

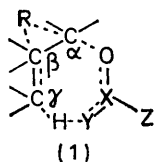
1,3-Elimination with Rearrangement during Ester Pyrolysis. A Simple Route to Protoadamantene and 2,4-Didehydroadamantane †

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Pyrolysis of 2-adamantyl methane- or toluene-*p*-sulphonate (16) affords a mixture (2:3) of protoadamantene (17) and 2,4-didehydroadamantane (18) in 95% yield. Hydroboration of (17) gives a mixture of 4- [(20), (21)] and 5-[(24), (25)] protoadamantanols. Epoxidation of protoadamantene gives a mixture (6:1) of the *exo*- (26) and *endo*- (27), epoxides the former rearranging spontaneously to 2a,4a-dihydroxyadamantane (28). Protoadamantan-5-one (23) with lithium aluminium hydride gives a 95:5 *endo*:*exo* alcohol mixture, but lithium-ammonia gives 70:23 *exo*:*endo* alcohols.

THE pyrolytic 1,2-elimination of carboxylic esters, xanthates, and *N*-oxides to furnish alkenes is a time-honoured procedure of wide synthetic utility.¹ It is experimentally simple and clean and often gives rise to single products which do not rearrange under the conditions which generate them. The list of synthetically useful alcohol derivatives has recently been extended.²⁻⁴

In a much less familiar mode of ester pyrolysis, olefin formation is accompanied by skeletal rearrangement. The process under discussion can be pictured as proceeding *via* a seven-membered transition state [as (1)], 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. As will be seen in the sequel, 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.

Intervention in such circumstances of a seven-membered cyclic transition state was first invoked by Bunton⁵ to account for the formation of optically pure camphene (3) as the major product from the pyrolysis of isobornyl methyl xanthate (2, arrows). Interestingly in this case the elimination-rearrangement process competes successfully with the apparently favourable *cis*-1,2-elimination, the camphene:bornylene ratio being 3:2. The formation of tricyclene (5) from

bornyl methyl xanthate (4, arrows), observed in the same study,⁵ exemplifies a cognate process. Several previously observed examples of both reactions are recorded in the older literature.⁶⁻⁸

More recently Kwart and Hoster have explicitly implicated⁹ a seven-membered transition state to account for the preferential formation of the unconjugated isomer $CH_2=CMe\cdot CH_2Ph$, during the pyrolysis of 2-methyl-2-phenylpropyl acetate. The timely appearance of this work led us¹⁰ to attempt and to effect a pyrolytic rearrangement of the atisane to the 7,20-secoaconane skeleton.

Several further instances of the two processes first identified by Bunton are to be found in the recent literature. They include the celebrated and initially misleading pyrolytic rearrangement¹¹ of patchouli acetate to α - and γ -patchoulenes (6, arrows); the rearrangement¹² of *trans*-1-hydroxy-2-acetoxycyclohexanes to alkyl cyclopentyl ketones [(7) \rightarrow (8)] and the conversion^{13,14} of 2-acetoxycycloalkanones into norcycloalkenes (loss of CO from an intermediate cyclopropanone) [*e.g.* (9) \rightarrow (10) \rightarrow (11)¹³].

In a formal sense the mechanisms of the three modes of ester pyrolysis are closely related: (i) 1,2-elimination (12) is, of course, an example of the retro-ene reaction;¹⁵ (ii) 1,3-elimination with formation of a three-membered ring (13) may be regarded as a 'homo' retro-ene reaction; and (iii) 1,3-elimination with rearrangement (14) is an extension of (ii).

The few examples which at present constitute the group of pyrolytic 1,3-elimination with rearrangement appear to have in common a steric situation as indicated in (15); the C-O and C-H bonds that cleave are coplanar while the C-C bond which migrates from the intermediate carbon atom is anti-periplanar to both.

It occurred to us that if this geometry is optimal for the

† Preliminary communication, J. Boyd and K. H. Overton, *Chem. Comm.*, 1971, 211.

¹ C. H. De Puy and W. King, *Chem. Rev.*, 1960, **60**, 431.

² D. B. Denney, C. J. Rossi, and J. J. Vill, *J. Amer. Chem. Soc.*, 1961, **83**, 3336.

³ M. S. Newman and F. W. Hetzel, *J. Org. Chem.*, 1969, **34**, 3604.

⁴ L. C. Roach and W. H. Daly, *Chem. Comm.*, 1970, 606.

⁵ C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Nature*, 1961, **190**, 715.

⁶ W. Qvist, *Annalen*, 1918, **417**, 278.

⁷ G. Komppa and R. H. Roschier, *Annalen*, 1922, **429**, 175.

⁸ G. Komppa and G. A. Nyman, *Annalen*, 1938, **585**, 252.

⁹ H. Kwart and D. P. Hoster, *Chem. Comm.*, 1967, 1156.

¹⁰ J. P. Johnston and K. H. Overton, *Chem. Comm.*, 1969, 329; *J.C.S. Perkin I*, 1972, 1490.

¹¹ G. Buchi, R. E. Erickson, and N. Wakabayashi, *J. Amer. Chem. Soc.*, 1961, **83**, 927; M. Dobler, J. D. Dunitz, B. Gubler, H. P. Weber, G. Buchi, and J. Padilla O, *Proc. Chem. Soc.*, 1963, 383.

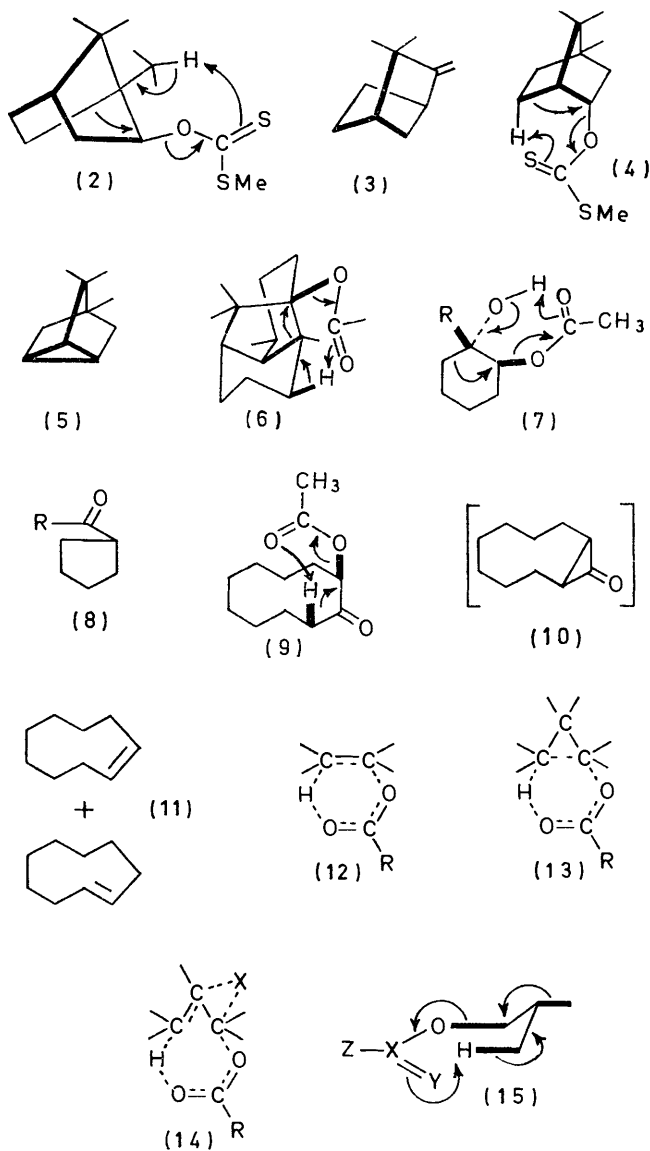
¹² J. C. Leffingwell and R. E. Shackleford, *Tetrahedron Letters*, 1970, 2003.

¹³ R. G. Carlsen and J. H. Bateman, *J. Org. Chem.*, 1967, **32**, 1608.

¹⁴ T. A. Spencer, A. L. Hall, and C. F. von Reyn, *J. Org. Chem.*, 1968, **33**, 3369 and references therein.

¹⁵ H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 556.

rearrangement, then the rigid framework of adamantane should provide an ideal test case and, in particular,



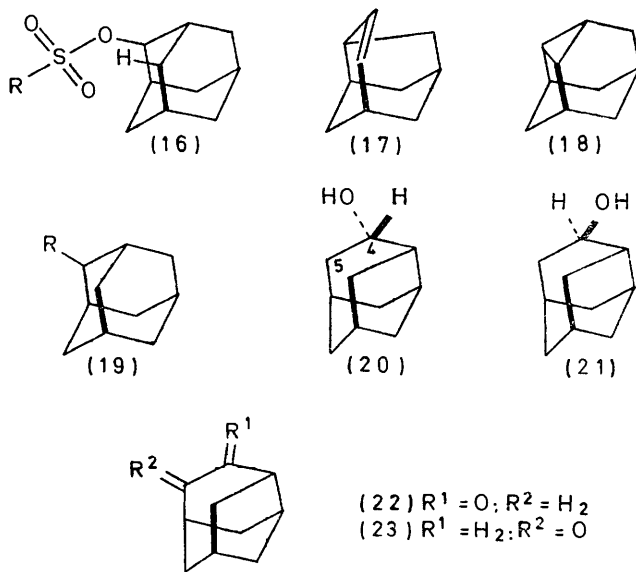
esters [*e.g.* (16)] of adamantane-2-ol should readily and smoothly rearrange to protoadamantene (tricyclo-[4,3,1,0^{3,8}]dec-4-ene) (17).¹⁶⁻¹⁸ At the same time, γ -hydrogen abstraction without rearrangement should as readily lead to 2,4-didehydroadamantane (18).¹⁹ Such a one-step synthesis of (17) and (18), whose potential for synthetic and mechanistic exploration interested us, would represent a distinct advance on syntheses for these substances recorded in the literature.

Our previous experience with this reaction¹⁰ persuaded us to concentrate on vapour phase rather than condensed phase pyrolysis. The apparatus, described in the

Experimental section consisted of a horizontal, electrically heated (460–560°), silica tube packed with glass wool. The substance to be pyrolysed was introduced into the furnace either as a dispersion in an inert solvent (10–100 mg) (method A), or by sublimation (100 mg–5 g) (method B) and the products were collected partly on the cold walls of the pyrolysis tube emerging from the furnace and partly in the cold trap placed in series with it. A forward flow of helium or nitrogen (0.05–0.5 mmHg) was maintained throughout the experiment.

Pyrolysis of 2-adamantyl acetate (19; R = OAc) (0.5 mmHg; 380, 500, and 560°) afforded recovered starting material in >90% yield. 2-Adamantyl xanthate (19; R = O-CS-SMe), m.p. 108–109.5° (0.5 mmHg; 550°), gave recovered xanthate (50%), the thiocarbonate (19; R = S-CO-SMe) (45%) [ν_{\max} 1649 and 870 cm⁻¹ (thiocarbonate²⁰)], protoadamantene (2%), didehydroadamantane (2%), and adamantane (1%).

However, 2-adamantyl toluene-*p*-sulphonate (16; R = *p*-C₆H₄Me) and 2-adamantyl methanesulphonate (16; R = Me), m.p. 67–68°, led to the desired products under the appropriate conditions. In small-scale experiments (10–100 mg), using the injection technique, the tosylate afforded (0.5 mmHg; 550°) >90% yield of C₁₀ hydrocarbons, consisting (>95%) of protoadamantene and didehydroadamantane in varying proportions (2 : 3 to 3 : 1), adamantane (<5%) and an unidentified hydrocarbon (M^+ , 314) (*ca.* 1%). At 760 mmHg and 550°, the



amount of adamantane formed rose dramatically to 80% of the hydrocarbon fraction (*ca.* 50% theoretical yield).

On a larger scale (250 mg–2 g) the sample was introduced by sublimation, and under these conditions at

¹⁶ R. M. Black and G. B. Gill, *Chem. Comm.*, 1970, 972.

¹⁷ M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Comm.*, 1969, 1000.

¹⁸ B. D. Cuddy, D. Grant, and M. A. McKerver, *J. Chem. Soc. (C)*, 1971, 3173.

¹⁹ H. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatman, *Chem. Comm.*, 1966, 657.

²⁰ R. A. Nyquist and W. J. Potts, *Spectrochim. Acta*, 1961, 17, 679.

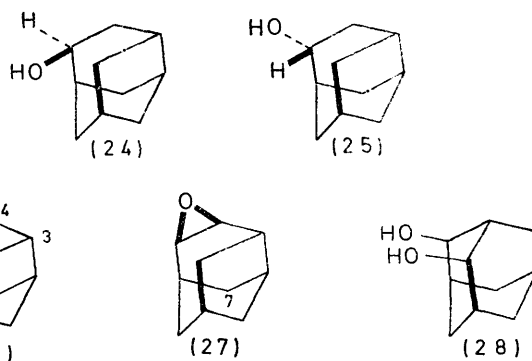
0.3–0.5 mmHg and 520–550° the recovery of monomeric hydrocarbon fell to *ca.* 50% while the ratio of protoadamantene : didehydroadamantane rose to 4 : 1. On the assumption that the didehydroadamantane formed was partially being destroyed by the toluene-*p*-sulphonic acid also formed during the pyrolysis, the inside of the pyrolysis tube and glass wool at the exit end of the furnace were coated with solid sodium carbonate. This resulted, on a 1–2 g scale, in reproducible yields >95% of hydrocarbon consisting of protoadamantene : didehydroadamantane 2 : 3, with <2% adamantane.

The pyrolysate, recovered with isopentane, was filtered through alumina to free it from sulphur compounds and then chromatographed over AgNO₃ (15%)–Al₂O₃. Isopentane eluted didehydroadamantane (57%), m.p. (before recrystallisation) 196–199° (lit.¹⁹ 202.5–203.5°), and ether eluted protoadamantene (37%), m.p. (before recrystallisation) 179–182° (lit.¹⁶ 183–185°).

An attempt was made to detect the incidence of an abnormal Cope elimination, analogous to the sulphate ester elimination–rearrangement, but proceeding through a six- rather than a seven-membered transition state. A relevant precedent exists in the pyrolysis²¹ of isoamylamine *N*-oxide to give appreciable amounts of 2-methylbut-2-ene apparently by γ -hydrogen abstraction and $\beta \rightarrow \alpha$ hydride shift. However, pyrolysis of 2-dimethylaminoadamantane *N*-oxide did not produce detectable quantities of protoadamantene or didehydroadamantane. Instead, a set of Meisenheimer rearrangement²² products were formed²³ and these will be reported separately.

Hydroboration of protoadamantene under standard conditions (diborane in THF at 0°) gave a mixture of the four protoadamantan-4- and 5-ols. The g.l.c. behaviour of this mixture was misleading since on eight different columns only peaks corresponding to the known 4-*exo*- (20) (*ca.* 60%) and 4-*endo*- (21) (*ca.* 40%) protoadamantanols could be detected, apart from minor amounts of 2-adamantanol (*ca.* 3%). However, oxidation of the mixture (RuO₂–NaIO₄–CCl₄) afforded two major ketones, separable by preparative t.l.c. (continuous development), protoadamantan-4-one (22),^{16,24–26} m.p. 212–214° (56.5% by g.l.c.), and protoadamantan-5-one (23),²⁷ m.p. 222–225° (40.5% by g.l.c.), and a minor amount (*ca.* 3%) of adamantan-2-one. Protoadamantan-5-one was reduced by the Caglioti method to a mixture of protoadamantene and protoadamantane (2 : 1), which supported its skeletal integrity. Preparative t.l.c. of the alcohol mixture from hydroboration afforded (i) 5-*endo*-protoadamantanol (24), m.p. 258–260°, identical with

the major product (95%) of lithium aluminium hydride reduction of both protoadamantan-5-one and protoadamantene *endo*-epoxide (see below); (ii) 4-*exo*-protoadamantanol (20); and (iii) a mixture of protoadamantan-4-*endo*- (21) and 5-*exo*- (25) ols. The approximate proportions of the four alcohols from hydroboration



were estimated from g.l.c. of the alcohols and the derived ketones (see Experimental section) to be 4-*endo* : 4-*exo* : 5-*endo* : 5-*exo* = 1 : 2.5 : 1 : 1.5. The 5-*exo*-alcohol could not be obtained pure from the hydroboration mixture, since it was inseparable both by t.l.c. and g.l.c. from the 4-*endo*-alcohol. Attempts to obtain it by equilibration of the 5-*endo*-alcohol failed under a variety of conditions.^{28–30} This signal failure to obtain by equilibration what is surely the thermodynamically more stable alcohol must reflect the difficulty of transferring hydride ion to the more encumbered (*endo*) side of C-5. The 5-*exo*-alcohol (25) was finally obtained in 70% yield by reduction with lithium in ammonia of the 5-ketone; the 5-*endo*-alcohol and unchanged 5-ketone were readily removed from the product by preparative t.l.c.

Oxymercuration of protoadamantene gave results similar to those obtained by McKervey³¹ and Schleyer.³²

The configurations assigned on a chemical basis by us and others to the protoadamantan-4-^{25,26} and -5-ols were well supported by (i) their Eu(dpm)₃-shifted n.m.r. spectra; in each case the resonances of at least eight of the sixteen protons could be identified individually with the aid of double resonance,³³ and (ii) application of the Karplus equation to the 5-proton system at C-3, C-4, C-5, and C-6 in the Eu(dpm)₃-shifted spectra (see Table 1). The latter results are in good agreement with a similar analysis³² of the 4-*endo*- and -*exo*-alcohols by Schleyer and his colleagues.

Epoxidation of protoadamantene (17) (*m*-chloroperbenzoic acid–Na₂CO₃–CH₂Cl₂; 20°) afforded the *exo*- and *endo*-epoxides [(26) and (27)] (6 : 1), of which only

¹⁹ E. L. Eliel and M. N. Rerick, *J. Amer. Chem. Soc.*, 1960, **82**, 1367.

²⁰ A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Turnbull, *J. Amer. Chem. Soc.*, 1952, **74**, 4867.

²¹ B. D. Cuddy, D. Grant, and M. A. McKervey, *Chem. Comm.*, 1971, 27.

²² D. Lenoir, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, in the press. We are grateful to Professor Schleyer, for showing us the manuscript of this paper before publication.

²³ C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; J. K. M. Sanders and D. H. Williams, *ibid.*, 1971, **93**, 641. A detailed account of this work will appear elsewhere.

²⁴ A. C. Cope, N. A. LeBel, H. H. Lee, and W. R. Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 4720.

²⁵ R. A. W. Johnstone in 'Mechanism of Molecular Migration,' vol. 2, Interscience, New York, 1969, p. 249.

²⁶ E. S. Lopez and K. H. Overton, unpublished results.

²⁷ W. H. W. Lunn, *J. Chem. Soc. (C)*, 1970, 2124.

²⁸ D. Lenoir and P. von R. Schleyer, *Chem. Comm.*, 1970, 941.

²⁹ J. R. Alford and M. A. McKervey, *Chem. Comm.*, 1970, 615.

³⁰ H. W. Whitlock and M. W. Siefken, *J. Amer. Chem. Soc.*, 1968, **90**, 4929.

³¹ E. L. Eliel and R. S. Rao, *J. Amer. Chem. Soc.*, 1957, **79**, 5992.

the minor *endo*-epoxide (27), m.p. 212–214°, could be isolated. The major *exo*-epoxide (26) decomposed either on attempted preparative t.l.c. or on fractional crystallisation, to furnish a more polar substance, which could be conveniently obtained by chromatographing the epoxide mixture over Grade II acid alumina.

The adamantane-2a,4a-diol (28),³⁴ m.p. 341–344°, thus generated by concerted epoxide opening and skeletal rearrangement for which the *exo*-epoxide is ideally constituted, was similarly obtained^{35,36} by Schleyer and his

the major *exo*-epoxide affords 4-*exo*-alcohol (80%) and 5-*exo*-alcohol (20%).

EXPERIMENTAL

The following instruments were used: i.r., Perkin-Elmer 225 and 257; n.m.r., Varian T60 and HA 100; mass spectrometry, A.E.I. MS9; g.l.c., Perkin-Elmer F11; g.l.c.-m.s., LKB 9000A. Solvents for spectroscopy: i.r., CCl₄; n.m.r., CDCl₃ with internal tetramethylsilane.

Merck Kieselgel G was used for analytical and preparative

TABLE I
Configurational assignment of the protoadamantan-4- and -5-ols from vicinal coupling constants

	θ_{obs} (°)	Compound				θ_{calc} (°)
		(20)	(21)	(24)	(25)	
		J_{obs} (Hz)				
3,4- <i>endo</i>	55 ^a	3.5 ^b		3	<i>c</i>	55–60
3,4- <i>exo</i>	70		3.5 ^b	<i>c</i>	<i>c</i>	53–56
4- <i>endo</i> , 5- <i>endo</i>	40	6.5, 6.5 ^b			6, 6.5 ^b	30–42
4- <i>endo</i> , 5- <i>exo</i>	85–90	<2, <1 ^b		<1		90
4- <i>exo</i> , 5- <i>endo</i>	145		8.5, 8		6.5, 6.5 ^b	150–160
4- <i>exo</i> , 5- <i>exo</i>	25		8, 8 ^b	8.5, 8 ^b		20–30
5- <i>endo</i> , 6	85	<2	<2		<2	90
5- <i>exo</i> , 6	35	8	9	8 ^b		20–35

^a Measured on Prentice-Hall models. ^b From carbinol proton of unshifted spectrum. ^c Not observable. ^d Calculated from J_{obs} by the Karplus equation.

colleagues shortly after we had isolated it in our laboratory.

In the major epoxide (26) (n.m.r. spectrum of unseparated mixture), the epoxide protons appear as triplets ($J_{4,5} = J_{3,4} = J_{5,6} = 4$ Hz) centred at δ 3.06 and 2.82. A clean 1H quartet centred at δ 1.22 ($J_{7,7}$ 12, $J_{7,6}$ 5, $J_{7,8} < 1$ Hz) is assigned to the 7-H *anti* to the epoxide ring, since in this case the vicinal coupling with 8-H ($\theta \cong 90^\circ$) should disappear, as is observed. This is in agreement with the anisotropic long-range shielding effect of epoxides previously observed.³⁷ In the n.m.r. spectrum of the minor epoxide (27) the epoxide hydrogens centred at δ 3.34 and 3.12 appear as quartets ($J_{4,5}$ 4, $J_{3,4}$ 7, $J_{5,6}$ 6 Hz).

The observed coupling constants of the oxiran protons in the two epoxides, when referred to Prentice-Hall models, clearly support the configurations assigned to the epoxides as above. These, in turn, provide independent support for the configurations of the four protoadamantan-4- and -5-ols when taken together with the following results of lithium aluminium hydride reduction. Reduction of the minor *endo*-epoxide afforded the 5-*endo*-alcohol (95%), 4-*endo*-alcohol (3%) and adamantan-2-ol (2%). Reduction of the epoxide mixture showed that

t.l.c. and Woelm alumina, deactivated to the appropriate Brockmann grade, for column chromatography. Horizontal preparative t.l.c. was done in a Desaga (Heidelberg) continuous development apparatus (No. 63621).

Microanalyses were by Mr. J. M. L. Cameron and his staff.

2-Adamantyl Acetate (19; R = OAc).—This was prepared from 2-adamantanol (207 mg) with sodium acetate (300 mg) and acetic anhydride (10 ml) (12 h; reflux) and isolation by preparative t.l.c. in 75% yield (homogeneous by t.l.c. and g.l.c. on 1% AP-L and 5% QF1), ν_{max} (film) 1730 cm⁻¹; δ 4.92 (1H, m), 2.2–1.4 (17H, m, including 3H at 2.08). Lithium aluminium hydride reduction (ether; 4 h; reflux) gave quantitative recovery of 2-adamantanol, m.p. 295–297° (lit.,³⁸ 296.2–297.7°).

2-Adamantyl Xanthate (19; R = O-CS-SMe).—2-Adamantanol (0.61 g, 4.02 mmol) in hot dry benzene (10 ml) was added to a suspension of sodium hydride (0.12 g, 5.0 mmol) in dry benzene (2 ml) and the suspension was stirred at reflux under N₂ for 6 h. On cooling this formed a thick gelatinous paste which turned bright red on dilution with CS₂ (5 ml) and this was stirred for 4 h at 50°. Addition of methyl iodide (6 ml) caused almost immediate discharge of the red colour, but stirring with reflux was continued for 14 h more. The mixture, diluted with benzene, was filtered through Celite and solvent removal afforded 2-adamantyl xanthate (0.885 g, 91%), m.p. 104–108°. Recrystallised from ether-methanol (1:2) it had m.p. 108–109.5°, ν_{max} 1222, 1212s, 1053s, 959, and 918m cm⁻¹, δ 5.7 (1H, m), 2.6 (3H, s), and 2.4–1.6 (14H, m) (Found: C, 59.35; H, 7.3. C₁₂H₁₈OS₂ requires C, 59.5; H, 7.5%).

³⁷ K. Tori, K. Kitahonaki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 1964, 559, 1965, 896.

³⁸ P. von Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, 83, 182.

³⁴ D. Faulkner and M. A. McKervey, *J. Chem. Soc. (C)*, 1971, 3906.

³⁵ D. Lenoir, P. von R. Schleyer, C. A. Cupas, and W. E. Heyd, *Chem. Comm.*, 1971, 26.

³⁶ D. Lenoir, R. Glaser, P. Mison, and P. von R. Schleyer, *J. Org. Chem.*, 1971, 36, 1821. We are grateful to Professor Schleyer for showing us the manuscript of this paper before publication.

2-Adamantyl Toluene-*p*-sulphonate (16; R = *p*-C₆H₄Me).³⁸—Prepared from 2-adamantanol by the usual method in 88% yield this had m.p. 79–82° and after one crystallisation from methanol, 82–83° (lit.,³⁸ m.p. 82.7–83.7°).

2-Adamantyl Methanesulphonate (16; R = Me).—Prepared from 2-adamantanol (2.03 g, 13.4 mmol) by the usual method in 90% yield this had m.p. 67–68° (from methanol), δ 4.76 (1H, m), 2.92 (3H, s), and 2.3–1.3 (14H, m) (Found: C, 57.3; H, 7.65. C₁₁H₁₈O₃S requires C, 57.4; H, 7.9%).

Pyrolysis Experiments

General Method.—The apparatus consisted of an electrically heated silica tube (70 × 2.5 cm) with provision for sample introduction by either injection (method A) or sublimation (method B). The heated part of the silica tube was lightly packed with glass wool. Injection was from a glass syringe through a 6 in hypodermic needle direct into the glass wool at the furnace entrance. Pyrolyses were carried out in a slow stream of He gas at 0.5–0.05 mmHg and at temperatures ranging from 460–560°. At the end of the pyrolysis, the part of the product condensed at the cold exit end of the pyrolysis tube was driven over into the U-tube trap with warm air from a hair dryer. The contents of the U-tube, recovered with isopentane (10

such that a maximum temperature of 150° was reached over 15 min. Heating was continued for 15 min more and then the product was recovered and analysed as before. See Table 2, entries 6 and 7.

Pyrolysis of 2-Adamantyl Methanesulphonate.—(a) The methanesulphonate (150 mg) was pyrolysed by method B as for the toluene-*p*-sulphonate above. See Table 2, entry 8.

(b) **Preparative pyrolysis.** See Table 2, entries 9 and 10. Method B was used, but the inside of the pyrolysis tube and the glass wool packing were coated at the exit end of the furnace (10 cm) with sodium carbonate. This was applied as a slurry, excess of water being removed by rotation in a Bunsen flame. The coated tube and packing were kept at 520° for at least 4 h before use.

The methanesulphonate (2.20 g) was sublimed (inlet temperature 220° reached over 15 min) into the pyrolysis tube as above maintained at 550° and 0.05 mmHg and heating continued for 20 min more. The product, recovered from the U-tube with isopentane (50 ml) was filtered through grade III alumina (10 g). Removal of solvent through a Vigreux column left a colourless crystalline hydrocarbon mixture (1.22 g 95%). This was chromatographed over silver nitrate-alumina (50 g). Isopentane (100 ml) eluted (solvent removal at 50° and 760 mmHg through a Vigreux

TABLE 2
Pyrolysis of 2-adamantyl sulphonates

Run	Ester	Method	Scale (mg)	Temp. (°C)	He pressure (mmHg)	Appr. conversion (%) ^b	Yield		
							(17)	(18)	Adamantane
1	Tosyl	A	20	450	0.5	80	60	37	3
2	Tosyl	A	20	550	0.5	90	50	50	2
3	Tosyl	A	20	550	0.5	90	40	60	2
4	Tosyl	A	20	450	760	50	35	20	50
5	Tosyl	A	20	550	760	50	10	5	80
6	Tosyl	B	100	550	0.5	50	80	13	5
7	Tosyl	B	250	520	0.3	50	70	28	2
8	Mesyl	B	150	520	0.3	40	80	16	2
9	Mesyl	B ^a	1040	520	0.5	90	40	60	1
10	Mesyl	B ^b	2200	550	0.05	95	40	60	1

^a Na₂CO₃, coated packing and tube. ^b Runs 1–5 from t.l.c.; 6–10 from weight of crude hydrocarbon fraction.

ml) and ether (10 ml) were filtered through grade I basic alumina (5 g) and analysed by t.l.c. and g.l.c.

Pyrolysis of 2-Adamantyl Toluene-*p*-sulphonate.—Method A. Portions of the sulphonate (20 mg) in ether (0.2 ml) were injected at a variety of temperatures and pressures. The extent of sulphonate conversion was judged by t.l.c. and the composition of the hydrocarbon fraction analysed by g.l.c. on a 2 m 1% AP-L column at 80°. Relative retention indices and molecular ions (*M*⁺ by g.l.c.–m.s.) of authentic hydrocarbon samples* under these conditions were: protoadamantene (1100; *M*⁺ 134), adamantane (1108; *M*⁺ 136), 2,4-didehydroadamantane (1126; *M*⁺ 134), and these were detected in the pyrolysis product in varying proportions. A fourth minor peak, r.r.i. 1085, *M*⁺ 134, was unidentified. The mass spectra of hydrocarbons having *M*⁺ 134 were indistinguishable.

Reaction conditions and product compositions are listed in Table 2, entries 1–5.

Method B. The sulphonate (100 mg) was placed in the boat and the furnace temperature and pressure were stabilised at 550° and 0.5 mmHg. The portion of the silica tube containing the boat was then heated by heating tape,

column) 2,4-didehydroadamantane containing a small amount of adamantane (730 mg, 57%), m.p. 196–199°, rising on sublimation to 198–202° (lit.,¹⁹ 202.5–203.5°). G.l.c.–m.s. showed this consisted of adamantane (1.5%) and 2,4-didehydroadamantane (98.5%).

Ether (100 ml) eluted substantially protoadamantene (475 mg, 37%), m.p. 179–180°, rising on sublimation to 180–182° (lit.,¹⁶ 183–185°). G.l.c.–m.s. showed this consisted of protoadamantene (99.5%) and the hydrocarbon *M*⁺ 134, r.r.i. 1085 (0.5%).

Pyrolysis of 2-Adamantyl Acetate (19; R = OAc).—Pyrolysis of the acetate (100 mg) by Method A at 380, 500, and 560° and 0.5 mmHg gave only unchanged starting material (t.l.c., g.l.c., >90% recovery).

Pyrolysis of 2-Adamantyl Xanthate (19; R = O-CS-SMe).—Pyrolysis of the xanthate (150 mg) by Method A at 500° and 0.5 mmHg afforded by g.l.c. (1% AP-L programmed

* 2,4-Didehydroadamantane was kindly furnished by Professor H. Wynberg, Groningen. Protoadamantene was prepared by Chugaev pyrolysis of the xanthates of protoadamantan-4-*exo*- and -4-*endo*-ols according to Black and Gill.¹⁶

³⁹ G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, **13**, 1.

80°/10 min; 80—180° at 8°/min) protoadamantene (2%; r.t. 5.8 min), adamantane (5%; 6.4 min), 2,4-didehydroadamantane (2%; 7.2 min), 2-adamantyl xanthate (48%; 23.6 min), and a fifth product (43%; 27.4 min). The last component was separated by preparative t.l.c. [ethyl acetate–light petroleum (1 : 3)] as a colourless oil. This had M^+ 242, ν_{\max} 1649 and 870 cm^{-1} , typical of dithiocarbonates.²⁰

Hydroboration³⁹ of Protoadamantene (14).—Into protoadamantene (265 mg) dissolved in tetrahydrofuran (5 ml) stirred magnetically under nitrogen in a two-neck flask equipped with reflux condenser and rubber septum, was injected an excess of diborane in THF (2 ml of 1M solution; Alpha Inorganics) at 0°. The mixture was stirred at 0° for 1 h and at 23° for 5 h. An alkaline solution of hydrogen peroxide (1 ml 30% H_2O_2 + 1 ml 10% NaOH) was added dropwise, followed by stirring at 30—40° for 15 min and 20—23° for 1 h. Potassium carbonate (1 g) was added, the suspension stirred for 5 min, and the aqueous layer was separated from THF and extracted with ether. Removal of solvent from the dried ether–THF solution gave an oil (400 mg) which on preparative t.l.c. [ethyl acetate–light petroleum (1 : 3)] afforded a crystalline mixture (250 mg, 82% calculated as protoadamantanols). G.l.c. analysis (50 m \times 0.5 mm; Carbowax 1540; 135°) showed three peaks corresponding to adamantan-2-ol (3%), protoadamantan-4-*exo*-ol (58%) and protoadamantan-4-*endo*-ol (39%). Analysis on the following g.l.c. columns failed to reveal additional peaks: QF 1, SE 30, AP-L, butanediol succinate, dinonyl phthalate, bis-(2-ethylhexyl) sebacate–sebacic acid, polyethylene glycol adipate, and Bentone 34. On keeping in air the samples developed additional peaks, later shown to correspond to protoadamantan-4- and -5-ones. Preparative t.l.c. of the mixture [ethyl acetate–light petroleum (1 : 4)] furnished three bands of R_F 0.35, 0.43, and 0.48. Each band was separately oxidised with Jones reagent. T.l.c. and g.l.c. comparison with authentic specimens of each band before and after oxidation, showed that the three fractions obtained by preparative t.l.c. of the hydroboration product consisted of (i) R_F 0.48: protoadamantan-5-*endo*-ol (oxidised to protoadamantan-5-one); (ii) R_F 0.43: protoadamantan-4-*exo*-ol (oxidised to protoadamantan-4-one); (iii) R_F 0.35: mixture of protoadamantan-4-*endo*- and -5-*exo*-ol [oxidised to protoadamantan-4- and -5-ones (7 : 10)]. Authentic samples of protoadamantan-4-*exo*- and -*endo*-ol for comparison were obtained from protoadamantan-4-one (prepared by the published methods^{16,24}) by lithium aluminium hydride reduction.^{16,25} (We are grateful to Dr. G. B. Gill, Nottingham, for sending us a mixture of the two alcohols used in early comparisons.) Protoadamantan-5-*endo*-ol was obtained by lithium aluminium hydride reduction of either protoadamantan-5-one or the 4,5-*endo*-epoxide (see below).

The proportions of protoadamantanols formed in the hydroboration were computed as follows. Let A = 4-*endo* (21), B = 4-*exo* (20), C = 5-*endo* (24), and D = 5-*exo* (25). Then (i) $(A + B)/(C + D) = 1.4$ (ratio by g.l.c. of 4- and 5-ones obtained from oxidation of hydroboration product), (ii) $(A + D)/(B + C) = 0.67$ (from g.l.c. of hydroboration product), and (iii) $A/D = 0.71$ [from g.l.c. of oxidation product obtained from band (iii) R_F 0.35 of hydrobor-

ation product]. These ratios lead to A : B : C : D = 1 : 2.5 : 1.1 : 1.4.

Oxidation^{40,41} of the Hydroboration Product.—The mixed alcohols (200 mg) were dissolved in CCl_4 (10 ml) and ruthenium dioxide (20 mg; Johnson-Matthey) added. Aqueous sodium periodate (10%) was run in dropwise with stirring until a permanent yellow colour persisted. On adding MeOH (0.5 ml) after 15 min, the clear mixture immediately became black. The product, obtained by solvent extraction as usual, consisted of a crystalline mixture (200 mg, 92%) of adamantan-2-one (3%; r.r.i. 1325), protoadamantan-5-one (23) (40.5%; 1338) and protoadamantan-4-one (22) (56.5%; 1364) (g.l.c., 4 m capillary; 2% SE30; 150°).

The major ketones were separated by preparative t.l.c. [ethyl acetate–light petroleum (1 : 9)] using horizontal elution with continuous development, Sudan Yellow serving as a tracking dye]. Protoadamantan-5-one (23) (80 mg) thus obtained had after sublimation (110°; 14 mmHg), m.p. 222—225° (lit.,²⁷ 226—227°); ν_{\max} 1727 cm^{-1} (Found: C, 79.85; H, 9.4. Calc. for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.95; H, 9.4%). Protoadamantan-4-one (100 mg), m.p. 210—212° (lit.,¹⁸ 212—214°) was identical (n.m.r. and i.r.) with authentic material.

Caglioti Reduction^{42,43} of Protoadamantan-5-one.—The ketone (12 mg, 0.08 mmol) and toluene-*p*-sulphonyl hydrazine (17 mg, 0.091 mmol) were refluxed for 12 h in methanol (5 ml) containing hydrochloric acid (1 drop; conc.). The product obtained from a dried ether solution, was reduced with excess (6 mg) of lithium aluminium hydride in refluxing dry dioxan for 3 h, according to Djerassi.⁴³ The hydrocarbon product (20%) was separated by filtration through Grade II neutral alumina (2 g) in light petroleum. G.l.c. analysis (2 m 1% AP-L; 80° and 50 m Carbowax 1540; 65°) showed that this consisted of protoadamantene (32%) and protoadamantane (68% compared with an authentic sample prepared from protoadamantene).

Lithium Aluminium Hydride Reduction of Protoadamantan-5-one.—The ketone (50 mg) was reduced with an excess of lithium aluminium hydride in refluxing ether for 3 h. The product (48 mg) afforded on preparative t.l.c. and sublimation, protoadamantan-5-*endo*-ol (24) (35 mg), needles, m.p. 258—260°, ν_{\max} 3600 cm^{-1} (Found: C, 78.85; H, 10.55. $\text{C}_{10}\text{H}_{16}\text{O}$ requires C, 78.9; H, 10.6%).

G.l.c. (50 m Carbowax 1540; 135°) of the crude reduction product showed a major peak (95%) of protoadamantan-5-*endo*-ol, inseparable from protoadamantan-4-*exo*-ol and a minor peak (5%) of protoadamantan-5-*exo*-ol, inseparable from protoadamantan-4-*endo*-ol.

Lithium-Ammonia Reduction of Protoadamantan-5-one (with MR. KONG LUK).—Protoadamantan-5-one (0.10 g) in ether (15 ml) was added to a stirred slurry of lithium (0.05 g) in refluxing ammonia (30 ml; redistilled from sodium). Stirring was continued for 1 h more under reflux and then ammonium chloride (1.0 g) was added. Evaporation of ammonia gave an ether-soluble crystalline residue (0.09 g) which was analysed by g.l.c. (50 m Carbowax 1540; 120°). It consisted of protoadamantan-5-one (3%), protoadamantan-5-*endo*-ol (27%), and protoadamantan-5-*exo*-ol (70%) [r.r.t. to protoadamantan-5-one 7 and 11.5 respectively]. Protoadamantan-5-*exo*-ol (25) (40 mg), m.p. 204—207°, was obtained by preparative t.l.c. [ethyl acetate–light

⁴⁰ V. M. Parikh and J. K. N. Jones, *Canad. J. Chem.*, 1965, **43**, 3452.

⁴¹ R. M. Moriarty, H. Gopal, and T. Adams, *Tetrahedron Letters*, 1970, 4003.

⁴² L. Caglioti, *Tetrahedron*, 1966, **22**, 487.

⁴³ M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, *Chem. Ber.*, 1965, **98**, 3236.

petroleum (1 : 4)] and sublimation, ν_{\max} 3630 cm^{-1} (Found: C, 79.05; H, 10.55. $\text{C}_{10}\text{H}_{16}\text{O}$ requires C, 78.9; H, 10.6%).

*Epoxidation*⁴⁴ of *Protoadamantene*.—Protoadamantene (350 mg, 2.6 mmol), *m*-chloroperbenzoic acid (600 mg 3.5 mmol), and sodium carbonate (280 mg, 2.6 mmol) in methylene dichloride (15 ml) were stirred for 16 h at 20°. Washing with aqueous sodium sulphite, hydrogen carbonate, and brine, and solvent removal from the dried organic layer gave a crystalline product (316 mg 81%, calculated as epoxides) consisting of two major components by t.l.c., both more polar than protoadamantene. G.l.c. (1% AP-L; 110°) showed two peaks in the proportions 1 : 6.

Preparative t.l.c. [ethyl acetate–light petroleum (1 : 19); continuous horizontal development with Sudan Yellow tracker] effected separation of the minor component R_F 0.5, 4,5-endo-epoxyprotoadamantane (30 mg), m.p. 212–214° (after sublimation), ν_{\max} 3005, 2975, 1114, 1038, 932, 883, 862, and 843 cm^{-1} , δ 3.34 and 3.12 (2 q, 1H each, –CH–O–CH–), 2.7–1.1 (12H, m) (Found: C, 79.75; H, 9.1. $\text{C}_{10}\text{H}_{14}\text{O}$ requires C, 79.95; H, 9.47%).

The major *exo*-epoxide decomposed during attempts to isolate it by preparative t.l.c. and also by fractional crystallisation. It was characterised by its conversion into adamantan-2a,4a-diol by acid (see below).

The n.m.r. spectrum of the epoxide mixture showed in addition to signals from the minor epoxide, the following multiplets assignable to the major epoxide: δ 3.06 and 2.82 (2 t, 1H each, –CH–O–CH–), 1.1 (1H, q, J 12, 4 Hz, H-7), and 2.7–1.3 (11H, m).

Conversion of exo-4,5-Epoxyprotoadamantane into 2a,4a-Dihydroxyadamantane.—Since the *exo*-epoxide could not be isolated, the rearrangement was effected with the epoxide mixture obtained as above. The epoxide mixture (120 mg) in ether (0.5 ml) was adsorbed on grade II acid alumina (10 g). Light petroleum eluted the minor epoxide (12 mg) followed by mixtures of intermediate polarity eluted with

ether–light petroleum (1 : 50). Methanol–ether (1 : 9) eluted 2a,4a-dihydroxyadamantane (80 mg, 59%), m.p. 341–344° (sealed evacuated capillary) (from light petroleum–ethyl acetate) (lit.³⁶ 312–326°; lit.³⁴ 305–312°) ν_{\max} ($5 \times 10^{-3}\text{M}$) 3616, 3530, 2912, 2868, 2854, 1233, 1100, 1077, 1056, 1007, 970, and 922 cm^{-1} , δ (CDCl_3) 3.86 (4H, m) and 2.5–1.2 (12H, m), δ ($\text{CDCl}_3\text{-D}_2\text{O}$) 3.89 (2H, m), and 2.5–1.2 (12H, m).

Lithium Aluminium Hydride Reduction of endo-4,5-Epoxyprotoadamantane.—The epoxide (10 mg) was refluxed with excess of lithium aluminium hydride in ether for 14 h. Work-up as usual gave crystalline material (8 mg), identical by t.l.c. with the lithium aluminium hydride reduction product of protoadamantan-5-one. G.l.c. showed in addition to protoadamantan-5-endo-ol (95%) peaks for adamantan-2-ol (3%) and protoadamantan-4-endo-ol (2%). The Jones oxidation product showed on g.l.c. protoadamantan-5-one (95%), adamantan-2-one (3%), and protoadamantan-4-one (2%).

Lithium Aluminium Hydride Reduction of the Mixture of exo- and endo-4,5-Epoxyprotoadamantane.—The epoxide mixture (25 mg) obtained from epoxidation of protoadamantene as above, was reduced as for the *endo*-epoxide. G.l.c. analysis of the product, and of the mixture of ketones obtained from it by Jones oxidation, allowed an estimate of the percentages of alcohols formed in the reduction (as for the hydroboration product, above): 4-*exo* (67%), 5-*exo* (17%), 5-*endo* (16%). The minor amount (<0.3%) of 4-*endo*-ol has been ignored. Reduction of the major *exo*-epoxide thus affords 4-*exo* : 5-*exo*-ol in the ratio 4 : 1.

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⁴⁴ M. Korach, D. R. Nielson, and W. H. Rideout, *J. Amer. Chem. Soc.*, 1960, **82**, 4328.