1.2 g), m.p. 244 - 245° (sublimation), $\nu_{max.}$ 3640, 1100, and 1040 cm^{-1}, δ 4.04(1H, approx. dd), 2.31(1H, exchangeable with D_2O), and 1.10 - 2.60(12H, m), m/e (relative intensity) 138(16, $\underline{M}^+$), 120(45), 105(13), 95(31), 91(28), and 79(100) (Found: $\underline{M}^+$ 138.104. $C_9H_{14}O$ requires $\underline{M}^+$ 138.104).

2-Axial-noradamantyl Methanesulphonate (30). -- Methane sulphonylchloride (6 ml) was added to a stirred solution of (38) (1.1 g) in pyridine (25 ml) and the mixture was stirred at room temperature for 72 h. The usual work-up gave a yellow oil, which, after repeatedly crystallisation from ether-pentane, afforded (30) (1.1 g), m.p. 25 -26°, $\nu_{max.}$ 1368, 1348, 1180, 1100, 950, 890, and 850 cm^{-1}, δ 4.78 (1H, approx. dd), 3.03(3H, s), and 1.20 - 2.70(12H, m), m/e (relative intensity) 216(2, $\underline{M}^+$), 132(3), 120(93), 105(15), 91(32), and 79(100) (Found: C, 55.85; H, 7.6; S, 14.6%. $C_{10}H_{16}O_3S$ requires C, 55.55; H, 7.45; S, 14.85%).

Pyrolysis of 2-Axial-noradamantyl Methanesulphonate (30). -- The compound (30) (0.5 g) was pyrolysed under identical conditions as in its epimer (26); a similar work-up gave a mixture (0.17 g) of (28) and (31) in the ratio of 1:4. The mixture was separated by preparative g.l.c. as before and each component was found to be identical with the authentic sample (i.r. and ^1H n.m.r. comparisons).

Pyrolysis of 10-Protoadamantyl Methanesulphonates

Pyrolysis of 10-Equatorial-protoadamantyl Methanesulphonate (41). -- The compound (41) (0.7 g, m.p. 76 - 78°, from Professor C. Cupas) was sublimed slowly during 20 min at 220° into the pyrolysis tube (530±20°) at a pressure of 0.04±0.01 torr. The pyrolysate, collected at -196°, was extracted with isopentane (3 x 5 ml), which, after being filtered through a column of basic alumina (grade II, 10 g), was shown by g.l.c. analysis (2m x 1/8in 1% ApL, 80°) to contain two compounds in the ratio of 3:2 and having retention time 5 and 4 min respectively. The isopentane solution was then concentrated at 50° under a vigreux column to 10 ml which was chromatographed over silver nitrate-alumina (30 g). Elution of the column with isopentane (75 ml) gave adamantane (43) (0.29 g), m.p. 267 - 269° (sublimation), $\nu_{max.}$ 2924, 2900, 2842, 1445, 1345, and 1090 cm^{-1}, $\delta(CFCl_3)$ 1.81(m); elution with ether (150 ml) gave tricyclo[5.3.0.$0^{4,9}$]dec-5-ene (45) (0.105 g), $\nu_{max.}$ ($CDCl_3$) 3020, 2940, 2860, 1635, and 850 cm^{-1}, $\delta(CFCl_3)$ 5.89(1H, approx. dd, J = 9.5 and 6.5 Hz), 5.20(1H, approx. dd, J = 9.5 and 3.0 Hz), and 1.20 - 2.80(12H, m), m/e (relative intensity) 134(66, M^+), 117(35), 105(31), 92(100), and 79(75) (Found: M^+ 134.1095. $C_{10}H_{14}$ requires M^+ 134.1095).

Oxidation of Tricyclo[5.3.0.$0^{4,9}$]dec-5-ene (45). -- The compound (45) (0.05 g) was added to a stirred solution of sodium periodate (4.2 g) in acetone (20 ml) and water (18 ml). To the stirred mixture under nitrogen atmosphere at 0^{o}, a solution of potassium permanganate (0.13 g) in water (5 ml) was added dropwise over 0.5 h which was then stirred at room temperature for 12 h. The acetone was then removed under reduced pressure and the residual aqueous phase was extracted continuously with ether. The dried ethereal solution was treated dropwise with diazomethane in ether (ca. 0.04 M) at 0^{o} until a permanent yellow colour developed which was then kept at room temperature for 0.5 h. The excess diazomethane and most of the ether were then removed under reduced pressure at room temperature. The residue was purified by preparative t.l.c. (developed in light petroleum-ethyl acetate 3:1, R_f = 0.40) to give dimethyl bicyclo[3.2.1]octane-2α,6α-dicarboxylate (48) (0.04 g), $\nu_{max.}$ 2950, 2870, 1740, 1470, 1435, 1370, 1283, 1195, and 1165 cm^{-1}, δ 3.68(3H, s), 3.67(3H, s), and 1.20 - 2.98(12H, m), m/e (relative intensity) 226(19, M^+), 195(38), 194(43), 166(95), 162(15), 134(100), 107(45), 106(35), and 79(71) (Found: M^+ 226.1208. $C_{12}H_{18}O_4$ requires M^+ 226.1205). G.l.c. analysis on the purified (48) showed that the sample contained 98% of one compound (using 2m x 1/8in 1% SE30 column at 110^{o}, 2m x 1/8in 1½% QF1 column at 150^{o}, 2m x 1/8in 1% ApL column at 160^{o}, 2m x 1/8in 8% Carbowax 1540 column at 150^{o}, and 2m x 1/8in 8% 1,4-butanediol succinate column at 150^{o}) and it was not 2α-carbomethoxybicyclo[2.2.1]heptane-5α-acetate (46) synthesised later.

5β,6α-Dihydroxybicyclo[2.2.1]heptane-2α-carboxylic 6α-Lactone (50). -- Aqueous hydrogen peroxide (30%, 10 ml) was added during 5 min to a stirred solution of bicyclo-

[2.2.1]hept-5-ene-2-carboxylic acid (49) (Aldrich, 10 g) in 98% formic acid (20 ml) at 45°. The mixture was stirred at 50° for 1 h during which it became homogeneous. It was then steam-distilled until no more formic acid came over and the residue was saturated with sodium carbonate and extracted continuously with ethyl acetate to give (50) (6.35 g), m.p. 157 - 158° (from ether), $\nu_{max.}$ ($CHCl_3$) 3612, 1770, 1054, 1012, and 890 cm^{-1}, δ 4.43(1H, d, _J_ = 5 Hz), 3.73(1H, broad s), 3.16(1H, m), and 1.50 - 2.70(7H, m) (Found: C, 62.3; H, 6.6%. Calc. for $C_8H_{10}O_3$: C, 62.3; H, 6.55%).

6α-Hydroxy-5-oxobicyclo[2.2.1]heptane-2α-carboxylic 6α-Lactone (51). -- A slurry of ruthenium dioxide (0.3 g) in carbon tetrachloride (130 ml) was added to a stirred solution of (50) (6.32 g) and sodium periodate (15 g) in water (130 ml) at 0°. The mixture was then stirred at room temperature for 48 h. Ether was added dropwise to the stirred mixture until the yellow colour was permanently discharged. The aqueous layer was then separated, filtered through celite and extracted continuously with ether to give a mixture (5.4 g) indicated by g.l.c. analysis (6ft x 1/8in 1% OV17 glass column, 110°) to contain (50) and (51) in the ratio of 1:4. The mixture was chromatographed over silica gel (grade II, 500 g) and elution with 1% methanol in chloroform afforded (51) (3.8 g), m.p. 201 - 203° (from ether), $\nu_{max.}$ ($CHCl_3$) 1790, 1767, 1170, 1128, 1080, 1034, 1020, and 988 cm^{-1}, δ 4.25(1H, d, _J_ = 6 Hz), 3.46(1H, m), 2.62 - 2.94(2H, m), and 1.62 - 2.40(4H, m), _m/e_ (relative intensity) 152(33, $\underline{M}^+$), 124(60), 95(60), 83(100), 67(75), and 55(30) (Found: C, 63.4; H, 5.55%. Calc. for $C_8H_8O_3$: C, 63.15; H, 5.3%).

Methyl 5-Oxobicyclo[2.2.1]heptane-2α-carboxylate (52). -- To a slurry of barium (16 g) in refluxing ammonia (distilled from sodium, 500 ml) was added a solution of (51) (3 g) in 1,4-dioxan (50 ml). After stirring the reaction mixture under reflux for 1 h, methanol (17 ml) was added rapidly, which on further stirring for 0.5 h, ammonium chloride (17 g) was added. The ammonia was allowed to evaporate and water (200 ml) was added to the residue, which, after being acidified to pH 4 by dropwise addition of 5M hydrochloric acid, was extracted with ether. The dried ethereal solution was treated dropwise with diazomethane in ether (ca. 0.04M) at 0° until a permanent yellow colour developed which was then kept at room temperature for 0.5 h. The excess diazomethane and most of the ether were then removed under reduced pressure at room temperature. T.l.c. analysis (developed in ethyl acetate-chloroform 1:1) showed this to be a mixture of at least five compounds; attempts to separate these cleanly by preparative t.l.c. proved difficult. The mixture (2.2 g) in acetone (200 ml) was treated dropwise with Jones reagent[31] until a permanent red colour appeared. Propan-2-ol was added dropwise to remove the excess reagent and the mixture was then diluted with ether (200 ml). Excess anhydrous sodium carbonate was added to remove the acid and the mixture was then dried by anhydrous sodium sulphate and filtered. The filtrate was evaporated and the residue was further treated with excess diazomethane and ether followed by purification of the residue by preparative t.l.c. (developed in chloroform) afforded (52) (1.83 g) as an oil, $\nu_{max.}$ 1755, 1743, 1435, 1412, 1197, and 1028 cm^{-1}, δ 3.68 (3H, s), 2.88 - 3.16(2H, m), 2.64(1H, m), and 1.60 - 2.22 (6H, m),<u>m/e</u> (relative intensity) 168(72, <u>M</u>$^+$), 140(20), 137 (52), 127(94), 109(24), 108(33), 99(46), 95(46), 81(100), and 67(80) (Found: <u>M</u>$^+$ 168.0795. $C_9H_{12}O_3$ requires <u>M</u>$^+$ 168.0786).

<u>Ethyl 2α-Carbomethoxy-5-bicyclo[2.2.1]heptylidene-acetate (53)</u>. -- To a stirred suspension of sodium hydride (Institute of Synthesis, Prague; 94%, 0.036 g) in benzene (2 ml) under nitrogen at 30 - 35°, redistilled triethyl phosphonoacetate (0.22 g) in benzene (1 ml) was added over a period of 45 min. The mixture was stirred at room temperature for 1 h. The compound (52) (0.13 g) in benzene (1 ml) was added slowly over a period of 20 min while the reaction mixture was kept at 20 - 30°. After the addition of (52) was completed, the reaction mixture was kept at 60° for 0.5 h. Ether (10 ml) was added to the cooled reaction mixture which was then washed with water (3 x 15 ml) and dried. Evaporation of the solvent afforded a mixture (0.12 g) which upon separation by preparative t.l.c. (developed in ethyl acetate-light petroleum 1:4) afforded (53) (R_f = 0.42, 0.09 g) as an oil, $\nu_{max.}$ (thin film) 1733, 1708, 1660, 1440, 1420, 1204, 1040, and 860 cm^{-1}, $\lambda_{max.}$ 226 nm (log ε <u>ca</u>. 4), δ 5.73(2/3H, m), 5.53(1/3H, m), 4.09(2H, q,

_J_ = 7 Hz), 3.62(3H, s), 2.80(2H, m), 2.48(1H, m), 1.41 - 2.22(6H, m), and 1.22(3H, t, _J_ = 7 Hz), _m/e_ (relative intensity) 238(2, _M_$^+$), 207(8), 192(27), 152(39), 133(14), 124(30), 91(100), and 79(50) (Found: C, 65.45; H, 7.7%. $C_{13}H_{18}O_4$ requires C, 65.55; H, 7.6%).

Methyl 2α-Carbomethoxy-5-bicyclo[2.2.1]heptylideneacetate (54). -- A mixture of (53) (0.06 g) and 5% aqueous sodium hydroxide (5 ml) was boiled under reflux for 15 min which was then acidified, saturated with sodium chloride, and extracted with ether (3 x 10 ml). To the stirred ethereal extract, an ethereal solution of diazomethane (_ca_. 0.04 M) was added dropwise until a yellow colour persisted. Evaporation of the ethereal solution gave an oil which on purification by preparative t.l.c. (developed in chloroform) afforded (54) (0.02 g), $\nu_{max.}$ (thin film) 1734, 1718, 1708, 1661, 1656, 1440, 1208, 1035, and 868 cm^{-1}, $\lambda_{max.}$ 226 nm (logε _ca_. 4), δ 5.75(2/3H, m), 5.57(1/3H, m), 3.62(6H, s), 2.80(2H, m), 2.49(1H, m), and 1.24 - 2.22 (6H, m), _m/e_ (relative intensity) 224(10, _M_$^+$), 193(35), 192(67), 163(32), 161(10), 152(10), 138(83), 133(24), 123(14), 106(100), 91(38), and 79(70) (Found: _M_$^+$ 224.1048. $C_{12}H_{16}O_4$ requires _M_$^+$ 224.1048).

Methyl 2α-Carbomethoxybicyclo[2.2.1]heptane-5α-acetate (46). -- A solution of (54) (0.015 g) in n-pentane (5 ml) was hydrogenated at atmospheric pressure and temperature in the presence of Adams catalyst (0.005 g) overnight. The solution was then filtered and the filtrate evaporated to give (46) (0.01 g) as an oil, $\nu_{max.}$ 1739, 1435, 1417, 1194, and 1177 cm^{-1}, δ 3.64(3H, s), 3.62(3H, s), 2.75(1H, m), 2.48 (2H, m), and 1.22 - 2.34(9H, m), m/e (relative intensity) 226(11, M^+), 195(57), 194(100), 176(12), 166(65), 162(40), 152(30), 134(38), and 107(62) (Found: M^+ 226.120. $C_{12}H_{18}O_4$ requires M^+ 226.120).

Ethyl 2α-Carbomethoxybicyclo[2.2.1]heptane-5α-acetate (55). -- A solution of (53) (0.02 g) in n-pentane (5 ml) was hydrogenated at atmospheric temperature and pressure in the presence of Adams catalyst (0.005 g) overnight. The solution was then filtered and the filtrate evaporated to give (54) (0.015 g) as an oil, $\nu_{max.}$ (thin film) 1735, 1442, 1199, 1190, and 1035 cm^{-1}, δ 4.11(2H, q, J = 7 Hz), 3.66(3H, s), 2.72(1H, m), 2.50(2H, m), 1.46 - 2.34(9H, m), and 1.24 (3H, t, J = 7 Hz), m/e (relative intensity) 240(10, M^+), 209(22), 208(42), 195(34), 194(31), 181(10), 180(19), 167 (22), 166(47), 162(29), 152(24), 135(24), 134(34), and 107(55) (Found: M^+ 240.1360. $C_{13}H_{20}O_4$ requires M^+ 240.1361).

Methyl 2α-Carbomethoxybicyclo[2.2.1]heptane-5α-acetate (46) from Ethyl 2α-Carbomethoxybicyclo[2.2.1]heptane-5α-acetate (55). -- A mixture of (55) (0.01 g) and 5% aqueous sodium hydroxide (2 ml) was boiled under reflux for 15 min which was then acidified, saturated with sodium chloride, and extracted with ether (3 x 10 ml). To the stirred ethereal extract, an ethereal solution of diazomethane (ca. 0.04 M) was added dropwise until a yellow colour persisted. Evaporation of the ether then gave an oil which on purification by preparative t.l.c. (developed in chloroform) afforded (46) (ca. 0.003 g) as an oil identical with the sample obtained earlier (i.r., t.l.c., and g.l.c. comparisons).

Pyrolysis of 10-Axial-protoadamantyl Methanesulphonate (42). -- The compound (42) (0.02 g, from Professor C. Cupas) was pyrolysed under similar conditions as its epimer (41) and upon the same work-up gave a mixture of four compounds (g.l.c. analysis using 2m x 1/8in 1% ApL column, 80°) in the ratio of 1:1:4:1 and having retention time of 7.2, 6.6, 5.4, and 4.1 min respectively. G.c.m.s. analysis (6ft x 1/8in 5% ApL column, 65°) showed all the four compounds had $\underline{M}^+$ 134. Another pyrolysis of a larger sample (0.17 g) under the same conditions and upon the same work-up gave adamantane (43) and (45) in the ratio of 1:1. The mixture was separated by preparative g.l.c. and each component was identified with the authentic sample (i.r. and n.m.r. comparisons).

Hydrogenation of Tricyclo[5.3.0.0^{4,9}]dec-5-ene (45). -- A solution of (45) (ca. 0.03 g) in ether (1 ml) was hydrogenated at atmospheric pressure and temperature in the presence of Adams catalyst (0.005 g) for 2 h. The solution was then filtered and g.l.c. analysis (2m x 1/8in 1% ApL, 80°) on the filtrate showed 90% of one compound, retention time 6 min. The compound was purified by preparative g.l.c. (14ft x 1/4in 20% ApL, 170°) and the ^{13}C n.m.r. spectrum was measured which failed to give any informative result owing to the small amount of compound present.

Synthesis of Deuterium-Labelled 2-Adamantyl Esters

4-Oxahomoadamantan-5-one (79) from Adamantanone (78). -- Adamantanone (78) (Aldrich, 12 g) was added during 0.5 h to a stirred solution of 30% aqueous hydrogen peroxide (9 g) in t-butanol (50 ml) containing selenium dioxide (0.5 g) at 80°. After being kept at this temperature for a further 1.5 h, the reaction mixture was poured into ice-water (60 ml) which was then saturated with sodium chloride and extracted with dichloromethane (3 x 100 ml). The dichloromethane extract was washed with water, dried, and evaporated to give (79) (12.2 g), m.p. 284 - 286° (sublimation), $\nu_{max.}$ 1734, 1723, 1264, 1169, and 1038 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-Oxahomoadamantan-5-one (79) to 4-Hydroxyadamantan-2-ones (80) and (81). -- A solution of (79) (12 g) in 50% v/v sulphuric acid (400 ml) was stirred at 90° overnight. The cooled reaction mixture was poured into water (400 ml) and neutralised with 50% aqueous sodium hydroxide which was then extracted with chloroform (4 x 400 ml). The chloroform extract was washed with saturated brine, dried, and evaporated to give a solid (10 g) which was adsorbed onto silica gel (100 g) and chromatographed on silica gel (1 kg). Elution with light petroleum-acetone (10:1) gave the starting material (79) (1.8 g) followed by 4*e*-hydroxyadamantan-2-one (81) (0.8 g), m.p. 324 - 332° (sublimation), $\nu_{max.}$ 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(10H, m), m/e (relative intensity) 166(32, M$^+$), 148(16), 138(53), 96(76), and 79(100). Further elution of the column gave 4a-hydroxyadamantan-2-one (80) (6.2 g), m.p. 321 - 329° (sublimation), $\nu_{max.}$ 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).

Adamantan-2,4-dione (82). -- A solution of (80) (4 g) and (81) (0.8 g) in acetone (100 ml) was treated dropwise with Jones reagent until the first permanent red colour appeared. The usual work-up afforded (82) (4 g), m.p. 292 - 294° (sublimation), $\nu_{max.}$ ($CHCl_3$) 1780 and 1708 cm^{-1}, δ 3.37(1H, m), 2.77(1H, m), 2.40(2H, m), and 1.62 - 2.26 (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 (82). -- To a stirred solution of (82) (4 g) in ether (250 ml), a slurry of lithium aluminium hydride (1 g) in ether (100 ml) was added. The mixture was boiled under reflux overnight. The usual work-up gave a solid (3.8 g), showing two spots on t.l.c. developed with 10% methanol in chloroform, which was adsorbed onto silica gel (40 g) and then chromatographed over silica gel (400 g). Elution with 2% methanol in chloroform afforded adamantane-2a,4a-diol (83) (1.5 g), m.p. 332 - 334° (sublimation), $\nu_{max.}$ (ca. 3 x

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, $\underline{M}^+$), 150(100), 132(10), and 79(82). Further elution of the column gave a solid diol mixture (2.1 g) which showed only one spot on t.l.c. developed in the following solvent systems: 10% methanol in chloroform. 50% acetone in light petroleum, 10% methanol in ether, three times with ethyl acetate, and four times with 20% acetone in light petroleum. The trimethylsilyl ethers of the diols (0.01 g) were prepared by the usual method which revealed two compounds on g.l.c. (4m 2.5% SE30 capillary column, 180°), retention time 10, 11 min, in the ratio of 7:3 respectively. The acetates of the diols were prepared by the usual method, which, though homogeneous on t.l.c., showed two compounds on g.l.c. in the same ratio (retention time 18.3 and 21.4 min). These diol derivatives, on g.l.c. comparison with those of the separated pure diols obtained later, showed that the major diol is adamantane-2*e*,4*a*-diol (84) and the minor adamantane-2*e*,4*e*-diol (85). The bis(3,5-dinitrobenzoyl)-derivatives of the diols (0.01 g), prepared in the usual way, were also homogeneous on t.l.c.

Mono-3,5-dinitrobenzoylation of the Mixture of Adamantane-2e,4a- and 2e,4e-diols (84) and (85). -- 3,5-dinitrobenzoyl chloride (3.3 g) in pyridine (50 ml) was added slowly during 5 h to a stirred solution of the above diol mixture (2.0 g) in pyridine (100 ml) at 60°. After being kept at this temperature for a further 1 h, the reaction mixture was poured into ice-water (200 ml) and extracted with ether (3 x 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 t.l.c. developed twice in 10% ethyl acetate in chloroform. The first band (R_f = 0.9) afforded a mixture of 2e,4a- and 2e,4e-bis(3,5-dinitrobenzoyloxy)adamantanes (0.3 g), $\nu_{max.}$ 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 x 0.4 H, m), and 1.48 - 2.66(12H, m). The second band (R_f = 0.51) gave 4a-(3,5-dinitrobenzoyloxy)adamantan-2e-ol (86) (0.6 g), m.p. 115 - 118° (from acetone-light petroleum), $\nu_{max.}$ 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 (86) (0.01 g) on reduction with lithium aluminium hydride followed by acetylation in the usual way gave a single peak on g.l.c. (conditions as before) with retention time of 18.3 min. The third band (R_f = 0.41) afforded a mixture of at least two mono-3,5-dinitrobenzoates (2.0 g), $\nu_{max.}$ 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 indicated by g.l.c. (conditions as before) to be (84)-diacetate and (85)-diacetate in the ratio of 3:2. The fourth band (R_f = 0.05) gave the starting material (0.3 g),whose acetate on g.l.c.

analysis (conditions as before), was shown to be a mixture of (84)- and (85)-diacetate in the ratio of 4:1.

<u>Adamantane-2e,4a-diol (84)</u>. — To a stirred solution of (86) (0.1 g) in ether (100 ml), a slurry of lithium aluminium hydride (0.06 g) in ether (50 ml) was added. 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 x 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 t.l.c. (developed in 10% methanol in chloroform) gave (84) (0.025 g), m.p. 321 - 325° (sublimation), $\nu_{max.}$ (<u>ca</u>. 3 x 10^{-3} M) 3620 cm^{-1}, δ (pyridine) 4.89(1H, m), 4.34(1H, m), and 1.20 - 2.80(12H, m), <u>m/e</u> (relative intensity) 168(<0.5, <u>M</u>$^+$), 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%).

<u>Lithium-Ammonia Reduction of 4a-Hydroxyadamantan-2-one (80)</u>. — To a stirred slurry of lithium (0.03 g) in refluxing ammonia (distilled from sodium, 20 ml) was added a solution of (80) (0.05 g) in ether (10 ml). After stirring the reaction mixture under reflux for 1 h, solid ammonium chloride (0.6 g) was added. The ammonia was evaporated and the residue was extracted with ether. Evaporation of the ethereal extract to dryness gave a solid (0.03 g) which was indicated by g.l.c. analysis (conditions as before) through

the bistrimethylsilyl ether and the diacetate derivatives to contain (83) and (84) in the ratio of 99:1.

Lithium Aluminium Hydride Reduction of 4e-Hydroxyadamantan-2-one (81). -- Lithium aluminium hydride (ca. 0.002 g) was added to a stirred solution of (81) (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 indicated by g.l.c. analysis (conditions as before) through the bistrimethylsilyl ether and the diacetate derivatives to contain (84) and (85) in the ratio of 3:2.

Meerwein-Ponndorf-Verley Reduction of Adamantane-2,4-dione (82). -- A stirred solution of (82) (0.84 g) and aluminium isopropoxide (2 g) in isopropanol (10 ml) was distilled under 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 h when the distillate was found free of acetone, most of the isopropanol was removed under reduced pressure. The cooled residue was hydrolysed by 5% aqueous hydrochloric acid (20 ml), saturated with sodium chloride, and then extracted with chloroform (3 x 20 ml). The chloroform extract, dried and evaporated, gave a diol mixture (0.65 g) separated by preparative t.l.c. (developed in 10% methanol in chloroform) into (83) (0.08 g), identical with authentic sample (i.r., n.m.r., and t.l.c. comparisons), and a mixture of (84) and (85) (0.4 g) in the ratio of 7:3 (g.l.c. comparisons on the bistrimethylsilyl ethers and diacetates).

Attempted Equilibration of Adamantane-2,4-diols. -- (a) Adamantane-2a,4a-diol (83). Acetone (0.0005 ml) was added to a solution of (83) (0.018 g) and aluminium isopropoxide (0.04 g) in isopropanol (0.2 ml) in an ampelle which was then sealed and kept at 150° for 168 h. The cooled content was poured into 5M aqueous hydrochloric acid (5 ml) which was saturated with sodium chloride and then extracted with chloroform (3 x 5 ml). The chloroform extract, after being dried and concentrated, gave a mixture containing ca. 95% of the starting material (g.l.c. on diacetates and t.l.c.).

(b) Adamantane-2e,4a- and 2e,4e-diols (84) and (85). A similar equilibration as in (a) on a mixture of (84) and (85) (4:1, 0.018 g) gave the same product mixture as in (a).

2e-Toluene-p-sulphonoxy-4a-(3,5-dinitrobenzoyloxy)-adamantane (89). -- Toluene-p-sulphonyl chloride (0.1 g) was added to (86) (0.072 g) in pyridine (2 ml) at 0°. The reaction mixture was then kept at room temperature for 72 h. The usual work-up gave (89) (0.095 g), m.p. 200 - 201° (from acetone-light petroleum), $\nu_{max.}$ 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 (89). --

To a solution of (89) (0.09 g) in ether (20 ml), a slurry of lithium aluminium deuteride (Isotopic Products Canada, isotopic purity ⩾99 atom % ^{2}H, 0.1 g) in ether (10 ml) was added. The mixture was boiled under reflux overnight. The usual work-up afforded a pale yellow oil (0.025 g) which was purified by preparative t.l.c. (developed in 25% ethyl acetate in light petroleum) to give bicyclo[3.3.1]non-2-ene-7α-deuteromethanol (91) (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 with (92) obtained later in g.l.c. and t.l.c. comparisons.

<u>Monotoluene-p-sulphonation of the Mixture of Adamantane-2e,4a- and 2e,4e-diols (84) and (85)</u>. -- Toluene-p-sulphonyl chloride (1.75 g) in pyridine (10 ml) was added to a stirred solution of (84) and (85) mixture (3:2, 1.5 g) in pyridine (10 ml) over 5 h at 0°. The reaction mixture was then kept stirred at room temperature overnight. The usual work-up gave a mixture of mono- and bistoluene-p-sulphonates (2.7 g) which was separated by preparative t.l.c. developed four times in 30% ethyl acetate in light petroleum. The first band (R_f = 0.72) afforded a mixture of 2e,4a- and 2e,4e-bis(toluene-p-sulphonoxy)adamantane (96) and (97) (0.8 g), $\nu_{max.}$ 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 x 0.4 H, m), 2.46(6H, s), and 1.25 - 2.20(12H, m). The second band (R_f = 0.48) gave 4a-toluene-p-sulphonoxyadamantan-2e-ol (93) (0.25 g), m.p. 68 - 70° (from ether-light petroleum), $\nu_{max.}$ 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, disappeared 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<u>e</u>-toluene-<u>p</u>-sulphonoxyadamantan-4<u>a</u>-ol (94) (0.6 g), m.p. 83 - 85° (from ether-light petroleum), $\nu_{max.}$ 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, disappeared 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<u>e</u>-toluene-<u>p</u>-sulphonoxyadamantan-4<u>e</u>-ol (95) (0.6 g), m.p. 87 - 90° (from ether-light petroleum), $\nu_{max.}$ 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%).

<u>2e,4e-Bis(toluene-p-sulphonoxy)adamantane (97)</u>. -- Toluene-<u>p</u>-sulphonyl chloride (0.03 g) was added to a solution of (95) (0.03 g) in pyridine (1 ml) at 0° which was then kept at room temperature overnight. The usual work-up afforded (97) (0.03 g), m.p. 115 - 117 (from ether-light petroleum), $\nu_{max.}$ 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%).

<u>2e,4a-Bis(toluene-p-sulphonoxy)adamantane (96)</u>. --

(a) <u>From 2e-Toluene-p-sulphonoxyadamantan-4a-ol (94)</u>.

Toluene-p-sulphonyl chloride (0.03 g) was added to a solution of (94) (0.03 g) in pyridine (1 ml) at 0° which was then kept at room temperature overnight. The usual work-up gave (96) (0.03 g), m.p. 97 - 99° (from ether-light petroleum), $\nu_{max.}$ 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 (93). The compound (93) (0.03 g) on similar toluene-p-sulphonation as in (a) gave (96) (0.03 g), m.p. 97 - 99°, identical with the one obtained in (a) (i.r. and n.m.r. comparisons).

Lithium Aluminium Hydride Reduction of 4e-Toluene-p-sulphonoxyadamantan-2e-ol (95). -- To a solution of (95) (0.433 g) in ether (30 ml), a slurry of lithium aluminium hydride (0.2 g) in ether (10 ml) was added. The mixture was boiled under reflux overnight. The usual work-up afforded bicyclo[3.3.1]non-2-ene-7α-methanol (92) (0.21 g) as an oil, homogeneous on t.l.c. (developed in 30% ethyl acetate in light petroleum) and g.l.c. (50m x 0.5mm capillary Carbowax 1540 column, 120°), $\nu_{max.}$ 3640, 3020, 1643, 1430, 1032, and 1020 cm^{-1}, δ 5.78(1H, m), 5.49(1H, m), 3.51(2H, d, J = 6 Hz), 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 (94). -- Lithium aluminium hydride (0.005 g) was added to a stirred solution of (94) (0.01 g) in ether (2 ml) which was then boiled under reflux overnight. The usual work-up afforded an oil, indicated by g.l.c. (conditions as before) to contain (92) and adamantan-2-ol (101) in the ratio of 93:7, identical with (92) (i.r. and t.l.c. comparisons).

Lithium Aluminium Deuteride Reduction of 4a-Toluene-p-sulphonoxyadamantan-2e-ol (93). -- To a solution of (93) (0.08 g) in ether (10 ml), a slurry of lithium aluminium deuteride (0.04 g) in ether (5 ml) was added which was then boiled under reflux overnight. The usual work-up gave a mixture indicated by g.l.c. analysis to contain (92) and adamantan-2-ol (101) in the ratio of 3:7. G.c.m.s. analysis (10ft x 1/8in 5% Carbowax 1540 column, 140°) showed that both compounds contain one deuterium ($\underline{M}^+$ 153, $\underline{M}^+ - 15$ 135) when compared to the unlabelled compounds. The mixture was separated by preparative t.l.c. (developed twice in 25% ethyl acetate in light petroleum) to give 4*e*-deuteroadamantan-2*e*-ol (100) (0.013 g), m.p. 294 - 296° (sublimation), $\nu_{max.}$ 3632, 2162, 2145, 1052, and 1020 cm^{-1}, identified by $Eu(dpm)_3$-shifted n.m.r.; and (91) (*ca*. 0.006 g), identified by n.m.r. and m.s. comparisons.

2-Tetrahydropyranoxyadamantane (104). -- Dihydropyrane (0.084 g) and phosphoryl chloride (0.01 ml) was added to a stirred solution of adamantan-2-ol (101) (0.01 g) in benzene (1 ml) under nitrogen at room temperature which was then kept at room temperature overnight. Ether (2 ml) was added to the reaction mixture which was then washed with water, saturated aqueous sodium carbonate, saturated brine, and dried over anhydrous magnesium sulphate. Evaporation of the solvent gave (104) as an oil (0.12 g), $\nu_{max.}$ 1023 cm^{-1}, δ 4.92(0.2H, m), 4.68(0.8H, m), 3.32 - 4.02(3H, m), and 1.36 - 2.28(20H, m), m/e (relative intensity) 152(11), 151 (5), 150(6), 134(87), 92(55), 84(74), 79(54), and 55(100) (Found: C, 76.4; H, 10.3%. $C_{15}H_{24}O_2$ requires C, 76.2 H, 10.25%).

4e-Tetrahydropyranoxy-2e-toluene-p-sulphonoxyadamantane (102). -- Dihydropyrane (0.021 g) and phosphoryl chloride (0.01 ml) was added to a stirred solution of (95) (0.052 g) in benzene (1 ml) in nitrogen at room temperature which was then kept at room temperature overnight. The similar work-up gave (102) as an oil (0.072 g), $\nu_{max.}$ 1367, 1188, 1178, 1026, 945, 925, 908, and 862 cm^{-1}, δ 7.84(2H, d), 7.35(2H, d), 4.88(1/3H, m), 4.57(5/3H, m), 3.28 - 4.12(3H, m), 2.42 (3H, s), and 1.20 - 2.22(18H, m) (Found: C, 65.25; H, 7.35%. $C_{22}H_{30}O_5S$ requires C, 65.0; H, 7.45%).

Lithium Aluminium Hydride Reduction of 4e-Tetrahydropyranoxy-2e-toluene-p-sulphonoxyadamantane (102). -- (a) In Tetrahydrofuran. Lithium aluminium hydride (0.05 g) was added in small portions to a stirred solution of (102) (0.046 g) in tetrahydrofuran (10 ml) which was then boiled under reflux overnight. The reaction mixture was treated by successive dropwise addition of water (0.05 ml), 15% aqueous sodium hydroxide (0.05 ml), and water (0.15 ml) and then dried over anhydrous magnesium sulphate and filtered. Evaporation of the solvent and purification of the residue by preparative t.l.c. (developed in ethyl acetate-light petroleum 1:1) afforded 4*e*-tetrahydropyranoxyadamantan-2*e*-ol (103) as an oil (0.025 g), $\nu_{max.}$ 3630 and 1020 cm^{-1}, δ 4.68 (1H, m), 3.32 - 4.12(4H, m), and 1.20 - 2.30(19H, m), *m/e* (relative intensity) 252(13, *M*$^+$), 234(8), 188(6), 167(14), 151(29), 133(86), 91(60), 85(100), and 79(34) (Found: C, 71.5; H, 9.8%. $C_{15}H_{24}O_3$ requires C, 71.4; H, 9.6%).

(b) *In Ether*. Lithium aluminium hydride (0.03 g) was added to a stirred solution of (102) (0.063 g) in ether (10 ml) which was then boiled under reflux overnight. The usual work-up gave a mixture indicated by t.l.c. comparison (developed in ethyl acetate-light petroleum 1:3) with authentic samples to contain (102), (103), and (104) in the ratio of *ca*. 17:2:1. This was further proved by i.r. comparisons after separating the mixture by preparative t.l.c.

Adamantane-2e,4e-diol (85). -- Hydrochloric acid (5M, 1 drop) was added to a stirred solution of (103) (0.01 g) in methanol (1 ml) which was kept at room temperature overnight. Saturated brine (1 ml) was added which was then extracted with ethyl acetate (3 x 2 ml). Evaporation of the solvent gave (85) as a crystalline solid (*ca*. 0.007 g), which was homogeneous on t.l.c., m.p. 338 - 342^{o} (sublimation), $\nu_{max.}$ 3623, (KBr disc) 1016 and 1027 cm^{-1}, δ (pyridine) 4.07(2H, m) and 1.37 - 2.68(14H, m), *m/e* (relative intensity) 168(6, *M*$^+$), 150(100), 132(16), 117(19), 107(20), 91(24), and 79(50) (Found: *M*$^+$ 168.1146. $C_{10}H_{16}O_2$ requires *M*$^+$ 168.1150).

The g.l.c. retention time of the diacetate (4m 2.5% SE30 capillary column, 180^o) was found to be 21.4 min.

4a-Tetrahydropyranoxy-2e-toluene-p-sulphonoxyadamantane (105). -- Dihydropyrane (0.04 g) and phosphoryl chloride (0.01 ml) was added to a stirred solution of (94) (0.127 g) in benzene (3 ml) in nitrogen at room temperature which was then kept at room temperature overnight. The usual work-up gave (105) (0.155 g), m.p. 119 - 121^o (from light petroleum-ether), $\nu_{max.}$ 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 (105). -- (a) With Slight Excess of Lithium Aluminium Hydride. Lithium aluminium hydride (0.014 g) was added to a stirred solution of (105) (0.083 g) in ether (10 ml) which was then boiled under reflux overnight. The usual work-up gave a mixture indicated by t.l.c. (developed in 20% ethyl acetate in light petroleum) to contain the starting material and a more polar product in the ratio of ca. 3:7. Separation by preparative t.l.c. (developed in 50% ethyl acetate in light petroleum) afforded the starting material, identified by i.r. comparison, and 4a-tetrahydropyranoxyadamantan-2e-ol (106) (0.028 g) as an oil, $\nu_{max.}$ 3628 and 1022 cm^{-1}, δ 4.68(1H, m), 3.30 - 4.24(4H, m), and 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) In Large Excess of Lithium Aluminium Hydride. Lithium aluminium hydride (0.025 g) was added to a stirred solution of (105) (0.011 g) in ether (3 ml) which was then boiled under reflux overnight. The usual work-up gave (106) identified by i.r. and t.l.c. comparisons.

Acid Hydrolysis of 4a-Tetrahydropyranoxyadamantan-2e-ol (106). -- Hydrochloric acid (5M, 1 drop) was added to a solution of (106) (0.01 g) in methanol (1 ml) which was stirred at room temperature overnight. The usual work-up gave (84) (0.005 g), m.p. 321 - 325° (sublimation), identified by t.l.c. and i.r. comparison.

Acetylation of 4a-Hydroxyadamantan-2-one (80). -- Pyridine (2 ml) was added to a stirred solution of (80) (2.7 g) in acetic anhydride (200 ml) which was then kept at room temperature for 48 h. The usual work-up gave 4a-acetoxyadamantan-2-one (107) (2.35 g) as an oil, $\nu_{max.}$ 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 (107). -- Sodium borodeuteride (Koch-Light, isotopic purity $\geqslant$98 atom % ^{2}H, 0.5 g) in aqueous 1,4-dioxan (1:1, 150 ml) was added to a stirred solution of (107) (2.35 g) in 1,4-dioxan (150 ml) which was kept at room temperature for 2 h. The mixture was then saturated with sodium chloride and the organic layer was separated. The aqueous layer was extracted with ether (3 x 50 ml). The combined organic extract was dried and concentrated to give a mixture indicated by g.l.c. analysis (4m 2.5% SE30 capillary column, 180°) to contain two compounds in the ratio of 17:3. Further acetylation and g.l.c. comparison (similar conditions) with unlabelled samples showed that the mixture contained 4*a*-acetoxy-2*e*-deuteroadamantan-2*a*-ol (108) and 4*a*-acetoxy-2*a*-deuteroadamantan-2*e*-ol (109) with (108) as the major component. Separation by preparative t.l.c. (developed in 2% methanol in chloroform) gave (108) (1.40 g) as an oil, $\nu_{max.}$ 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 (109) (0.25 g), m.p. 78 - 82° (sublimation), $\nu_{max.}$ 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(18), 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-deutero-2a-toluene-p-sulphonoxyadamantane (110). -- Toluene-p-sulphonyl chloride (2.5 g) was added to (108) (1.38 g) in pyridine (20 ml) at 0°. The mixture was then kept at room temperature for 72 h. The usual work-up gave pure (110) (2.37 g), m.p. 83 - 85° (from ether), $\nu_{max.}$ 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(12H, m) (Found: C, 6.25; 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-deutero-2a-toluene-p-sulphonoxyadamantane (110). -- To a solution of (110) (1.2 g) in ether (200 ml), a slurry of lithium aluminium hydride (0.8 g) in ether (20 ml) was added which was then boiled under reflux overnight. The usual work-up gave a mixture containing (t.l.c.) three products having the same R_f values as (101), (92), and (83). The mixture was adsorbed onto alumina (10 g) which was then chromatographed over alumina (50 g). Elution of the column with ether-pentane (3:7) afforded 4a-deuteroadamantan-2a-ol (113) (0.4 g), m.p. 292 - 296° (sublimation), $\nu_{max.}$ 3628, 2155, 1048, and 1020 cm^{-1}, identical with 2-adamantanol on t.l.c. and g.l.c. comparisons. Further elution of the column with ether-pentane (1:1) gave 2-deuterobicyclo[3.3.1]-non-2-ene-7α-methanol (114) as an oil (0.03 g), $\nu_{max.}$ 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 (92) on t.l.c. and g.l.c. comparisons. The third more polar compound was not eluted.

Lithium Aluminium Deuteride Reduction of 4a-Acetoxy-2e-deutero-2a-toluene-p-sulphonoxyadamantane (110). — To a solution of (110) (1.14 g) in ether (200 ml), a slurry of lithium aluminium deuteride (0.8 g) in ether (20 ml) was added which was then boiled under reflux overnight. The usual work-up gave a mixture similar to the lithium aluminium hydride reduction products (t.l.c.) which was then chromatographed over alumina in the same way. Elution with ether-pentane (3:7) afforded 4,4-dideuteroadamantan-2a-ol (111) (0.4 g), m.p. 292 - 295° (sublimation), $\nu_{max.}$ 3628, 2200, 2088, 1048, and 1020 cm^{-1}, identical with 2-adamantanol on t.l.c. and g.l.c. comparisons. Further elution of the column with ether-pentane (1:1) gave 2-deuterobicyclo[3.3.1]non-2-ene-7α-deuteromethanol (112) as an oil (0.03 g), $\nu_{max.}$ 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 (92) and (114) on t.l.c. and g.l.c. comparisons. The third more polar compound was not eluted.

4a-Deutero-2a-adamantyl Methanesulphonate (116). — Methane sulphonyl chloride (0.6 ml) was added to a stirred solution of (113) (0.1 g) in pyridine (6 ml) at 0° and the mixture was stirred at room temperature for 72 h. The usual work-up afforded (116) (0.14 g), m.p. 65.5 - 66.5° (from pentane), $\nu_{max,}$ 2170, 1174, 922, and 916 cm^{-1}, identical with 2-adamantyl methanesulphonate in t.l.c.

4a-Deutero-2a-adamantyl Trifluoroacetate (117). -- Trifluoroacetic anhydride (2 ml) was added slowly over 5 min to a stirred solution of (113) (0.2 g) in pyridine (15 ml) at 0° and the mixture was stirred at room temperature overnight. The usual work-up gave (117) (0.31 g) as an oil, $\nu_{max.}$ (thin film) 2165, 1780, 1372, 1359, 1330, 1255, 1215, 1150, 1100, 1090, 1036, 1007, 970, and 920 cm^{-1}, *m/e* (relative intensity) 249(<0.8, $\underline{M}^+$), 135(100), 120(8), 106(10), 93(70), and 79(30), identical with the unlabelled ester in t.l.c. and g.l.c.

4,4-Dideutero-2a-adamantyl Methanesulphonate (118). -- Methane sulphonylchloride (1 ml) was added to a stirred solution of (111) (0.15 g) in pyridine (10 ml) at 0° and the mixture was stirred at room temperature for 72 h. The usual work-up gave (118) (0.21 g), m.p. 66 - 67° (from pentane), $\nu_{max.}$ 2200, 2120, 2100, 2085, 1365, 1340, 1174, and 920 cm^{-1}, identical with 2-adamantyl methanesulphonate on t.l.c.

4,4-Dideutero-2a-adamantyl Trifluoroacetate (119). -- Trifluoroacetic anhydride (1.7 ml) was added slowly over 5 min to a stirred solution of (111) (0.18 g) in pyridine (15 ml) at 0° and the mixture was stirred at room temperature overnight. The usual work-up gave (119) (0.25 g) as an oil, $\nu_{max.}$ (thin film) 2210, 2130, 2110, 1780, 1225, and 1170 cm^{-1}, *m/e* (relative intensity) 250(1, $\underline{M}^+$), 136(100), 121(5), 107(5), 106(5), 94(30), 93(28), 92(26), and 79(19), identical with the unlabelled ester on t.l.c. and g.l.c.

2-Deuteroadamantan-2-ol (121). -- To a stirred solution of adamantanone (78) (3.0 g) in ether (250 ml), a slurry of lithium aluminium deuteride (0.8 g) in ether (50 ml) was added. The mixture was boiled under reflux overnight. The usual work-up gave (121) (3.0 g), m.p. 295 - 297° (sublimation), $\nu_{max.}$ 3632, 2135, 2123, 2105, 1110, 1050, 1022, and 936 cm^{-1}, δ 1.48 - 2.26(m), identical with 2-adamantanol on g.l.c. and t.l.c. comparisons.

2-Deutero-2-adamantyl Methanesulphonate (120). -- Methane sulphonylchloride (15 ml) was added to a stirred solution of (121) (3.0 g) in pyridine (60 ml) at 0° and the mixture was stirred at room temperature for 72 h. The usual work-up afforded (120) (3.9 g), m.p. 66 - 67° (from ether-isopentane), $\nu_{max.}$ 2182, 1360, 1343, 1176, and 917 cm^{-1}, δ 3.00(3H, s) and 1.48 - 2.24(14H, m), identical with 2-adamantyl methanesulphonate on t.l.c.

4a-Deuteroadamantan-2-one (122). -- A solution of (113) (0.5 g) in acetone (100 ml) was treated dropwise with Jones reagent until the permanent red colour appeared. The usual work-up afforded (122) (0.5 g), m.p. 280 - 282° (sublimation), $\nu_{max.}$ 2150, 1727, and 1055 cm^{-1}, identical with adamantanone on t.l.c. and g.l.c.

The 1:1 Mixture of 4a- (74) and 4e-Deuteroadamantan-2a-ol (73). -- To a stirred solution of (122) (0.5 g) in ether (50 ml), a slurry of lithium aluminium hydride (0.06 g) in ether (10 ml) was added. The mixture was boiled under reflux overnight. The usual work-up gave a 1:1 mixture of (73) and (74) (0.5 g), m.p. 295 - 297^{o} (sublimation), identical with 2-adamantanol on t.l.c. and g.l.c. comparisons.

The 1:1 Mixture of 4a- and 4e-Deuteroadamantyl Methanesulphonate (124). -- Methane sulphonylchloride (2.5 ml) was added to a stirred solution of the 1:1 mixture of alcohols (73) and (74) (0.5 g) in pyridine (10 ml) at 0^{o} and the mixture was stirred at room temperature for 72 h. The usual work-up afforded the mixture of esters (124) (0.7 g), m.p. 66 - 67^{o} (from ether-isopentane), identical with 2-adamantyl methanesulphonate on t.l.c.

Pyrolyses of the Labelled Esters. -- The apparatus, with either the commercial or the improved furnace, is described in Fig. 30, 31, and 33. The reaction conditions are listed in Table 11 and 12 together with the obtained products. The general procedure of these pyrolyses follows that of (180) described in page 144.

Cyclohexyl Methanesulphonate (162). -- Methane sulphonylchloride (8 ml) was added to a stirred solution of (161) (6 g) in pyridine (70 ml) at 0^{o} and the mixture was stirred at room temperature for 72 h. The usual work-up gave (162) (9.8 g) as an oil, $\nu_{max.}$ 1370, 1345, 1180, 970, 935, and 865 cm^{-1}, δ 4.70(1H, m), 3.00(3H, s), and 1.05 - 2.30(10H, m), m/e (relative intensity) 135(9), 99(7), 83 (59), 82(100), and 67(75).

Cyclohexyl Trifluoroacetate (163). -- Trifluoroacetic anhydride (12 ml) was added slowly over 5 min to a stirred solution of (161) (6 g) in dry pyridine (80 ml) and the mixture was stirred at room temperature for 24 h. The usual work-up gave (163) (9.2 g) as an oil, b.p. 148 - 149^{o}, $\nu_{max.}$ 1787, 1221, 1169, and 1150 cm^{-1}, δ 4.97(1H, m) and 0.8 -2.2(10H, m), m/e (relative intensity) 83(100), 82(9), 69(19), 67(74), 55(31), and 54(38).

Synthesis of Protoadamantan-5-exo-ol

2-Adamantanol (179). -- To a solution of (178) (6.0 g) in ether (100 ml), a slurry of lithium aluminium hydride (1.5 g) in ether (100 ml) was added. The mixture was boiled under reflux for 18 h. The usual work-up afforded (179) (5.5 g), m.p. 295 - 297^o (sublimation), $\nu_{max.}$ 3630, 1095, 1050, and 930 cm^{-1}, δ 3.86(1H, m), 1.55(1H, s, exchangeable with D_2O), and 1.30 - 2.30(14H, m), m/e (relative intensity) 152(9, $\underline{M}^+$), 151(5), 150(3), 134(100), 119(14), 105(12), 92(58), and 79(62).

2-Adamantyl Methanesulphonate (180). -- Methane sulphonylchloride (30 ml) was added to a solution of (179) (5.0 g) in pyridine (100 ml) and the mixture was stirred at room temperature for 72 h. The reaction mixture was then poured into water. The precipitate, recrystallised from methanol, gave (180) (6.5 g), m.p. 67 - 68^o, $\nu_{max.}$ 1360, 1340, 1170, 1095, 955, 920, 900, and 840 cm^{-1}, δ 4.87(1H, m), 3.03(3H, s), and 1.40 - 2.50(14H, m).

Pyrolysis of 2-Adamantyl Methanesulphonate (180). -- The compound (180) (2.0 g) was sublimed slowly during 20 min at 220^o into the pyrolysis tube (530$\pm$20^o) in an atmosphere of helium at 0.05$\pm$0.03 torr. The pyrolysate, collected at -196^o, was extracted with isopentane (3 x 20 ml), which, after being filtered through a column of basic alumina (grade II, 50 g), was shown by comparison with authentic samples on g.l.c. analysis to contain (182), (183), and an unidentified hydrocarbon [M^+(g.c.m.s.) 134] in the ratio of 59.5:39.5:1. The isopentane solution was then concentrated at 50° under a vigreux column to 10 ml which was chromatographed through a column of silver nitrate-alumina (100 g). Elution of the column with isopentane (150 ml) afforded a mixture of (182) and adamantane (0.6 g) in the ratio of 99:1, m.p. 199 - 202° (sublimation), $\nu_{max.}$ 3030, 3000, 1462, 1450, 1440, and 1330 cm^{-1}, $\delta(CCl_3F)$ 1.09 - 2.61(m); elution with ether (250 ml) gave (181) (0.4 g), m.p. 181 - 184° (sublimation), $\nu_{max.}$ 3040, 1635, and 900 cm^{-1}, $\delta(CDCl_3)$ 6.18(2H, m), 2.18 - 2.82(2H, m), and 1.36 - 1.98(8H, m). Another pyrolysis at a temperature of 530±20° without a helium atmosphere while the system was kept at a pressure of 0.04±0.03 torr and upon the same work-up gave a similar yield of a mixture of (182), (181), and the unknown hydrocarbon in the ratio of 48:51:1.

Oxidation of Dehydroadamantane (182). -- (a) With Ozone. Ozonised oxygen was bubbled through a solution of (182) (1.0 g) in pyridine (2 ml) and methylene chloride (20 ml) at -30° for 10 h. The mixture, after being flushed thoroughly with dry nitrogen to remove the excess ozone, was then washed successively with 15% hydrochloric acid, saturated sodium carbonate, water, and dried. The methylene chloride was evaporated under a vigreux column at 60° and the residue was chromatographed over alumina (grade II, 100 g). Elution with pentane gave the starting material identified by g.l.c. comparison, and elution with ether-pentane (1:4) gave a complex mixture (0.22 g) which was not investigated. Further elution with the same solvent mixture yielded (183) (0.3 g), m.p. 204 - 206^{0} (sublimation), $\nu_{max.}$ 3040, 1707, 1050, 1025, 948, 890, and 870 cm^{-1}, δ 1.20 - 2.60(m), identical with an authentic sample (g.l.c. and t.l.c. comparisons).

(b) With Chromic Anhydride-Aqueous Acetic Acid. The compound (182) (0.007 g) was added to a solution (0.6 ml) of 5% chromic anhydride in acetic acid containing 3% water and 10% carbon tetrachloride at room temperature for 3 h. Water (1 ml) was added to the reaction mixture which was then extracted with ether (3 x 1 ml). The ethereal extract was washed with sodium bicarbonate, dried, and filtered. The filtrate was concentrated and found to contain (178) and (173) in the ratio of 1:1 in addition to unreacted starting material (g.l.c.)

(c) With Chromic Anhydride-Pyridine Complex. Chromic anhydride (0.15 g) was added to a solution of pyridine (0.25 ml) in methylene chloride (3.5 ml) and the mixture was stirred at room temperature for 15 min; a solution of (182) (0.013 g) in methylene chloride (0.5 ml) was then added. After stirring the mixture for 96 h, ether (2 ml) was added, and the organic solution was washed with three 5 ml portions of 5% aqueous sodium hydroxide solution, 5 ml of 5% hydrochloric acid, 5 ml of saturated aqueous sodium carbonate solution, dried, and filtered. The filtrate was concentrated and found to contain(183) and (182) in the ratio of 3:2 (by g.l.c. and t.l.c.).

Lithium-Ammonia Reduction of Dehydroadamantanone (183). --

To a stirred slurry of lithium (0.15 g) in refluxing ammonia (distilled from sodium, 150 ml) was added a solution of (183) (0.25 g) in ether (50 ml). After stirring the reaction mixture under reflux for 1 h, solid ammonium chloride (2.5 g) was added. The ammonia was evaporated and the residue was extracted with ether. Evaporation of the ethereal extract to dryness gave a solid (0.22 g) which was indicated by g. l.c. analysis (50m x 0.5mm capillary Carbowax 1540 column, oven temperature 120°) to contain (173) (4%), (179) (2%), (177) (4%), (176) (65%), and (184) (25%). Jones Reagent (1 drop) was added to a stirred solution of the mixture (0.01 g) in acetone (1 ml), which, on the usual work-up, gave a mixture containing 70% (173) (g.l.c.). The mixture was adsorbed onto alumina (activity II, 20 g) and chromatographed over alumina (200 g) using pentane and varying amounts of ether as eluents. The compound (176) (g.l.c. and t.l.c. identical with the pure compound obtained later) was eluted with 30% ether in pentane but was contaminated with (184) (same g.l.c. retention time on comparison with an authentic sample) in all the fractions collected. A mixture (1.02 g) of (184) and (176) in the ratio of 1:4 was thus obtained. Further attempts to obtain a pure sample of (176) from the mixture by preparative t.l.c. was not very successful.

Hydroboration-Oxidation of Protoadamantene (181). -- A slurry of lithium aluminium hydride (0.14 g) in ether (10 ml) was added slowly over a period of 15 min to a stirred solution of (181) (1.0 g) and redistilled boron trifluoride etherate (0.65 ml) in ether (10ml) at 0° in an atmosphere of nitrogen. The mixture was stirred at 0° for 1 h and then at room temperature for 5 h. The excess hydride was destroyed by water (2 ml) and a chromic acid solution prepared from sodium dichromate dihydrate (1.5 g), water (1 ml), and 96% sulphuric acid (5 ml) was added. After the mixture was heated under reflux for 2 h, water (10 ml) was added and the ether layer was separated. The aqueous layer was extracted twice with ether and the combined ethereal solution was dried and evaporated to give a ketone mixture (1.0 g), which was dissolved in n-pentane and filtered through a column of silica gel (100 g). Elution of the column with 3% ether in n-pentane (150 ml) gave (178) (0.06 g), m.p. 279 -281° (sublimation); further elution with 3% ether in n-pentane (250 ml) gave a mixture (0.06 g) of (178) and (173). Elution with 4% ether in n-pentane (250 ml) gave (173) (0.32 g), m.p. 222 -225° (sublimation), $\nu_{max.}$ 1723 and 1416 cm^{-1}, δ 1.12 - 2.85(m), m/e (relative intensity) 150(100, M^+), 132(10), 107(14), 93(29), and 79(99), identical with an authentic sample (t.l.c. and g.l.c. comparisons). Elution with 5% ether in n-pentane (500 ml) afforded (172) (0.5 g), m.p. 210 - 212° (sublimation).

Protoadamantan-5-endo-ol (177) from Protoadamantan-5-one (173). -- A slurry of lithium aluminium hydride (0.025 g) in ether (10 ml) was added to a stirred solution of (173) (0.1 g) in ether (10 ml). The mixture was heated under reflux for 3 h. The usual work-up gave (177) (0.085 g), m.p. 258 - 260° (sublimation), $\nu_{max.}$ 3635 and 1045 cm^{-1}, δ

4.18(1H, t, $\underline{J}$ = 7 Hz), 1.82(1H, s, exchangeable with D_2O), and 1.18 - 2.74(14H, m), m/e (relative intensity) 152(10, $\underline{M}^+$), 134(100), 119(17), 110(16), 105(21), 92(56), and 79(86).

Attempted Equilibration of Protoadamantan-5-endo-ol (177). -- Sodium (0.02 g) in small pieces was added to a solution of (177) (3 mg) in methanol (2 ml) in an ampelle. A small amount of (173) (ca. 0.1 mg) was added and the ampelle was sealed with an argon atmosphere inside, which was then kept at 70° for 325 h. The cooled content was poured into water (10 ml) which was then extracted with ether (3 x 10 ml). The ethereal extract, after being dried and concentrated, gave a mixture containing 88.5% Of the starting material (g.l.c.).

Protoadamantan-5-exo-ol (176) from Protoadamantan-5-one (173). -- To a stirred slurry of lithium (0.05 g) in refluxing ammonia (distilled from sodium, 30 ml) was added a solution of (173) (0.1 g) in ether (15 ml). After stirring the reaction mixture under reflux for 1 h, solid ammonium chloride (1 g) was added. The ammonia was evaporated and the residue was extracted with ether. Evaporation of the ethereal extract to dryness gave a solid (0.09 g) which was indicated by g.l.c. analysis (50m x 0.5mm capillary Carbowax 1540 column, oven temperature 120°) to contain (173) (3%), (177) (17%), and (176) (70%, relative retention time to protoadamantan-5-one 11.5 min). The mixture was separated by preparative t.l.c. in ethyl acetate-light petroleum (1:4). The band with R_f = 0.35 afforded

(176) (0.04 g), m.p. 204 - 207° (sublimation), $\nu_{max.}$ 3620 cm^{-1}, m/e (relative intensity) 152(43, M^+), 134(90), 119 (32), 110(49), 105(38), and 79(100) (Found: C, 79.05; H, 10.55%. $C_{10}H_{16}O$ requires C, 78.9; H, 10.6%).

Synthesis and Pyrolysis of the Esters of Adamantane-2,6-diol

Adamantane-2,6-dione (185). -- Adamantane (50 g) was added to stirred fuming sulphuric acid (20%, 400 ml) at 0° and then the temperature was maintained at 25 - 28° for 0.5 h. The mixture was poured on to crushed ice (1.2 kg) which was then extracted with methylene chloride (2 x 1 l). The aqueous layer was heated to 50° under reduced pressure to remove residual methylene chloride and sulphur dioxide and then at atmospheric pressure at 100° for 2 h. Water (2 l) was added, and after the addition of chromic anhydride (30 g) in water (100 ml), the mixture was again heated at 70° for 0.5 h. The cooled solution was extracted continuously with chloroform overnight. The extract was evaporated to dryness and the residue (40 g) was dissolved in methylene chloride (60 ml) and chromatographed over alumina (grade IV, 2 kg). Elution of the column with ether-methylene chloride (1:9) gave adamantanone (0.5 g), m.p. 254 - 256° (sublimation); further elution of the column with the same solvent mixture gave (185) (4.5 g), m.p. 312 - 314° (sublimation), $\nu_{max.}$ ($CHCl_3$) 1720, 1450, 1346, 1300, 1075, and 989 cm^{-1}, δ 2.66 (4H, m) and 2.28(8H, m), m/e (relative intensity) 164(62, M^+), 149(15), 136(14), 118(22), 109(24), 95(100), 79(81), 67(60), and 55(62).

Adamantane-2,6-diol (186). -- To a solution of (185) (4 g) in ether (500 ml), a slurry of lithium aluminium hydride (2 g) in ether (50 ml) was added. The mixture was boiled under reflux overnight. The usual work-up afforded

(186) (3.1 g), m.p. 337 - 339° (sublimation), $\nu_{max.}$ (KBr disc) 3330 (broad), 1100, 1085, 1070, 1060, 1025, 955, and 927 cm^{-1}, δ(DMSO-d_6) 4.42(2H, d), 3.58(2H, m), and 1.14 - 2.22(12H, m), m/e (relative intensity) 168(8, M^+), 150(100), 132(57), 107(57), 104(40), 91(70), 79(68), and 67(32) (Found: C, 71.4; H, 9.85%. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.6%).

2,6-Adamantyl Bistrifluoroacetate (192). -- Trifluoroacetic anhydride (7 ml) was added slowly over 5 min to (186) (0.2 g) in dry pyridine (50 ml) at 0° and the mixture was stirred at room temperature for 24 h. The usual work-up gave (192) (0.3 g), m.p. 66 - 67° (from pentane-ether at -78°), $\nu_{max.}$ (KBr disc) 1778, 1225, and 1165 cm^{-1}, δ 5.13 (2H, m) and 1.51 - 2.55(12H, m), m/e (relative intensity) 246(46), 150(5), 132(49), 117(32), 91(100), 79(42), and 69(53) (Found: C, 46.85; H, 4.1%. $C_{14}H_{14}O_4F_6$ requires C, 46.65; H, 3.9%).

2,6-Adamantyl Bismethanesulphonate (191). -- Methanesulphonylchloride (8 ml) was added to a solution of (186) (0.8 g) in dry pyridine (50 ml) at 0° and the mixture was stirred at room temperature for 72 h. The usual work-up gave (191) (1.0 g), m.p. 203 - 204° (from methanol), $\nu_{max.}$ (KBr disc) 3025, 2940, 2870, 1360, 1168, 975, 950, 915, 862, 844, 824, and 755 cm^{-1}, δ(pyridine-d_5) 4.91(2H, m), 3.24 (6H, s), and 1.24 - 2.28(12H, m), m/e (relative intensity) 228(15), 132(58), 117(18), 104(16), 91(100), and 79(42) (Found: C, 44.6; H, 6.2%. $C_{12}H_{20}O_6S_2$ requires C, 44.45; H, 6.2%).

Pyrolysis of 2,6-Adamantyl Bismethanesulphonate (191). -- The compound (191) (0.2 g) was sublimed slowly during 20 min at 220° into the pyrolysis tube (530±20°) at 0.02±0.03 torr. The pyrolysate, collected at -196°, was extracted with isopentane (3 x 5 ml), which, after being filtered through a column of basic alumina (grade II, 1 g), was shown by g.l.c. analysis (2m x 1/8 in 1% ApL, 80°) to contain *ca*. 95% of one compound. Purification by preparative g.l.c. (14ft x 1/4in 20% ApL, 180°) gave an olefin (0.01 g), δ 5.81 (Found: M^+ 132.0942. $C_{10}H_{12}$ requires M^+ 132.0939). Another similar pyrolysis gave a mixture (*ca*. 30% yield) of adamantane and the same olefin in the ratio of 6:1.

Pyrolysis of 2,6-Adamantyl Bistrifluoroacetate (192). -- The compound (192) was pyrolysed under similar conditions as (191) and upon the same work-up gave a very complex mixture of hydrocarbons (g.l.c.) in *ca*. 10% yield.

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