Thermolysis of Highly Congested Tri-*tert*-alkylmethanes. Rearrangement of a 3-Noradamantylmethyl† Radical

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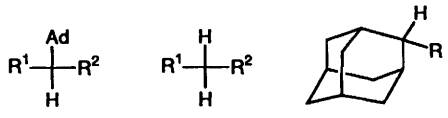
Activation energies for C–Ad fission in the thermolysis of di-1-adamantyl-*tert*-alkylmethanes and 1-adamantyl-di-1-bicyclo[2.2.2]octylmethane, AdR^1R^2CH, in toluene are best correlated with the strain energy difference (MMP2 force field) between the methane and the corresponding radical, $R^1R^2C^{\bullet}H$; difficulties were encountered in the application of MM3 to certain of these trialkylmethanes. Normally, the major thermolysis product is the di-*tert*-alkylmethane, $R^1R^2CH_2$, but when a 3-noradamantyl group is present (**1d**) the initially formed radical ring opens to give 1,2′-biadamantyl in amounts which depend on the temperature and the solvent (normal or octadeuteriated). This rearrangement is readily explained by MMP2 calculations. Since the cross-product yield is low (less than 3%, even in deuteriated solvent at the highest temperature) the thermodynamic parameters for the hydrogen transfer and ring opening reactions of the 1-adamantyl-3-noradamantylmethyl radical can be compared directly. Both the activation enthalpy and entropy are much greater for ring opening than for hydrogen abstraction from the solvent. Isotope effects on hydrogen abstraction are high and satisfy certain criteria for tunnelling, as do data on the analogous reaction of $Ad_2C^{\bullet}H$. A more sophisticated treatment of the product composition for **1d** thermolysis, using kinetic simulation, leads to essentially the same conclusions as the simpler treatment.

We recently showed that it was possible to convert tri-1-adamantylmethanol into the corresponding methane, **1a**, by



1 **2** **3**

1,2a $R^1 = R^2$ = 1-Adamantyl (Ad)
b R^1 = Ad; R^2 = 222Oc
c R^1 = Ad; R^2 = 321Oc
d R^1 = Ad; R^2 = 3-Noradamantyl
e R^1 = Ad; R^2 = 1-Norbornyl
f $R^1 = R^2$ = 222Oc

3a R = Ad
b R = Bu^t

treatment with oxalyl bromide followed by Bu_3SnH reduction of the resulting bromide.[1] Thermolysis of tri-1-adamantylmethane follows a rather simpler scheme than that of the alcohol,[2] because in $Ad_2C^{\bullet}H$ there is no labile hydrogen atom which can be transferred to another radical. We felt that such a simplification could be useful in studies on the ring opening of strained bi- or tri-cyclic alkyl groups in thermolysis. Work on the thermolysis of di-1-adamantyl-1-norbornylmethanol[3] has shown that, as the number of possible elementary processes in the overall scheme grows, it becomes increasingly difficult to use kinetic simulation as a means of estimating the rate constants of the most critical of these processes.

The reduction of alcohols to methanes by the above procedure is limited to alcohols bearing bi- and tri-cyclic alkyl groups, acyclic groups such as *tert*-butyl being likely to suffer rearrangement in the first step of the synthesis. We chose therefore to study a short series of di-1-adamantyl-*tert*-alkylmethanes (**1a–e**) and 1-adamantyldi-1-bicyclo[2.2.2]-octylmethane (**1f**) (222Oc = 1-bicyclo[2.2.2]octyl; 321Oc = 1-bicyclo[3.2.1]octyl) the thermolysis of which should result essentially in C–Ad homolysis. It is known that the 1-Ad$^{\bullet}$ radical reacts rapidly with the solvent, toluene, so that secondary reactions of this radical with other species are absent from the reaction scheme.[1] An incidental advantage of this set is that the presence of bulky *tert*-alkyl substituents ensures that the kinetics of the reaction can be measured in a convenient temperature range not exceeding 300 °C.

Results and Discussion

Synthesis and Thermolysis Kinetics.—Two new alcohols, denoted **1c**-OH and **1d**-OH (Table 1), were synthesized by the one-pot Barbier organolithium procedure.[4] Hydrocarbons **1a–f** were synthesized from the corresponding alcohols in yields ranging from 38% to 90% by the oxalyl bromide–Bu_3SnH procedure.

First-order rate constants for the thermolysis of the new alcohols and methanes were determined by following the rate of appearance of the termination product, bibenzyl, or, for the least reactive alkane, **1e**, by following its disappearance directly. The methanes are substantially less reactive than the corresponding alcohols[5] (Tables 1 and 2), the activation energies at a given temperature being about 5–6 kcal mol^{-1} higher (Table 3).§ The activation entropies are, however, very similar, albeit slightly higher on average for the alkanes (19.9 ± 1.2 cal mol^{-1} K^{-1}) than for the alcohols (18.1 ± 2.7 cal mol^{-1} K^{-1}). Because of this difference any comparison between the two sets will depend somewhat on the temperature chosen. At 225 °C (being approximately the mean temperature of all the kinetic determinations) the activation energy values show a good linear correlation (r = 0.9982) of $\Delta G^{\ddagger}$ (H) against $\Delta G^{\ddagger}$ (OH) with slope 1.17 ± 0.04 and intercept −0.38 ± 1.21 (Fig. 1).

Molecular Mechanics Calculations.—Correlation of thermolysis rates with strain energy changes. In previous work devoted to alcohol thermolysis,[5,6] for the purpose of calculating the strain energy change associated with C–C bond homolysis,

† Noradamantane = 2,5-methanooctahydropentalene.

§ 1 cal = 4.184 J.

Table 1 Kinetics of the thermolysis of di-1-adamantyl-*tert*-alkylmethanols (**1c**-OH and **1d**-OH) in toluene [$k_1/10^{-4}$ s^{-1} (T/°C)] (R^1 = Ad)

Cpd.	R^2	T_1	T_2	T_3	T_4
1c-OH	321Oc[a]	0.416 (174.5)	2.31 (190.0)	11.0 (204.9)	41.6 (219.4)
1d-OH	Norad[b]	0.465 (174.7)	2.51 (189.7)	11.0 (204.7)	42.2 (219.6)

[a] 321Oc = 1-bicyclo[3.2.1]octyl. [b] Norad = 3-noradamantyl.

Table 2 Kinetics of the thermolysis of 1-adamantyldi-*tert*-alkylmethanes, AdR^1R^2CH, in toluene [$k_1/10^{-4}$ s^{-1} (T/°C)] (R^1 = Ad, unless stated)

Cpd.	R^2	T_1	T_2	T_3	T_4
1a	Ad[a]	0.610 (185.0)	3.02 (200.0)	12.9 (214.5)	60.0 (230.0)
1b	222Oc[b]	0.912 (204.7)	4.21 (219.7)	17.4 (234.6)	73.1 (249.5)
1c	321Oc	0.596 (235.5)	2.89 (249.4)	10.5 (264.7)	40.5 (279.5)
1d	Norad	0.499 (234.6)	2.22 (249.5)	8.59 (264.7)	32.9 (279.6)
1e	Norb[c]	0.0665 (244.5)	0.320 (259.5)	2.15 (279.5)	5.41 (289.5)
1f	222Oc[b,d]	0.673 (219.8)	3.47 (235.0)	13.4 (249.8)	50.4 (264.8)

[a] Ad = 1-adamantyl. [b] 222Oc = 1-bicyclo[2.2.2]octyl: 92.5, 91.9, 91.2, 90.6% C–Ad fission at T_1 to T_4, respectively; the rest is C–Oc. [c] Norb = 1-norbornyl. [d] R^1 = 222Oc: 72.2, 71.3, 69.8, 69.4% C–Ad fission at T_1 to T_4, respectively; the rest is C–Oc.

Table 3 Thermodynamic parameters for C–Ad fission in the thermolysis of AdR^1R^2CX ($\Delta H^\ddagger$ and $\Delta G^\ddagger$ in kcal mol^{-1}, $\Delta S^\ddagger$ in cal mol^{-1} K^{-1}) (R^1 = Ad unless stated)

Cpd.	R^2	X	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$(225 °C)
1a-OH	Ad	OH	39.7 ± 0.2	16.4 ± 0.5	31.53[b]
1b-OH	222Oc	OH	42.1 ± 0.5	19.3 ± 1.1	32.48[b]
1c-OH	321Oc	OH	43.5 ± 0.4	16.5 ± 0.8	35.27
1d-OH	Norad	OH	43.0 ± 0.7	15.5 ± 1.5	35.27
1e-OH	Norb	OH	49.7 ± 0.6	22.8 ± 1.1	38.34[b]
1f-OH	222Oc[a]	OH	42.4 ± 0.4	17.7 ± 0.9	33.58[b]
1a	Ad	H	45.7 ± 0.4	18.9 ± 0.9	36.31[c]
1b	222Oc[d]	H	47.3 ± 0.6	19.4 ± 1.1	37.63
1c	321Oc	H	50.7 ± 1.2	19.7 ± 2.2	40.91
1d	Norad	H	50.8 ± 0.5	19.4 ± 0.9	41.14
1e	Norb	H	55.4 ± 0.3	22.3 ± 0.5	44.28
1f	222Oc[a,e]	H	48.8 ± 0.9	19.8 ± 1.7	38.95

[a] R^1 = 222Oc. [b] Ref. 5. [c] Ref. 1, revised. [d] For C–Oc fission: 50.0 ± 0.5; 21.5 ± 1.0; $\Delta G^\ddagger$(225 °C) = 39.31. [e] For C–Oc fission: 50.5 ± 0.9; 19.9 ± 1.7; $\Delta G^\ddagger$ 19.9 ± 1.7; $\Delta G^\ddagger$(225 °C) = 40.56.

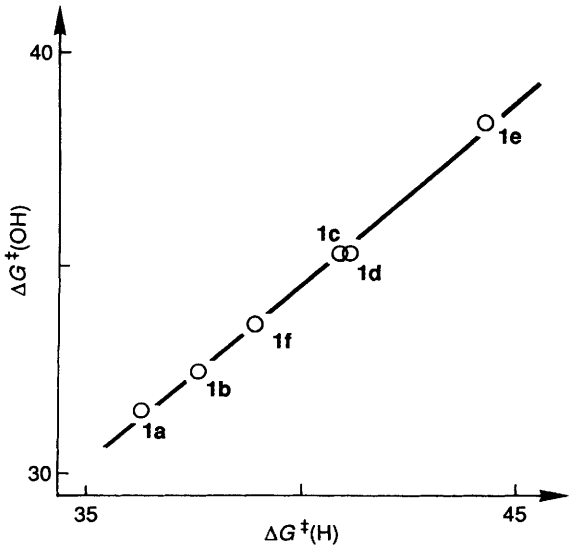


Fig. 1 Correlation of activation energies (kcal mol^{-1}) for thermolysis of AdR^1R^2CH and AdR^1R^2COH in toluene at 225 °C

the corresponding secondary alcohol was considered a reasonable surrogate for the transition state. The analogous approach in the present case would be to take the corresponding dialkylmethane. However, since the molecular mechanics program, MMP2,[7] which has been used in previous work, and MM3[8] are both parametrized for alkyl radicals, it is possible to represent the reaction as AdR^1R^2CH ⟶ R^1R^2C·H + Ad·, or, since Ad· is common to all members of the series, to seek a correlation between the activation energy and the difference between the strain energies of AdR^1R^2CH and R^1R^2C·H, bearing in mind, however, that the latter is an intermediate and not a transition state. The fact that the slope of the correlation is close to unity for the alcohols has, however, been taken as indicating that the transition state for thermolysis is energetically close to the intermediate and that, therefore, the kinetics can be used to obtain thermodynamic information about radical species.[6]

The strain energy correlation for the methanes in terms of the difference between the trialkyl- and dialkyl-methanes (Tables 4 and S1)¶ calculated by MMP2(85) is moderately satisfactory, the slope being acceptable at −0.94 but the correlation coefficient somewhat low at 0.9710. The MM3 version of this correlation is distinctly poorer (slope −0.87; r 0.9366). When the radical is taken as the transition state surrogate the MMP2 correlation is much improved (slope −0.97 ± 0.05; r 0.9937) (Fig. 2) but the MM3 version is as bad as before (slope −0.83; r 0.9401). The principal reason for the poor quality of the MM3 correlations is that neither the 3-noradamantyl nor the bicyclo[2.2.2]octyl derivatives seem to be handled correctly, all lying well above the plot through the three remaining points,

¶ Tables S1, S2 and details of procedures for determining rate constants are available as a supplementary publication (Supp. Pub. no. 57061 [5 pp.]). For details of the deposition scheme, see 'Instructions for Authors (1995),' *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

Table 4 Strain energies (kcal mol^{-1}) of trialkyl- and dialkyl-methanes and methanols and dialkylmethyl radicals calculated by molecular mechanics (R^1 = Ad unless stated)

	AdR^1R^2CH		$R^1R^2CH_2$		$R^1R^2C^{\bullet}H$		AdR^1R^2COH	R^1R^2CHOH
R^2	MMP2 (85)	MM3 (89)	MMP2	MM3	MMP2	MM3	MMP2	MMP2
Ad	76.00	69.83	28.31	22.75	26.45	20.48	82.12	31.80
222Oc	78.83	75.31	32.06	28.60	30.30	26.37	84.80	35.22
321Oc	72.46	68.03	30.37	26.34	28.03	23.71	79.69	32.66
Norad	80.96	77.91	37.16	33.63	36.11	31.17	88.18	39.75
Norb	73.20	69.43	33.17	29.99	31.49	27.83	79.76	35.37
222Oc[a]	81.90	80.76	36.00	34.53	34.53	32.29	88.16	39.09

[a] R^1 = 222Oc.

Table 5 Activation energies and strain energy calculations for Bu^t_2RCH thermolysis ($\Delta G^{\ddagger}$ and strain energies in kcal mol^{-1})[a]

		MMP2 strain energy		
R	$\Delta G^{\ddagger}$(250 °C)[b]	Bu^t_2RCH	$Bu^tRC^{\bullet}H$	Δstrain
H	64.53	9.16	0.99	8.17
Me	57.68	15.98	1.95	14.03
Et	54.60	21.98	2.26	19.72
Pr^i	50.17	29.01	3.53	25.48
Bu^t	39.97	40.38	7.45	32.93
Ad	37.05	52.04	16.37	35.67

[a] All points: $\Delta G^{\ddagger}$ = 72.7 − 0.975 Δstrain (n = 6, r = 0.9914). Not Pr^i: $\Delta G^{\ddagger}$ = 72.6 − 0.988 Δstrain (n = 5, r = 0.9969). Symm only: $\Delta G^{\ddagger}$ = 72.1 − 0.981 Δstrain (n = 4, r = 0.9994). [b] Calculated from data in ref. 9.

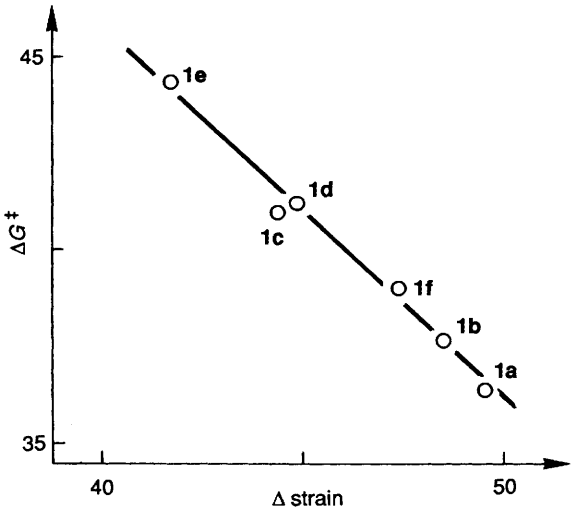


Fig. 2 Correlation of activation energy for AdR^1R^2CH thermolysis against strain energy change (MMP2) for the alkane–radical model (both in kcal mol^{-1})

which has almost unit slope. This would seem to indicate that the strain energies of the initial trialkylmethanes are overestimated by MM3. Even with MMP2 there appears to be a problem concerning 3-noradamantyl; the marked improvement on going from the alkane–alkane to the alkane–radical model is largely due to the fact that in the latter the Δstrain values for 3-noradamantyl and 1-bicyclo[3.2.1]octyl are similar, as is required, since the activation parameters for the corresponding hydrocarbons are virtually identical. No reason can be given at present for these anomalies in the handling of 3-noradamantyl derivatives. In the two force fields the minima correspond to the same conformation to within a few degrees.

In the case of the dibicyclo[2.2.2]octyl derivatives, minima can be found with the two systems screwed in the same or in opposite directions. Unlike the alcohol, the structure corresponding to the energy minimum for **1f** has the two bicyclo[2.2.2]octyl systems screwed in opposite directions; in MMP2 this conformation is 1.6 kcal mol^{-1} more stable than that where they were screwed in the same sense, but only 0.7 kcal mol^{-1} with MM3. In both **1b** and **f** the screw angles are 4–5° smaller for MM3 than for MMP2. Previous work on alcohols[5] did not reveal any particular problem with 1-bicyclo[2.2.2]octyl derivatives though the point for **1f**-OH does lie about 0.5 kcal mol^{-1} above the correlation. That for **1d**-OH, however, lies 1.5 kcal mol^{-1} above the correlation.

Table 6 Individual increments for AdR^1R^2CH (R^1 = Ad unless stated) with respect to the Rüchardt correlations, 'not Pr^i' (n = 5) and 'symm only' (n = 4)

R^2	n = 5	n = 4	Δstrain(corr)[a]	Diff. (5)	Diff. (4)
Ad	37.16	36.87	39.12	1.96	2.25
222Oc	35.91	35.62	38.10	2.19	2.48
321Oc	32.59	32.27	34.00	1.41	1.73
Norad	32.34	32.02	34.42	2.08	2.40
Norb	29.24	28.90	31.28	2.04	2.38
222Oc[b]	34.59	34.28	36.94	2.35	2.66

[a] SE(AdR^1R^2CH) − SE($R^1R^2C^{\bullet}H$) − 10.43. See Table 4. [b] 222Oc.

Estimation of strain in 1-*adamantyl and* 1-*bicyclo*[2.2.2]*octyl radicals.* Comparison of our set of alkanes, where Ad$^{\bullet}$ is formed, with Rüchardt's series, Bu^t_2RCH, where $Bu^{t\bullet}$ is formed,[9] should provide a new estimate of the strain in the 1-adamantyl radical. Again, the problem of finding a reasonable temperature for comparison arises, since Rüchardt's data cover a much greater range than ours (Table 5). However, as before, the fact that activation entropies are similar means that this is not too critical. The activation energies were therefore recalculated for 250 °C and plotted against the MMP2 Δstrain values corresponding to the alkane–radical model, our data having been 'corrected' for the strain energy of adamantane (10.43 kcal mol^{-1}) (Table 6). All our points lie above the Rüchardt plot, which indicates that this correction is too small, *i.e.* that the 1-adamantyl radical is more strained than adamantane.[5] By just how much is difficult to say because neither correlation is perfect. In particular, the Pr^i point in the correlation of Rüchardt's data appears wild; if it is neglected and the deviations are calculated for each adamantyl derivative, we find a fairly constant value of 2.0 ± 0.3 kcal mol^{-1}. We obtain a slightly higher value, 2.3 ± 0.3 kcal mol^{-1}, if only the trigonally symmetrical substituents of Rüchardt's set are used (Table 6). Both these values are consistent with our earlier estimate, 2.4 ± 0.5 kcal mol^{-1}, based on alcohol thermolysis.[5]

It is possible to estimate the strain energy difference between 1-bicyclo[2.2.2]octyl and 1-adamantyl radicals by using the competitive method.[5,10] This has the advantage that the strain energy of the initial alkane, likely to be the most difficult to calculate correctly, is not required. The previously described method was used, it being assumed that the strain energy

changes are completely expressed in the activation energies (*i.e.* unit slopes). From the differences in the strain energy changes for the two competing pathways, using MMP2 or MM3 and the secondary alkane or radical model for the transition state, the data for Ad_2OcCH (**1b**) and $AdOc_2CH$ (**1f**) give values of 1.6 ± 0.1 and 1.9 ± 0.1 kcal mol^{-1}, respectively. That is, the bicyclo[2.2.2]octyl radical is about 1.7 kcal mol^{-1} more strained than the 1-adamantyl radical, relative to the corresponding alkanes. The fact that this result is in reasonable agreement with previous estimates[5] (1.6 kcal mol^{-1}) and that both models and both force fields agree lends weight to our idea that the MM3 calculations fail for the highly strained trialkylmethanes. It should be noted that the value for the extra strain in the 1-adamantyl radical is referenced to Bu^t•/isobutane = 0, while the figure for bicyclooctyl is compared to adamantyl. Referenced to Bu^t•/isobutane, the bicyclooctyl radical is about 3.7 or 4.0 kcal mol^{-1} more strained than bicyclooctane, depending on the value adopted for the 1-adamantyl radical.

Effect of the OH *group on radical stability.* Since there are no parameters for radicals bearing OH groups at the radical centre we can only compare the alcohols and the alkanes using the trialkylmethane–dialkylmethane model. We have updated our earlier MM2 calculations[4] on the alcohols by using MMP2(85)[7] which takes into account the electronegativity effect on the C–O bond, so the figures given here will not correspond to those in the earlier publication. Whereas replacing the OH group by a hydrogen increases the activation energy by some 5.5 ± 0.5 kcal mol^{-1}, the strain energy difference is on average 3.8 ± 1.0 kcal mol^{-1} greater for the alcohols than for the alkanes (Table S2). This means therefore that the greater reactivity of the alcohols cannot be attributed entirely to the greater strain energy change but that part of it, *ca.* 1.7 kcal mol^{-1}, must be due to the polar effect of the OH group on the stability of the incipient radical, it being assumed that strain energy change is reflected entirely in the activation energy (*i.e.* unit slope, which is approximately the case for both alcohols and alkanes). This is somewhat smaller than data from classical studies[11] on much simpler radicals (*ca.* 2.6 kcal mol^{-1}). Our previous estimate[6] of about 4.7 kcal mol^{-1}, obtained by comparing Rüchardt's Bu^t_2RCH data with ours for $Bu^tR^1R^2COH$, should be revised downwards in the light of further data,[5,9c] but the difference in the slopes [1.13 for the Rüchardt correlation (alkane–alkane model) when Flamm's datum[9c] for $AdBu^t_2CH$ is included; 1.02 for our alcohols[5]] makes comparison difficult. Perhaps the best procedure is to compare alcohol–alkane pairs, whence values of 2.3 and 2.1 kcal mol^{-1} for Bu^t_3CX and $AdBu^t_2CX$, respectively. There is finally not such a greater difference between the result for the *tert*-butyl and the 1-adamantyl derivatives. Given that the latter are very highly strained, it is satisfying that the disagreement is no worse. In fact, we could see in these results a general trend for the contribution of the OH group to decrease as the crowding at the radical centre increases, but the limited results available hardly justify such a conclusion.

*Thermolysis Products and Kinetic Simulation.—Di-*1*-adamantyl-*3*-noradamantylmethanol* (**1d**-OH). In toluene the thermolysis of tri-*tert*-alkylmethanols generally gives bibenzyl (by the self-reaction of solvent-derived radicals), di-*tert*-alkyl ketone, di-*tert*-alkylmethanol and a cross-product, 1,1-di-*tert*-alkyl-2-phenylethanol.[2,3,5] Thermolysis of **1d**-OH under kinetic conditions gave similar amounts of ketone and secondary alcohol but little or no cross-product, while at higher concentration (which favours the cross-reaction)[2] a cross-product representing about 10% of the oxygen-containing products was detected by GC. Thermolysis of **1d**-OH in the presence of benzophenone (BP) to scavenge the AdNoradC$^•$OH radicals, followed by removal of excess BP by reaction with an organomagnesium compound, gave 1-adamantyl 3-noradamantyl ketone in good yield. The one-pot Barbier reaction[4] of this with benzyl bromide in the presence of lithium metal gave material identical with the cross-product. In contrast with what was observed for di-1-adamantyl-1-norbornylmethanol,[3] there was no evidence for the formation of ring-opened ketones or ring-opened cross-products.

1-*Adamantyldi*-tert-*alkylmethanes* (**1a–f**). The regular dialkylmethanes, **2a–f**, obtained by thermolysis of the trialkylmethanes were first identified by their GC/ITD (ion trap detector) and ^{13}C NMR spectra. Di-1-adamantylmethane (**2a**) was synthesized directly by reduction of Ad_2CHBr. The other hydrocarbons were isolated from preparative thermolysis experiments in the presence of benzenethiol. The addition of the thiol, a stronger hydrogen atom donor than the solvent, eliminates cross-products, bibenzyl and rearrangement products. Column chromatography on alumina in light petroleum allows the hydrocarbons, including adamantane, to be separated from the disulfide.

Tri-1-adamantylmethane (**1a**) has already been studied in detail and discussed briefly.[1] Its thermolysis corresponds to Scheme 1, where the solvent is represented by SL (L = H or D).

$$Ad_3CH \longrightarrow Ad_2C^•H + Ad^• \qquad k_1$$
$$Ad^• + SL \longrightarrow AdL + S^• \qquad k_2$$
$$Ad_2C^•H + SL \longrightarrow Ad_2CHL + S^• \qquad k_3$$
$$S^• + Ad_2C^•H \longrightarrow Ad_2CHS \qquad k_4$$
$$2\,S^• \longrightarrow S_2 \qquad k_5$$

Scheme 1

By kinetic simulation of the product composition, it being assumed that the rate constant, k_4, if the cross-reaction, S$^•$ + $Ad_2C^•H$, is the same as that, k_5, of the self-reaction of benzyl radicals, $\Delta H^‡$ is calculated as 12.9 and 15.0 kcal mol^{-1} and $\Delta S^‡$ −20 and −18.4 cal mol^{-1} K^{-1} for hydrogen transfer (k_3) to $Ad_2C^•H$ from normal and octadeuteriated toluene, respectively. Linear extrapolation of these data indicates an isotope effect of 16 ± 2 at 25 °C, consistent with proton tunnelling. The large difference between the activation enthalpies is also considered as a criterion for tunnelling,[12] as is the activation entropy trend, though this difference is in our opinion too small to be significant. If our results in normal toluene are combined with low-temperature data obtained by direct observation[13] of the decay of $Ad_2C^•H$, a curved Arrhenius plot is obtained, the Arrhenius energies in the two studies being quite different (Fig. 3). Our assumption about the rates of the radical–radical reactions affects only the position of our data on the log k_3[SH] axis, not the slope.[2] A curved Arrhenius plot, though infrequently observed, because of the difficulty of doing measurements over a sufficiently wide temperature range, is also considered to be an indication of tunnelling, but our plot suffers from a large window at intermediate temperatures. It would be very interesting to do rate measurements in this range and to determine the isotope effect at temperatures below 230 °C. Much greater deuterium isotope effects, satisfying all criteria for tunnelling, including curved Arrhenius plots over a very wide range of temperature, have been reported for intramolecular but not intermolecular hydrogen transfers.[14]

Of the new methanes, only **1d** (R^1 = Ad; R^2 = Norad) appeared to merit a complete investigation, the others giving simply the expected hydrocarbons, **2b–c** and **2e–f**, by loss of adamantyl radical, and small amounts of cross-products. Two methanes, **1b** and **f**, showed significant amounts of C–222Oc homolysis in addition to C–Ad, and the product hydrocarbons were, therefore, mixtures. The amount of C–321Oc fission in **1c** was so small (2–3%) that it was deemed negligible. In the thermolysis of **1f** without thiol the principal product, **2f**,

Table 7 Temperature and solvent isotope effect on product composition (%) from the thermolysis of di-1-adamantyl-3-noradamantylmethane (**1d**) in toluene

	Yield						
T/°C	AdH	Bibenzyl	**2d**	**3a**	CP/R[a]	CP/N[b]	**2d**/**3a**
In [$^1H_8$]toluene[c]							
235	(100)	(97)	74.4 (72)	25.4 (24)	0.2	—	2.93
250	(100)	(98)	66.8 (65)	32.6 (31)	0.5	0.1	2.05
265	(98)	(96)	58.6 (57)	40.3 (39)	0.8	0.3	1.46
280	(99)	(97)	50.2 (48)	47.6 (46)	1.7	0.5	1.05
In [$^2H_8$]toluene[d]							
235			37.5	60.9	1.2	0.4	0.616
250			30.8	67.4	1.4	0.4	0.457
265			24.6	72.6	2.2	0.6	0.344
280			20.4	76.4	2.6	0.6	0.267

[a] Several apparently rearranged cross-products. [b] Normal cross-product. [c] Normalized values; absolute yields in parentheses. [d] Normalized yields.

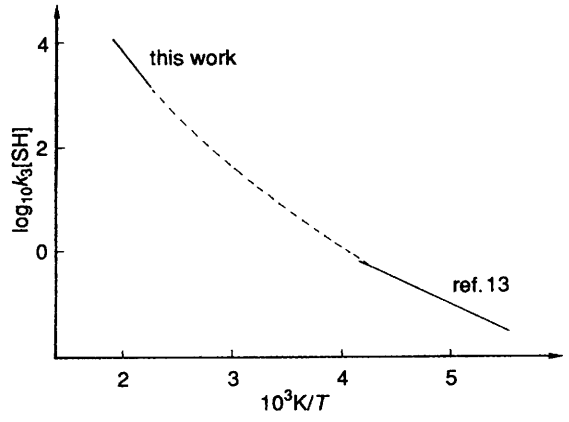


Fig. 3 Composite Arrhenius plot for the pseudo-first-order reaction of $Ad_2C^{\bullet}H$ with toluene

$$Ad_2NoradCH \longrightarrow AdNoradC^{\bullet}H + Ad^{\bullet} \quad k_1$$
$$Ad^{\bullet} + SL \longrightarrow AdL + S^{\bullet} \quad k_2$$
$$AdNoradC^{\bullet}H + SL \longrightarrow AdNoradCHL + S^{\bullet} \quad k_3$$
$$AdNoradC^{\bullet}H \longrightarrow (Ad\text{–}CH{=}331)^{\bullet} \quad k_{open}$$
$$(Ad\text{–}CH{=}331)^{\bullet} \longrightarrow (Ad\text{–}Ad)^{\bullet} \quad k_{close}$$
$$(Ad\text{–}CH\text{–}331)^{\bullet} \longrightarrow (Ad\text{–}CH{=}331)'' \quad k_{migr}$$
$$(Ad\text{–}Ad)^{\bullet} + SL \longrightarrow (Ad\text{–}Ad)L + S^{\bullet} \quad k_3'$$
$$S^{\bullet} + AdNoradC^{\bullet}H \longrightarrow AdNoradCHS\ (CP/N) \quad k_4$$
$$S^{\bullet} + (Ad\text{–}Ad)^{\bullet} \longrightarrow CP/R$$
$$S^{\bullet} + (Ad\text{–}CH{=}331)^{\bullet} \longrightarrow CP/R \quad k_5$$
$$S^{\bullet} + (Ad\text{–}CH{=}331)'' \longrightarrow CP/R$$
$$2\,S^{\bullet} \longrightarrow S_2 \quad k_6$$

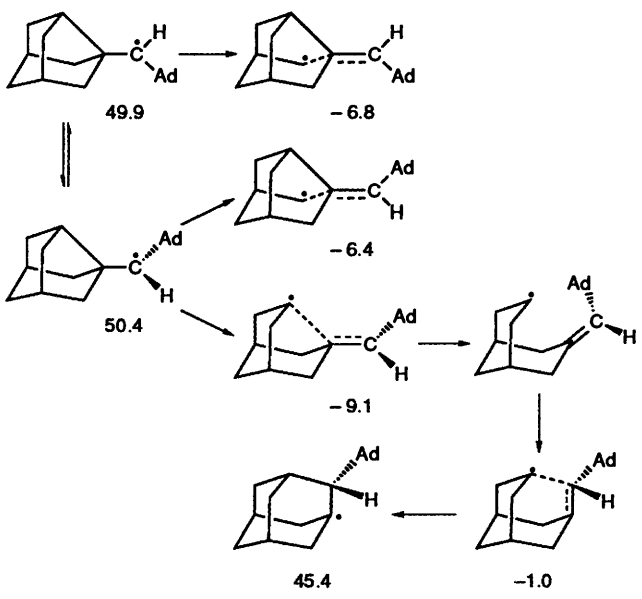
Scheme 2

Oc_2CH_2, was accompanied by 5–10% of an isomer, possibly a ring-opened product. Thermolysis of **1e** (R^2 = Norb), again without thiol, gave also a familiar pattern[3] of four probably ring-opened products emerging from the GC column before the usual product, **2e**, and a broad, poorly resolved multiplet of ring-opened cross-products. We did not attempt to study either of these systems further.

Di-1-adamantyl-3-noradamantylmethane (**1d**). (*i*) *General features.* Experiments on the thermolysis of **1d** (R^1 = Ad; R^2 = Norad) under kinetic conditions show that adamantane is formed quantitatively, that the bibenzyl yield is only a few percent short of quantitative and that 94–98% of the AdNoradC$^{\bullet}$H radical is accounted for by two products, a normal hydrocarbon, $AdNoradCH_2$ (**2d**), and a rearrangement product which we identified as 1,2′-biadamantyl (**3a**) (see below) (Table 7). The other outstanding feature of the reaction is the very low yield of cross-products (approximately 0–3%, depending on the temperature and the solvent, deuteriated or not). The cross-products consist of a multiplet of probably rearranged structures, denoted CP/R, and a well separated peak of longer retention time which, on the basis of previous experience, seems likely to be the normal cross-product, CP/N, derived directly from the AdNoradC$^{\bullet}$H radical. Several rearranged cross-products could perhaps be formed by interception of a ring-opened radical, before or after intramolecular hydrogen migration. Another possibility is that after ring closure the radical centre is scrambled over the 2-adamantyl system, before reaction with solvent or the solvent radical. The overall reaction Scheme 2 is therefore slightly more complicated than that for **1a** thermolysis. In this scheme, (Ad–CH=331)$^{\bullet}$ denotes the radicals formed by ring opening and (Ad–CH=331)'' a set of radicals derived from this by intramolecular hydrogen transfer. Ring closure gives the radical (Ad–Ad)$^{\bullet}$, the precursor of 1,2′-biadamantyl, but possibly also of rearranged cross-products. That there is little cross-product signifies that the rate of recombination of the benzyl radical with any other radical is slow compared to that of the alternative, reaction of the same radicals with the solvent. It was previously found that the cross-product yield decreases as the reaction temperature increases on going from a relatively reactive alcohol to a less reactive one,[15] this for the simple reason that the rate constant for hydrogen transfer from solvent to the radical increases with temperature faster than that for recombination. The cross-product yield is already small for Ad_3CH, **1a**, in the range 185–230 °C (1–3% in normal toluene)[1] and is even smaller at the higher temperature required for thermolysis of **1d** (235–280 °C).

It should be noted that ring opening has no effect upon the reactivity of the noradamantyl-substituted methane. Regardless of the calculational model chosen there is no indication of any abnormal rate enhancement. Furthermore, the fact that the presence of a hydrogen-donor radical scavenger, such as benzenethiol, totally suppresses the rearrangement indicates that this process occurs after the rate determining C–C homolysis. This situation is to be contrasted with the solvolysis of 1-(3-noradamantyl)ethyl and propyl sulfonates,[16] which ionize with participation and/or strong hyperconjugation.

(*ii*) *Molecular mechanics calculations on ring opening.* Molecular mechanics calculations on the AdNoradC$^{\bullet}$H radical reveal two conformers with similar steric energies, that with the AdC$^{\bullet}$H group approximately in the plane of the C(3)–C(7) bond being slightly less strained (49.9 kcal mol^{-1}) than that with this group orthogonal (50.4 kcal mol^{-1}) (Scheme 3). Calculations on the possible transition states[17] for ring opening (*endo-trig*) indicate a marked preference for C(3)–C(7) bond fission for the



Scheme 3

second conformer (−9.1 kcal mol^{-1}), with C(2)–C(3) fission from either conformer about 2.5 kcal mol^{-1} higher in energy (first −6.8 kcal mol^{-1}; second −6.4 kcal mol^{-1}).‖ Recyclization of the bicyclo[3.3.1]nonyl ene-radical to the more stable (45.4 kcal mol^{-1}) 1,2′-biadamantyl radical goes through the much less favoured *exo-trig* transition state (−1.0 kcal mol^{-1}). This is followed by hydrogen transfer from the solvent to give the observed 1,2′-biadamantyl.

The outstanding difference between alkane and alcohol thermolysis is that no such rearrangement is observed in the thermolysis of the corresponding alcohol, **1d**-OH, which goes through a very similar radical. The only products isolated were 1-adamantyl 3-noradamantyl ketone and the corresponding secondary alcohol, while a small amount of a cross-product, absent under kinetic conditions, was detected in a high-concentration, semi-preparative experiment. Calculations cannot be performed on the dialkylketyl radical, AdNoradC$^{\bullet}$OH, but we can take the dialkylethyl radical, AdNoradC$^{\bullet}$CH$_3$, as a reasonable surrogate, as we have done in the past,[3] and compare this with the rearranged species, the 2-(1-adamantyl)-2-methyl-1-adamantyl radical. Now we find that the steric energy of the rearranged radical is substantially higher (63.06 kcal mol^{-1}) than that of the initial radical (56.60, 56.63 or 57.30 kcal mol^{-1}, depending on the conformation), solely because of the geminal 2-methyl substituent. There is therefore no energetic advantage in the rearrangement process.

(*iii*) *Competition between ring opening and hydrogen transfer.* As expected from previous work, the amount of radical ring opening increases with the temperature and, more dramatically, on going from normal toluene to deuteriated toluene. The second phenomenon is easily understood by considering that ring opening of the initially formed radical is in competition with its reaction with the solvent. This latter, involving a hydrogen atom transfer, will be slower in deuteriated solvent. Why ring opening is favoured by increasing the temperature is related to the thermodynamic parameters of the two reactions, and is more difficult to appreciate intuitively. In a first approximation we ignored the small amounts of cross-products formed and assumed that the relative amounts of normal hydrocarbon, AdNoradCH$_2$ and of 1,2′-biadamantyl represented the rate constant ratio, $k_{rel} = k_3[SL]/k_{open}$. Plotting the appropriate data for the two solvents against temperature, either as Arrhenius plots (log k_{rel} *vs.* $1/T$) or Eyring plots ($\Delta\Delta G^{\ddagger}$ *vs.* T) enables us to determine the differences between the thermodynamic parameters for the two competing reactions in normal and labelled toluene. In both cases the activation enthalpies and entropies are greater for ring opening than for hydrogen transfer ($\Delta\Delta H^{\ddagger}$ is 12.8 and 10.4 kcal mol^{-1} and $\Delta\Delta S^{\ddagger}$ is 23.0 and 21.4 cal mol^{-1} K^{-1} in normal and labelled toluene, respectively). Similar, though somewhat greater, differences can be calculated from the data on AdNorbC$^{\bullet}$OH:[3] 16.3 and 12.8 kcal mol^{-1}, and 29.5 and 24.8 cal mol^{-1} K^{-1}, respectively. In this latter work there was evidence for a small isotope effect on the ring opening, but kinetic simulation involved so many unknowns that this apparently anomalous result cannot be considered conclusive. We shall assume that there is no isotope effect upon ring opening, in which case the isotope effects on AdNoradC$^{\bullet}$H concern only hydrogen transfer and amount to 2.4 kcal mol^{-1} on the activation enthalpy and 1.6 cal mol^{-1} K^{-1} on the activation entropy, *i.e.* the activation entropy is 1.6 cal mol^{-1} K^{-1} less negative in [$^2H_8$]toluene. Both these differences are closely similar to the corresponding data for Ad$_2$C$^{\bullet}$H (2.1 kcal mol^{-1} and 1.6 cal mol^{-1} K^{-1}). Linear extrapolation to 25 °C indicates an isotope effect of about 25, somewhat greater than that for Ad$_2$C$^{\bullet}$H because of the difference in the enthalpy term. It should be borne in mind, however, that if the large difference in the activation enthalpies is indicative of tunnelling, then the Arrhenius plots should be non-linear when examined over an extended temperature range.[12]

Kinetic simulation of the product data is difficult because the cross-product yields, which make it possible to 'anchor' the rate constants, are small and unreliable, particularly in normal toluene. For [$^2H_8$]toluene, however, optimization of the rate constants for hydrogen transfer from solvent and that for ring-opening (for the various assumptions involved in these calculations, see Experimental section and Table 8) gave k_3[SD], k_{open} and k_3'[SD] values showing fairly regular temperature dependence. The corresponding Arrhenius parameters are [rate constant, log (A/s^{-1}), E_a (kcal mol^{-1})]: k_3[SD], 9.2 ± 0.9, 13.0 ± 2.2; k_{open}, 14.0 ± 0.8, 23.7 ± 2.0; k_3'[SD], 11.5 ± 0.7, 19.0 ± 1.8. The values for k_3[SD] are not very different from those for the corresponding reaction of Ad$_2$C$^{\bullet}$H in the same solvent (9.8 and 15.1 kcal mol^{-1}, calculated from the data in ref. 1). Where the two plots are closest (about 230–235 °C) the difference in k_3 is a factor of about 1.5 in favour of the less congested AdNoradC$^{\bullet}$H radical. It should be remembered, however, that our treatment assumes that the rate constant of the cross-reaction with the solvent radical is in both cases equal to that of the self-reaction of the solvent radical. If, for example, the rate of the cross-reaction for Ad$_2$C$^{\bullet}$H were a factor of two less than that of AdNoradC$^{\bullet}$H, the resulting value of the hydrogen transfer reaction for Ad$_2$C$^{\bullet}$H would also be a factor of two lower, making it three times slower than that of AdNoradC$^{\bullet}$H.

The pre-exponential Arrhenius parameter for ring-opening is slightly greater than those for the opening of cyclobutylmethyl radicals[18] determined, at much lower temperatures, while the activation energy is substantially higher. Both parameters are notably smaller than those for ring opening of the 1-adamantyl-1-norbornylketyl radical studied previously (log A 16.0; E_a 31.8). Expressed in terms of the Eyring equation, the data on **1d** correspond to a small positive activation entropy (2.3 ± 3.8 cal mol^{-1} K^{-1}, while we can calculate from the Arrhenius parameters for the cyclobutylmethyl radicals values of about 0 to −4 cal mol^{-1} K^{-1} in the range 250–350 K. The data for AdNorbC$^{\bullet}$OH correspond to an activation entropy of *ca.* 12 cal mol^{-1} K^{-1}. Again, it must be stressed that the activation entropies obtained by kinetic simulation depend on the values

‖ Since the steric energies of radicals and transition states are not on the same scale, differences between the two are not meaningful.

Table 8 Kinetic simulation of product data for thermolysis of **1d** in toluene (Arbitrary: $k_4 = k_5 = k_6$. In [$^2H_8$]toluene k_3, k_3' and k_{open} optimized; in [$^1H_8$]toluene k_3 and k_{open} only).

T/°C	$[\mathbf{1d}]_{corr}/10^{-2}$ mol dm^{-3}	$[SL]_{corr}$/ mol dm^{-3}	k_1/s^{-1} [a]	$k_6/10^{11}$ dm^3 mol^{-1} s^{-1}	$k_3[SL]/10^4$ s^{-1}	$k_{open}/10^4$ s^{-1}	$k_3'[SL]/10^3$ s^{-1}	$k_3[SL]/k_{open}$
In [$^2H_8$]toluene								
234.6	0.299	6.83	5.06×10^{-5}	0.210	0.344	0.570	1.88	0.604
249.5	0.289	6.59	2.18×10^{-4}	0.229	0.588	1.31	3.85	0.449
264.7	0.278	6.34	8.79×10^{-4}	0.247	0.648	1.97	5.31	0.329
279.6	0.266	6.08	3.27×10^{-3}	0.267	1.07	4.14	9.25	0.258
In [$^1H_8$]toluene								
234.6	0.299	6.83	5.06×10^{-5}	0.210	1.74	0.570 [b]	6.46	2.919
249.5	0.289	6.59	2.18×10^{-4}	0.229	2.35	1.31 [b]	5.85	2.026
264.7	0.278	6.34	8.79×10^{-4}	0.247	3.14	1.97 [b]	8.20	1.427
279.6	0.266	6.08	3.27×10^{-3}	0.267	4.08	4.14 [b]	8.66	1.017

[a] Recalculated from Arrhenius plot. [b] Data for [$^2H_8$]toluene.

assumed for the rate constants of the cross-reactions (and also on the validity of the extrapolation of Fischer's data[19] for benzyl radical recombination).

Attempts to optimize the same rate constants for normal toluene gave values of the same order of magnitude as those for deuteriated solvent but tending to vary randomly with the temperature. Fixing k_{open} at the values calculated by kinetic simulation of the products formed in [$^2H_8$]toluene gave a more coherent set of k_3[SH] data, with log A and E_a equal to 8.8 ± 0.8 and 10.6 ± 2.0, respectively. The isotope effect varies smoothly from 4.8 at 235 °C to 3.9 at 280 °C. Nevertheless, k_3'[SH] still varies wildly, the apparent isotope effect on k_3' ranging from 0.9 to 3.5. The most important point to emerge from these calculations is that k_3[SH]/k_{open} remains fairly close to the naive value based on the product ratio, whatever the value of k_{open} used and regardless of whether three or two rate constants are optimized. This is due to the simple fact that k_3[SH]/k_{open} is determined to a large extent by the **2d**:**3a** ratio, the correction being less for normal toluene, where the cross-product yields are particularly small, than for the deuteriated solvent where the 'real' rate ratio is slightly higher than assumed. Corrected data are given in Table 8. Use of these data to compare the activation parameters of hydrogen transfer and ring opening and to estimate the solvent isotope effect at 25 °C gives values insignificantly different from those calculated above.

(*iv*) *Remarks concerning* 1,2'-*biadamantyl.* There are two previous reports of the isolation of 1,2'-biadamantyl (**3a**). The first[20] concerns the reaction of the 1-adamantyl cation with 2,4-didehydroadamantane, where a compound with mp 266–268 °C was formed in increasing amounts as the ratio of adamantane to didehydroadamantane was increased. The product was shown not to be 1,1'-biadamantyl by mixed mp, GC and MS comparison, while the mp was greater than that reported for 2,2'-biadamantyl. Later, in experiments designed to demonstrate the formation of adamantene by dehalogenation of 1,2-diiodoadamantane, McKervey *et al.*[21] obtained a mixture of head-to-head and heat-to-tail dimers which, when treated with $AlCl_3$ in CS_2, gave in 64% yield a product with mp 263 °C, identified by GC comparison with the cross-product obtained by Wurtz reaction[22] of 1- and 2-bromoadamantanes with sodium in xylene, reported to give a mixture (1:6:3) of the 1,1'-2,2'- and 1,2'-biadamantyls. There is no indication, however, that 1,2'-biadamantyl was actually isolated from the mixture. In our hands the ratio was approximately 1:7:5. Other authors mention this compound (equilibration studies,[23] ring enlargement of 3-noradamantyl carbene[24]) but provide no further information.

Thermolysis of **1d** gave $AdNoradCH_2$ (**2d**) identified by MS and ^{13}C NMR of the isolated product, and another hydrocarbon with retention time and MS identical with the cross-product from the mixed Wurtz reaction. Deoxygenation of 2-(1-adamantyl)adamantan-2-ol by oxalyl bromide–Bu_3SnH or Duddeck's procedure[25] gave material with the same GC–MS characteristics but with mp 166 °C (sealed capillary). The same product was obtained by applying Duddeck's procedure to 1-adamantyl-3-noradamantylmethanol, which clearly undergoes carbocation rearrangement. The ^{13}C NMR spectrum of this product is in full agreement with the structure of 1,2'-biadamantyl (**3a**), the relative intensities and the numbers of the various CH and CH_2 signals being as required for a 1-adamantyl group attached to the 2-position of another. The signals at 29.1, 37.1 and 42.5 ppm are characteristic of the 1-substituted Ad group (*cf.* Ad_2CH_2: 29.0, 37.2 and 44.6 ppm) while the 2-adamantyl group has four CH signals (2,1,1,1) and three CH_2 signals (2,2,1), the overall intensity pattern, but not the shifts, of course, being closely similar to that of the starting alcohol (except for the C_q-OH signal). The ^{13}C spectrum of the 2-substituted adamantane unit greatly resembled that of the corresponding 2-*tert*-butyl derivative **3b** and of various other 2-substituted adamantanes which have been the subject of detailed studies.[26] We feel therefore that 1,2'-biadamantyl has been unambiguously characterized for the first time but can offer no explanation for the previous results.

Conclusions

The thermolysis of highly strained tri-*tert*-alkylmethanes, AdR^1R^2CH, follows the same pattern as that of the corresponding alcohols, the higher reactivity of the latter being due to the greater relief of steric strain on going to the intermediate radical, clearly close to the homolysis transition state, and to the stabilization of both the transition state and the radical by the OH group. The activation free energies for thermolysis of the methanes are well correlated by MMP2 calculations in which the transition state is represented by the corresponding radical. Data concerning hydrogen abstraction from the solvent by the $Ad_2C^{\cdot}H$ radical, obtained by kinetic simulation of the product data for the thermolysis of tri-1-adamantylmethane in normal and deuteriated toluene, satisfy several of the criteria for proton tunnelling. When there is a 3-noradamantyl group amongst the three *tert*-alkyl groups, as in **1d**, the intermediate radical ring opens and then ring closes to give substantial amounts of 1,2'-biadamantyl, fully characterized for the first time, as well as the regular product, $AdNoradCH_2$. Since the cross-product yield is very small it is possible, to a very good approximation, to consider that the ratio of rearranged to normal product is that of the rate constants for ring opening and hydrogen abstraction from the solvent. The calculated isotope effects on hydrogen abstraction are of the same order of magnitude as for Ad_3CH

thermolysis. Comparison of the thermodynamic parameters for ring opening and hydrogen abstraction indicates that both the enthalpy and the entropy of activation are greater for ring opening. The energy required to break the C–C bond in ring opening is greater than that for hydrogen transfer from one carbon to another but, since the entropy term is much more favourable for ring opening, the two reactions proceed at comparable rates. Kinetic simulation of the product composition, taking into account the cross-products, leads to small modifications of the relative rate constants but to no change in the general conclusions. The cross-product yields are so small and difficult to determine accurately that it is not possible to establish whether there is an isotope effect on ring opening or not; paradoxically, simplifying the reaction scheme leads to a situation where kinetic simulation gives little more than relative rate constants.

Experimental

Equipment.—^{13}C NMR spectra were recorded on a Bruker AC 200 instrument operating at 50 MHz; chemical shifts of trialkylmethanes were obtained in [$^2H_8$]toluene at 80 °C and are referenced to the methyl carbon (δ = 20.5 at room temperature, relative to $CDCl_3$ δ = 77.0); other spectra were obtained in $CDCl_3$ at room temperature. Mass spectra were recorded on a Finnigan MAT ITD 800B instrument using chemical ionization (isobutane) (ITD = ion trap detector). Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}.

Noradamantane-3-carboxylic Acid.—Synthesized by the method of Black and Gill.[27]

Bicyclo[3.2.1]*octane-1-carboxylic Acid.*—Synthesized by the method of Chow, Jakas and Hoover.[28]

Alcohol Synthesis.—New alcohols, **1c**-OH (R^2 = 321Oc) and **1d**-OH (R^2 = Norad), were synthesized by reaction of the methyl ester of the appropriate carboxylic acid with excess 1-AdBr and lithium metal in THF at −20 °C and recrystallized from hexane–benzene mixtures.[4] **1c**-OH; 28%, mp 232 °C decomp. (Found: C, 85.3; H, 11.0. $C_{29}H_{44}O$ requires C, 85.23; H, 10.85%). **1d**-OH; 21%, mp 251 °C decomp. (Found: C, 85.4; H, 10.7. $C_{30}H_{44}O$ requires C, 85.65; H, 10.54%).

1-*Adamantyl* 3-*Noradamantyl Ketone* (**4**).—A solution of alcohol **1d**-OH (0.28 g, 0.67 mmol) and benzophenone (0.12 g, 0.66 mmol) in toluene (3 cm^3) was sealed in a thick-walled glass tube under vacuum. Three such samples were heated for 0.5 h at 220 °C, then cooled and opened carefully. The contents were combined, the solvent evaporated and the residue taken up in dry diethyl ether (40 cm^3). Under argon a solution of butylmagnesium bromide in diethyl ether (0.3 mol dm^{-3}; 10 cm^3, 3 mmol) was added to the stirred solution in about 5 min. This reacted only with residual benzophenone. Excess organomagnesium reagent was carefully quenched with alcohol and then water, and the mixture extracted with hexane; the hexane extract was washed and dried ($MgSO_4$), and the solvent evaporated. Chromatography on a short alumina column in light petroleum gave a fraction (0.51 g) from which the required ketone was isolated by recrystallization from hexane (0.455 g, 80%); mp 173 °C; *m/z* (ITD) 286, 285 (100%), 284, 283, 149, 136, 135, 121, 93 and 79; δ_C 28.2 (3 CH of Ad), 35.0 (CH_2), 36.6 (3 CH_2 of Ad), 37.3 (2 CH), 38.8 (3 CH_2 of Ad), 42.4 (CH), 43.4 (2 CH_2), 47.9 (2 CH_2), 47.9 (sh, C_q of Ad), 62.0 (C_q) and 216.9 (C=O) (Found: C, 84.3; H, 9.8. $C_{20}H_{28}O$ requires C, 84.45; H, 9.92%).

Semi-preparative Thermolysis of Di-1-adamantyl-3-noradamantylmethanol.—The alcohol (0.21 g, 5 mmol) was sealed after several pump–freeze–thaw cycles in a thick-walled pyrex tube with toluene (2.5 cm^3). After heating at 200 °C for 3 h the tube was cooled, opened and the solvent evaporated from the contents under reduced pressure. Chromatography of the residue on alumina with light petroleum, light petroleum–diethyl ether mixtures, diethyl ether and ethanol as eluents gave, in order of elution: adamantane (0.012 g, 18%), bibenzyl (0.043 g, 47%), 1-adamantyl 3-noradamantyl ketone (**4**) (0.044 g, 31%) and 1-adamantyl 3-noradamantylmethanol (**5**) (0.085 g, 59%), identical with the product obtained by $LiAlH_4$ reduction of the ketone; mp 196 °C; *m/z* (ITD) 285, 270, 269 (100%), 268, 267, 151, 136, 135, 121, 107, 93 and 79; δ_C 28.5 (3 CH of Ad), 35.8 (CH_2), 37.2 (3 CH_2 of Ad), 38.2 (CH), 38.4 (CH), 39.3 (C_q of Ad), 39.5 (3 CH_2 of Ad), 42.6 (CH_2), 43.4 (CH_2), 44.2 (CH_2), 46.0 (CH), 48.9 (CH_2), 54.7 (C_q) and 84.1 (CHOH) (Found: C, 83.8; H, 10.7. $C_{20}H_{30}O$ requires C, 83.86; H, 10.56%). A cross-product, representing about 10% of the total oxygen-containing products, identified as AdNoradBzCOH by comparison with the product of the following experiment, was also detected by GC, but could not be isolated. Under kinetic conditions at the same temperature **1d**-OH gave only compounds **4** and **5** in a ratio of 0.6 : 1 and a trace of cross-product.

1-(1-*Adamantyl*)-1-(3-*noradamantyl*)-2-*phenylethanol.*—A solution of 1-adamantyl 3-noradamantyl ketone (0.142 g, 0.5 mmol) and benzyl bromide (1.8 g, 11 mmol) in dry diethyl ether (15 cm^3) was run slowly onto finely chopped lithium metal (0.42 g, 0.06 g-atom) magnetically stirred in diethyl ether (10 cm^3) under argon at −20 °C. The reaction mixture was maintained at −20 °C for 30 min and then allowed to warm slowly to room temperature. The crude product (after quenching in water, hexane extraction, drying and evaporation of the solvents) was chromatographed on alumina in pentane–diethyl ether mixtures. The product was recrystallized (hexane) (0.17 g, 90%); mp 162 °C; *m/z* (ITD) 375, 357, 285, 240, 223, 149, 136, 135 (100%), 121, 91 and 79; δ_C 28.8 (3 CH of Ad), 36.1 (CH_2), 37.2 (3 CH_2 of Ad), 38.0 (CH_2), 38.1 (CH), 38.3 (3 CH_2 of Ad), 38.4 (CH), 43.2 (CH_2), 43.5 (CH_2), 44.2 (C_q of Ad), 44.4 (CH), 48.0 (CH_2), 48.3 (CH_2), 61.8 (C_q), 79.6 (C–OH), 125.8 (CH), 128.0 (2 CH), 131.3 (2 CH) and 140.0 (C_q) (Found: C, 85.9; H, 9.4. $C_{27}H_{36}O$ requires C, 86.11, H, 9.64%).

Methane Synthesis.—Methanes were prepared by treatment of the alcohols with excess oxalyl bromide in benzene at room temperature for 15 h, followed by reduction of the crude bromide by refluxing with excess Bu_3SnH and a trace of azoisobutyronitrile (AIBN) in benzene for 1–2 h. After evaporation of the solvent, the product was isolated by crystallization from benzene, hexane or mixtures thereof. **1a**: 90%, mp 283–284 °C decomp. (lit.,[1] 277 °C); δ_C 31.0 (9 CH), 38.0 (9 CH_2), 44.1 (3 C_q), 44.7 (9 CH_2) and 67.3 (CH) (Found: C, 88.7; H, 10.8. $C_{31}H_{46}$ requires C, 88.92; H, 11.08%). **1b**: 56%, mp 282 °C decomp.; δ_C 24.1 (CH), 27.7 (3 CH_2), 30.9 (6 CH of Ad), 33.9 (3 CH_2), 38.0 (6 CH_2 of Ad), 40.6 (C_q), 43.3 (2 C_q of Ad), 44.5 (6 CH_2 of Ad) and 67.1 (CH) (Found: C, 88.6; H, 11.5. $C_{29}H_{44}$ requires C, 88.70; H, 11.30%). **1c**: 37%, mp 275 °C decomp.; *m/z* (ITD) 391, 256, 255, 136, 135 (100%), 107, 93 and 79; δ_C 21.4 (CH_2), 30.1 (CH_2), 30.9 (6 CH of Ad), 32.4 (CH_2), 35.2 (CH_2), 36.0 (CH), 37.9 (CH_2 of Ad), 38.0 (CH_2 of Ad), 42.5 (CH_2), 42.8 (C_q of Ad), 44.2 (C_q of Ad), 44.4 (CH_2 of Ad), 44.8 (CH_2 of Ad), 50.4 (CH_2) 53.3 (C_q) and 69.4 (CH); note that the two adamantyl groups give separate C_q and CH_2 signals (Found: C, 88.3; H, 11.2. $C_{29}H_{44}$ requires C, 88.70; H, 11.30%). **1d**: 64%, mp > 300 °C; *m/z* (ITD) 403, 269, 268, 267, 136, 135 (100%), 121, 93 and 79; δ_C 30.8 (6 CH_2 of Ad), 36.4 (CH_2), 37.8 (2 CH), 38.0 (6 CH_2 of Ad), 42.6 (2 C_q of Ad), 43.7 (2 CH_2), 44.2 (6 CH_2 of Ad), 46.0 (CH), 53.5 (2 CH_2), 57.1 (C_q) and 69.7 (CH) (Found: C, 88.8; H, 11.0. $C_{30}H_{44}$ requires C, 89.04; H,

10.96%). **1e**: 68%, mp 267 °C decomp.; *m/z* (ITD) 377, 242, 241, 136, 135 (100%), 107 and 79; δ_C 30.8 (2 CH_2), 30.8 (6 CH of Ad), 35.4 (CH), 36.9 (br CH_2), 37.9 (6 CH_2 of Ad), 43.1 (2 C_q of Ad), 44.2 (6 CH_2 of Ad), 49.3 (CH_2), 55.1 (C_q) and 64.6 (CH) (Found: C, 88.7; H, 11.4. $C_{28}H_{42}$ requires C, 88.82; H, 11.18%). **1f**: 70% mp 241–243 °C decomp.; *m/z* (ITD) 365, 256, 255, 136, 135 (100%), 109, 93 and 79; δ_C 24.2 (2 CH), 27.6 (6 CH_2), 30.8 (3 CH of Ad), 33.8 (6 CH_2), 38.0 (3 CH_2 of Ad), 39.1 (2 C_q), 42.6 (C_q of Ad), 44.4 (3 CH_2 of Ad) and 66.8 (CH) (Found: C, 88.5; H, 11.5. $C_{27}H_{42}$ requires C, 88.45; H, 11.55%).

Kinetics and Products of Thermolysis.—General procedures for determining thermolysis rate constants[5,6] and analysis of the products[2] have been described elsewhere. For **1d**, internal standards were used in order to determine the absolute yields of the major products; these data are given in parentheses in Table 7 and are reproducible to ± 1–2%. The cross-product yields are estimates based on surface areas of ITD total ion current chromatograms, it being assumed that surface areas are proportional to molar ratios. This approximation was tested by comparing mixtures of **2a** and 1,1-diadamantyl-2-phenylethylene[1] under similar chromatographic conditions and was found to be valid in the relative concentration range concerned here. The ITD parent peaks were in all cases 359 (M − 1) and 366 (M − 1) for thermolysis in normal toluene and [$^2H_8$]toluene, respectively, corresponding to the general formula of AdNoradBzCH. There were also prominent peaks at *m/z* 269 (M − 91 or M − 98) and 135 (Ad^+). The percentages of **2d** and **3a** are normalized values corrected for the total cross-product estimate. The **2d**:**3a** ratios listed in the last column are based on calibration with standard mixtures of the authentic compounds and are reproducible to ± 2% or better.

Di-1-adamantylmethane (**2a**).—Di-1-adamantylmethanol was converted into the bromide by reaction with thionyl bromide in pyridine. The bromide was reduced by refluxing with Bu_3SnH and AIBN in benzene to give **2a** in 96% yield after chromatography on alumina in light petroleum: mp 184.5 °C (lit.,[29] 171–177 °C); *m/z* (ITD) 283, 148, 136, 135 (100%), 109, 95, 93 and 79; δ_C 29.0 (6 CH), 34.8 (2 C_q), 37.2 (6 CH_2), 44.6 (6 CH_2) and 59.5 (CH_2).

Semi-preparative Thermolysis Experiments.—Duplicate samples of the hydrocarbons (50 mg) dissolved in toluene (2.5 cm^3) with benzenethiol (0.05 cm^3) were sealed *in vacuo* in medium thick-walled pyrex tubes (total volume 9–10 cm^3) after 2–3 freeze–pump–thaw degassing cycles. The tubes were held in an oil bath at appropriate temperatures between 235 and 270 °C for times corresponding to 10 half-lives. The tubes were cooled before opening, the samples combined and the solvent and residual thiol evaporated at reduced pressure. Chromatography on alumina in light petroleum separated hydrocarbons (including some adamantane) from disulfide. The hydrocarbons were either taken up in $CDCl_3$ for NMR analysis or in hexane for crystallization. Alkanes **2b** and **c** could not be freed of **2a**, and **2f** could not be freed of **2b**, but all compounds were adequately identified by ITD MS and NMR spectroscopy. The ^{13}C NMR spectra are listed as follows: shifts of the 1-adamantyl group are given first, then those of the second moiety (if it is not also 1-Ad) and finally that of the 'central' methylene group.

1-*Adamantyl*-1-*bicyclo*[2.2.2]*octylmethane* (**2b**).—*m/z* (ITD) 257, 149, 136, 135 (100%), 122, 107, 93 and 79; δ_C 29.0 (3 CH), 34.6 (C_q), 37.1 (3 CH_2), 44.6 (3 CH_2); 24.2 (CH), 26.5 (3 CH_2), 31.9 (C_q), 32.8 (3 CH_2) and 57.0 (CH_2).

1-*Adamantyl*-1-*bicyclo*[3.2.1]*octylmethane* (**2c**).—*m/z* (ITD) 257, 149, 136, 135 (100%), 122, 107, 93 and 79; δ_C 29.0 (3 CH), 34.4 (C_q), 37.1 (3 CH_2), 44.3 (3 CH_2); 20.3, 29.6, 32.3, 37.4, 38.5 and 47.5 (6 CH_2), 35.6 (CH), 44.7 (C_q) and 57.2 (CH_2).

1-*Adamantyl*-3-*noradamantylmethane* (**2d**).—Yield 30%; mp 177 °C; *m/z* (ITD) 270, 269, 136, 135 (100%), 121, 107, 93 and 79; δ_C 28.9 (3 CH), 34.8 (C_q), 37.2 (3 CH_2), 44.1 (3 CH_2); 35.2 (CH_2), 38.7 (2 CH), 43.1 (2 CH_2), 48.5 (CH), 49.1 (C_q), 50.7 (2 CH_2) and 56.0 (CH_2) (Found: C, 88.8; H, 11.0. $C_{20}H_{30}$ requires C, 88.82; H, 11.18%).

1-*Adamantyl*-1-*norbornylmethane* (**2e**).—Yield 33%; mp 117 °C; *m/z* (ITD) 243, 215, 136, 135 (100%), 121, 108, 107, 93 and 79; δ_C 28.9 (3 CH), 34.4 (C_q), 37.2 (3 CH_2), 44.0 (3 CH_2); 31.6, 35.8 and 47.6 (3 CH_2), 35.2 (CH), 47.7 (C_q) and 51.7 (CH_2) (Found: C, 88.7; H, 11.4. $C_{18}H_{28}$ requires C, 88.45; H, 11.55%).

Di-1-bicyclo[2.2.2]*octylmethane* (**2f**).—*m/z* (ITD) 232, 231, 203, 161, 149, 148, 135, 123, 122, 121, 109 (100%), 108, 91, 81, 80 and 79; δ_C 24.2 (2 CH), 26.5 (6 CH_2), 31.8 (2 C_q), 32.7 (6 CH_2) and 54.5 (CH_2).

1,2′-*Biadamantyl* (**3a**).—*Method A.* 2-(1-Adamantyl)adamantan-2-ol[30] (0.41 g) in benzene (10 cm^3) was treated with oxalyl bromide (0.5 cm^3) at room temperature for 15 h. The solvent and residual oxalyl bromide was evaporated off and the crude bromide refluxed with Bu_3SnH (0.5 cm^3) and AIBN (20 mg) in benzene (10 cm^3) for 1.5 h. After evaporation of the solvent the residue was treated with a solution of bromine in carbon tetrachloride, added dropwise until a light yellow colouration persisted. The product was chromatographed on alumina in pentane, then crystallized from hexane (0.393, 73%); mp 166 °C (lit.,[20,21] 266–268, 263 °C); *m/z* (ITD) 270, 269, 136, 135 (100%), 134, 121, 107, 93 and 79; δ_C 29.1 (3 CH), 35.7 (C_q), 37.3 (3 CH_2), 42.5 (3 CH_2); 27.2 (CH), 28.4 (2 CH), 28.9 (CH), 33.8 (2 CH_2), 38.6 (CH_2), 41.8 (2 CH_2) and 55.9 (CH) (Found: C, 88.9; H, 11.2. $C_{20}H_{30}$ requires C, 88.82; H, 11.18%).

Method B.[25] Trifluoroacetic acid (1.8 cm^3) was added with magnetic stirring to dichloromethane (15 cm^3) at *ca.* 5 °C (ice bath). 2-(1-Adamantyl)adamantan-2-ol (0.25 g; 0.87 mmol) was washed in with a little dichloromethane (5 cm^3), followed by the immediate addition of triethylsilane (0.8 cm^3). The ice bath was removed and the mixture stirred for 2 h. Hexane was added to the reaction mixture which was then washed with water, dried ($MgSO_4$), and the solvent evaporated to leave the required product (0.232 g) as a slightly off-white solid, purified by chromatography on alumina in pentane (0.211 g, 89% yield, mp 166 °C), identical with material from method A.

Method C.[25] Trifluoroacetic acid (1.0 cm^3) was added with magnetic stirring to dichloromethane (10 cm^3) at *ca.* 5 °C (ice bath). The mixture was transferred to a flask containing 1-adamantyl-3-noradamantylmethanol (100 mg, 0.35 mmol), to which was then immediately added triethylsilane (0.4 cm^3). After 2 h stirring hexane was added to the reaction mixture which was then washed with water, dried ($MgSO_4$) and the solvent evaporated to leave **3a** (93 mg, 98% crude yield), identical with material from method A.

Wurtz Reaction of Bromoadamantanes.[21,22]—1-Bromoadamantane (0.5 g) and 2-bromoadamantane (0.5 g) were mixed in xylene (5 cm^3) and refluxed for 8 h with sodium metal (0.1 g). GC of the crude reaction product showed 1,1-, 2,2′- and 1,2′-biadamantyls in a ratio of 1:7:5. The last component has GC–ITD-MS characteristics identical with those of the synthetic 1,2′-biadamantyl and of the second product from thermolysis of **1d**.

2-tert-*Butyladamantane* (**3b**).—From 2-*tert*-butyladamantan-2-ol[31] by Duddeck's procedure,[25] followed by chromatography on alumina in pentane; *m/z* (ITD) 192, 191, 149, 135 (100%),

121, 107, 93 and 79; δ_C 27.8 (CH), 28.8 (CH), 29.5 (2 CH), 30.6 (3 CH_3), 33.1 (2 CH_2), 33.9 (C_q), 38.7 (CH_2), 41.9 (2 CH_2) and 54.1 (CH). These values are 0.1–0.4 ppm lower than those reported elsewhere.[32]

Molecular Mechanics Calculations.—Strain energies were calculated with Allinger's MMP2(85)[7] and MM3(89)[8] force fields, using block matrix minimization. In MM3 there is a full matrix minimization option but, while this converged correctly for dialkylmethanes, giving slightly improved energy minima, with congested trialkylmethanes it either aborted for computational reasons or failed to give the required six zero eigenvalues. Only the block matrix energy minima are given. In all cases the same preferred conformations, to within a few degrees, were found with both force fields. The steric energies of the transition states for ring opening are based on the MMP2 force field with the addition of Spellmeyer and Houk's parameter set.[17]

In calculating the heat of formation and the strain energy from the steric energy, the datum resulting directly from the minimization procedure in molecular mechanics, Allinger takes into account torsional motions of molecules by adding an increment of 0.36 kcal mol^{-1} for each torsional barrier below 7 kcal mol^{-1}, zero if it is higher. In the past we have generally allowed for two low torsional barriers in di-*tert*-alkylmethanols and zero in tri-*tert*-alkylmethanols. However, in the absence of sufficient information regarding these barriers (values of 10–15 kcal mol^{-1} were found for some tri-*tert*-alkylmethanols[33]), particularly in hydrocarbons and radicals, we have decided to neglect this correction. Since we are always comparing differences between similar structures, the slopes of strain energy correlations will be unchanged, and the effect on the intercept is of no great importance since it is never known with any degree of precision.

Kinetic Simulation by the SSAIKS Program.[3,5,15]—Calculations were based on Scheme 2 and the product data for thermolysis of **1d** in [$^1H_8$]toluene and [$^2H_8$]toluene. As usual, reactions (1) and (2) were expressed by a single reaction where the trialkylmethane thermolyses in toluene to give the radical AdNoradC$^{\bullet}$H, benzyl radical and adamantane. Ring closure (k_{close}) and intramolecular hydrogen migration (k_{migr}) were assumed to be fast compared with other processes and, for this reason, do not enter into the rate equations for simulation. Ring-opened and 1,2′-biadamantyl radicals were assigned the same rate constant for hydrogen abstraction from the solvent. Recombination rate constants, k_4 and k_5, were set arbitrarily equal to k_6, which was calculated by extrapolation of Fischer's data.[19] For [$^2H_8$]toluene three rate constants, k_3[SD], k_{open} and k_3'[SD], were optimized. The only effect of altering k_5 was to modify k_3[SD] in the same proportion; changing k_4 modified the optimized values of k_3[SD] and k_{open} in the same proportion. Surprisingly, k_3[SD] and k_{open} were very sensitive to variations in the relative amounts of CP/R and CP/N, but relatively insensitive to the total amount of cross-product. In no case, however, was the k_3[SD]/k_{open} ratio seriously affected. Attempts to optimize the same three constants for normal toluene showed random variations with the temperature. Values of the k_{open}, calculated for [$^2H_8$]toluene, were therefore used and the other two constants, k_3[SH] and k_3'[SH], optimized. The resulting values are listed in Table 8.

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