Clean Radical-induced Isomerisation of Homoadamantane to 1- and 2-Methyladamantane

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Homoadamantane slowly rearranges at 400 °C to a mixture of 1- and 2-methyladamantane (*ca.* 2.5:1 ratio) in a reaction which is accelerated by a radical initiator. The products from rearrangement of [4-^{13}C]-, [4,4-D_2]-, and [3,6-D_2]-homoadamantane are consistent with mechanisms involving initiation by abstraction of hydrogen from the 3- and 4-position of homoadamantane, rearrangement by elimination–readdition in the radicals formed, and chain transfer through hydrogen abstraction by the 1- and 2-adamantylmethyl radicals.

Tricyclic $C_{11}H_{18}$ hydrocarbons undergo extensive rearrangements *via* carbenium ions in the presence of protic[1-3] or Lewis[4,5] acids. Homoadamantane (**1**) plays an important role in these processes which ultimately[1,2,4,6] lead to 1- and 2-methyladamantane (**2**) and (**3**). The heats of formation, $\Delta H_f°$ (gas), of these hydrocarbons are calculated as (**1**) −114.5,[7] (**2**) −169.7, and (**3**) −154.5 kJ mol^{-1}, respectively.[8] It has recently been shown that the electron-impact induced fragmentation of homoadamantane involves reversible rearrangement between the radical cations of (**1**) and (**2**).[9a]

We have found that homoadamantane slowly rearranges to 1- and 2-methyladamantane on static thermolysis at 400 °C even though it is stable to flash vacuum pyrolysis at 1 500 °C and despite there being not enough activation energy available at 400 °C for homolysis of any C–H or C–C bond in homoadamantane. Studies on ^{13}C- and D-labelled (**1**) lead us to propose the radical-induced mechanisms shown in Scheme 1.[9b]

Experimental

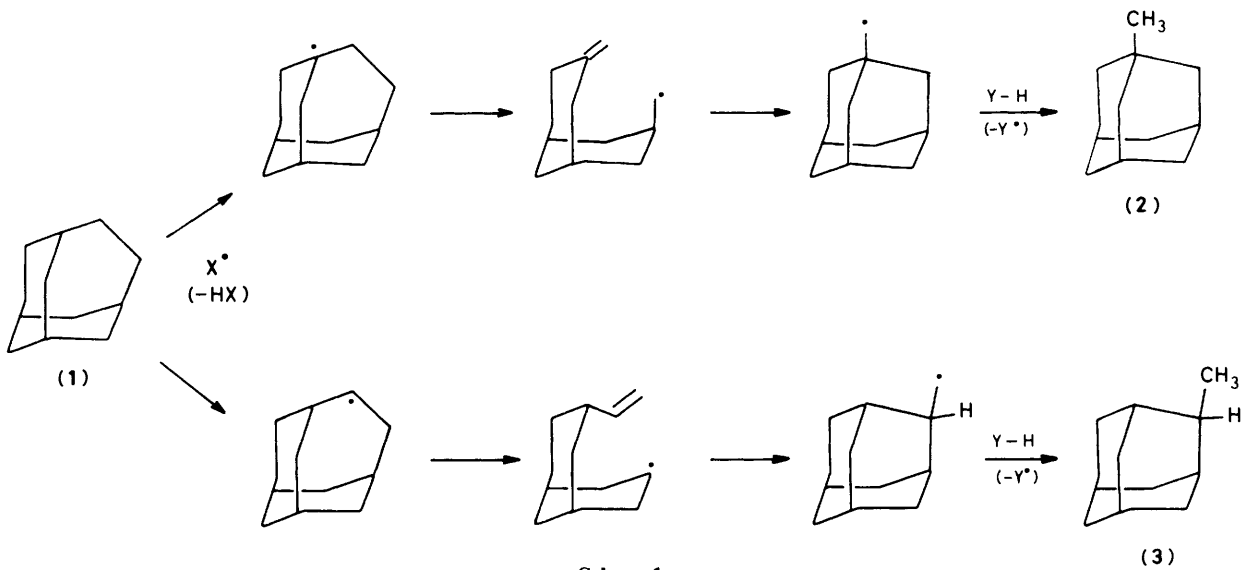
^{13}C N.m.r. spectra were recorded at 100.62 MHz on a Bruker WM400 instrument, and mass spectra were measured on a Finnigan MAT711A instrument. G.c.–m.s. work was performed on a Finnigan MAT112S mass spectrometer coupled to a Carlo Erba Fractovap instrument using glass capillary columns.

Homoadamantane (**1**) was prepared by a literature procedure,[10] δ_C ($CDCl_3$) 27.51 (C-1, C-8), 31.87 (C-3, C-6), 33.82 (C-4, C-5), 36.73 (C-9), and 38.26 p.p.m. (C-2, C-7, C-10, C-11).

[4-^{13}C]Homoadamantane (**4**) was prepared by Wolff–Kishner reduction of [5-^{13}C]homoadamantan-4-one[11] in 83% yield, m.p. 259 °C. C-4 was labelled to the extent of 80.3% (by m.s.).

[4,4-D_2]Homoadamantane (**5**) was prepared by the method of Rüchardt *et al.*[12] from 3-(dideuteriohydroxymethyl)adamantane by ring enlargement *via* Koch–Haaf synthesis and subsequent decarboxylation of the corresponding t-butyl perester. The product was 98.1% D_2, 1.9% D_1 by mass spectrometric measurement. Proton-decoupled ^{13}C n.m.r. gave δ_C ($CDCl_3$) 27.52 (C-1, C-8), 31.70 (C-3), 31.87 (C-6), 33.0 [C-4, *quintet*, J(C-D)$_C$ 19.18 Hz], 33.61 (C-5), 36.37 (C-9), 38.20 (C-2, C-10), and 38.27 p.p.m. (C-7, C-11).

[3,6-D_2]*Homoadamantane* (**6**). An oven-dried 100 ml steel autoclave was charged with D_2O (5 ml), closed, heated to 150 °C for several hours, and again dried. The autoclave was charged with dimethyl 2,7-dioxohomoadamantane-3,6-dicarboxylate[10] (460 mg, 1.56 mmol) and 20% DCl in D_2O (2 ml)



Scheme 1.

and heated for 40 min to 120 °C. The temperature was then increased to 280 °C and maintained there for 1.5 h. The reaction mixture was distributed between petroleum (b.p. 30—50 °C) and water, the petroleum solution dried ($MgSO_4$) and evaporated on a rotary evaporator in a cold water-bath. The yellow oil which resulted was chromatographed on silica gel and then subjected to Wolff–Kishner reduction yielding of pure [3,6-D_2]*homoadamantane* (**6**) (74.7 mg, 31.4%), m.p. 255—257 °C, 93.6% D_2, 6.4% D_1 by m.s. Proton-decoupled ^{13}C n.m.r. gave δ_C ($CDCl_3$) 27.43 (C-1, C-8), 31.36 [C-3, C-6, triplet, J (C-D) 19.22 Hz], 33.66 (C-4, C-5), 36.36 (C-9), and 38.14 p.p.m. (C-2, C-7, C-10, C-11). These assignments and labelling positions for (**4**)—(**6**) are in agreement with previous work.[13]

Thermolysis Procedure.—Compounds (**1**) and (**4**)—(**6**) (10 or 20 mg) were placed in Pyrex ampoules, which were cooled (liquid N_2) and sealed under vacuum (< 0.1 Torr). The ampoules had a volume of *ca.* 37 ml when sealed. Ampoules were heated at 400 ± 1 or 410 ± 1 °C in the oven of a gas chromatograph. In some experiments ampoules were pre-treated with D_2O or [$^2H_8$]toluene (see Results section). Product yields were determined by g.c. on a 2.5 m packed column of SE-52, at 120 °C. The deuterium content of the products from the thermolyses of (**5**) and (**6**) were obtained by g.c.—m.s. measurement using a 20 m glass capillary column coated with SE-30, at 180 °C.

Results

The products from thermolysis of homoadamantane (**1**) are shown in Table 1, which also demonstrates that the reaction products (**2**) and (**3**) are stable under the reaction conditions. The rearrangement is clearly stimulated by the addition of AIBN, although this is hardly an ideal initiator for these reaction conditions. Reactions are clean with high recovery of $C_{11}H_{18}$ material, but capillary g.c. revealed a small peak, just resolved from that of 1-methyladamantane, amounting to 2.5% of the products. G.c.—m.s. showed this to be a $C_{11}H_{18}$ isomer (*m/z* 150) with a base peak at *m/z* 93. Since the *m/z* 135 peak is small [7%; it is the base peak for (**2**) and (**3**)], this compound lacks a methyl group. As the unknown was not resolved from (**2**) on packed-column g.c., no attempt at isolation was made.

When thermolyses were carried out in ampoules pretreated with D_2O or [$^2H_8$]toluene, the products contained deuterium (20—37% D_1).

The rearrangement products from [4-^{13}C]homoadamantane (**4**) were analysed by ^{13}C n.m.r. spectroscopy.[14] In 1-methyladamantane, the ^{13}C label was equally distributed between the methyl group at δ_C 31.5 and the methylene group adjacent to the methyl-substituted bridgehead (δ_C 44.7 p.p.m.). The 2-methyladamantane product consisted, within experimental error, of equal portions of [2-^{13}C-methyl]adamantane (δ_C 18.9) and 2-methyl[2-^{13}C]adamantane (δ_C 33.9 p.p.m.). The label in the homoadamantane reisolated from thermolysis was not scrambled at all.

The products from thermolyses of [4,4-D_2]- (**5**) and [3,6-D_2]-homoadamantane (**6**) were analysed for their deuterium content by g.c.—m.s. and the results are in Table 2. The most significant finding is that from (**5**), the 1-methyladamantane is mainly doubly labelled but there is a substantial loss of label in the 2-methyladamantane, whereas from (**6**) the situation is reversed. [3,6-D_2]Homoadamantane (**6**) gives mainly [D_1]-1-methyladamantane but the 2-methyladamantane is still largely doubly labelled. Besides these main products, there is clearly some general exchange of deuterium, with both products and recovered starting material showing gain (D_3) and loss (D_1 and D_0) of deuterium.

Discussion

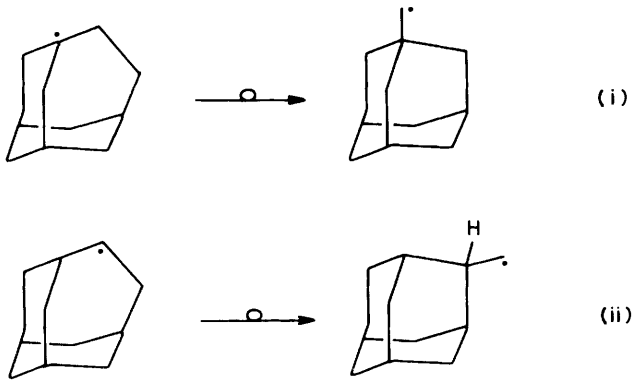
Several lines of evidence point to the rearrangement we have observed being a radical-induced process and not a simple unimolecular process. The apparent half-life for rearrangement translates into $\Delta G^{\ddagger}$ *ca.* 240 kJ mol^{-1}. Since the weakest C–C bond in homoadamantane probably has bond dissociation energy of > 330 kJ mol^{-1}, mechanisms involving bond cleavage to a biradical are improbable. The lack of rearrangement on flash thermolysis at *ca.* 1 500 °C is in agreement with this. The acceleration of rearrangement produced by AIBN points to a radical-induced process. The only plausible

Table 1. Thermolysis of homoadamantane (**1**) at 400 °C (20 mg) in Pyrex ampoules (37 ml)

	Reaction time (h)	Product ratio (%) 1-Methyladamantane	2-Methyladamantane	Homoadamantane
Homoadamantane	10	12.8	4.5	81.2
	20	21.2	8.7	67.9
	40	28.7	11.6	56.8
Homoadamantane + azobis-isobutyronitrile (3 mg)	40	63.4	19.5	17.1
1-Methyladamantane	20	100		
2-Methyladamantane	20		100	

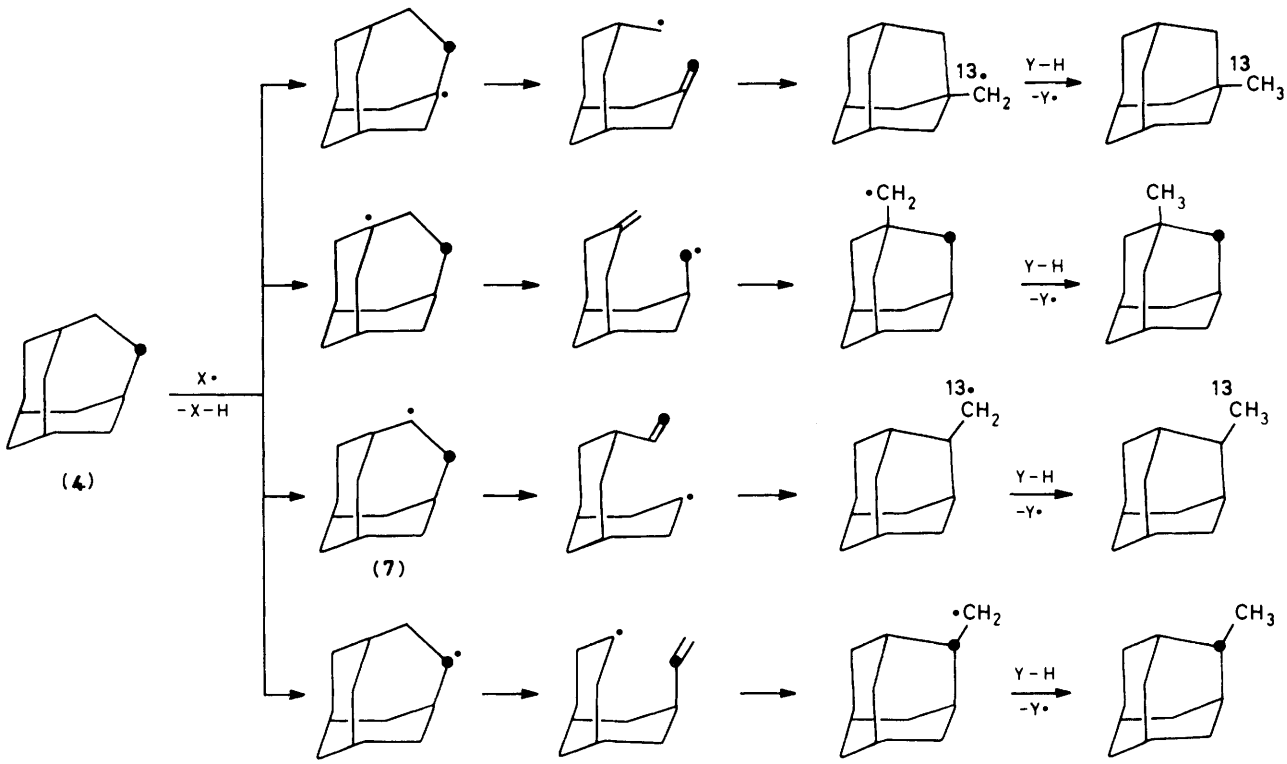
Table 2. Thermolysis of the deuteriated homoadamantanes (**5**) and (**6**) (10 mg; 410 °C; 10 h) in Pyrex ampoules (37 ml)

	Product ratio and deuterium distribution 1-Methyladamantane	2-Methyladamantane	Homoadamantane
[4,4-D_2]Homoadamantane; 98.1% D_2, 1.9% D_1	14.9% 4% D_3, 89.6% D_2, 4.5% D_1, 1.9% D_0	11.6% 2.7% D_3, 75.3% D_2, 20.8% D_1, 1.2% D_0	73.5% 0.2% D_3, 96.2% D_2, 3.1% D_1, 0.6% D_0
[3,6-D_2]Homoadamantane; 93.6% D_2, 6.4% D_1	15.2% 0.9% D_3, 14.2% D_2, 80.4% D_1, 4.5% D_0	12.1% 8.9% D_3, 79.7% D_2, 10% D_1, 1.4% D_0	72.7% 7.3% D_3, 81.0% D_2, 9.4% D_1, 2.3% D_0



reversible at the temperatures used here,[17,20] although the energetics of these processes will obviously be modified by strain effects in intramolecular cases. Thus we assume elimination–addition sequences in Schemes 1—4 because, although none of our evidence specifically requires this mechanism, it is energetically plausible.

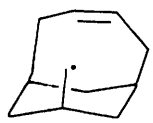
Routes to the observed products of thermolysis of [4-^{13}C]homoadamantane (**4**) are shown in Scheme 2; the labelling is precisely accounted for. It is interesting that for the radical (**7**), the alternative β-scission leading to symmetrical radical (**8**) does not compete. If (**8**) were formed, recovered homoadamantane would have some of its ^{13}C label scrambled to C-2. It should be noted that (**8**) is a primary radical whereas the productive β-scission gives a secondary radical.



Scheme 2.

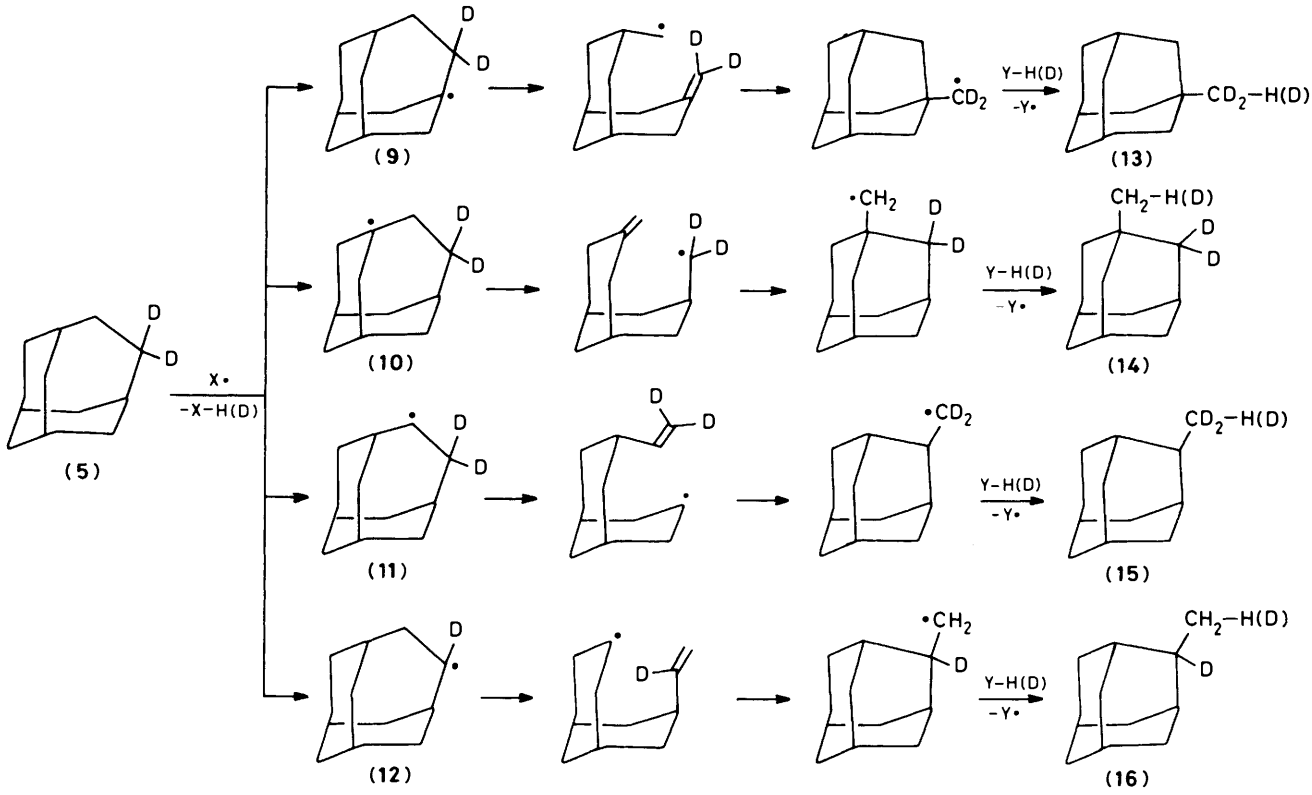
initiation process with homoadamantane is hydrogen abstraction and this is supported by the observation of deuterium incorporation from the ampoules which had been pretreated with D_2O or [$^2H_8$]toluene and by the gain and loss of deuterium in both starting materials and products during thermolysis of [4,4-D_2]- and [3,6-D_2]-homoadamantane (**5**) and (**6**).

The products from the thermolyses of ^{13}C and D_2-labelled homoadamantanes are in excellent accord (see below) with rearrangement of the 3-homoadamantyl radical to the 1-adamantylmethyl radical [equation (i)] and of the 4-homoadamantyl radical to the 2-adamantylmethyl radical [equation (ii)]. It is likely that these radical to radical rearrangements occur by elimination (β-scission)–addition processes rather than by direct 1,2-alkyl shift. The available evidence[15,16] indicates that the latter process has a very high activation energy at best, whereas the former occurs readily[15-17] and has been previously implicated in some radical-induced rearrangements.[18,19] Addition of alkyl radicals to alkenes is known to be

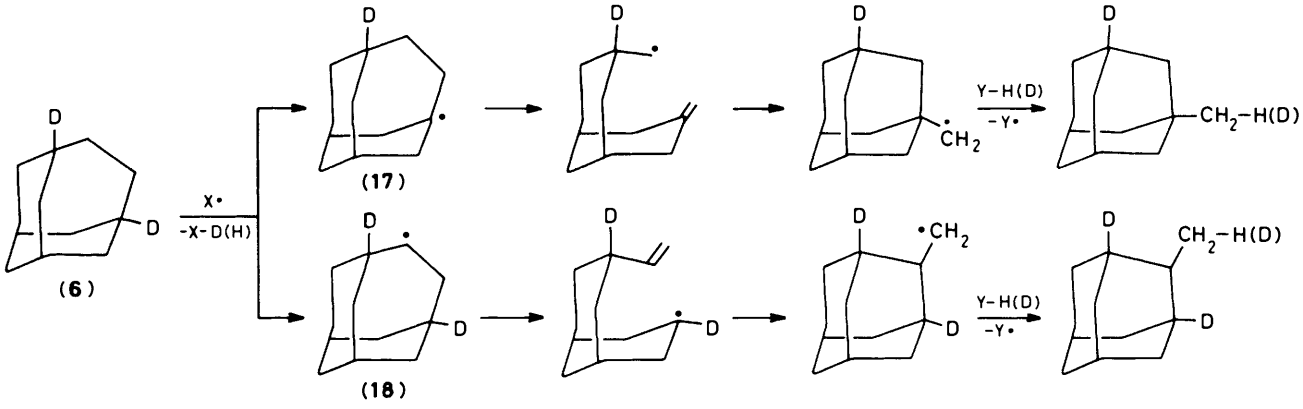


(**8**)

Hydrogen abstraction of [4,4-D_2]homoadamantane (**5**) can give the dideuteriated, isotopomeric, bridgehead radicals (**9**) and (**10**), the dideuteriated radical (**11**) and the monodeuteriated (**12**) (Scheme 3). The dideuterated 1-methyladamantanes (**13**) and (**14**) ultimately result from (**9**) and (**10**), whereas (**11**) and (**12**) give dideuteriated (**15**) and monodeuteriated (**16**), respectively, assuming hydrogen atom transfer in the final step. Small amounts of products containing three deuterium atoms are observed. These obviously come from the deuterium atom transfer which produces (**12**), and this indicates chain transfer in the reaction. The chain length is unknown but the majority of



Scheme 3.



Scheme 4.

products probably come from homogeneous reaction in the gas phase with bimolecular hydrogen (deuterium) transfer as the chain transfer step. The incorporation of deuterium from the walls of ampoules pretreated with D_2O or [$^2H_8$]toluene may indicate some hydrogen (deuterium) abstraction at the walls, although this exchange could be an independent (acid-catalysed?) reaction.

The ratio of mono- to di-deuteriated 2-methyladamantane (75.3/20.8 = 3.62) may be taken as approximately that of (**15**):(**16**) and thus of (**11**):(**12**), although a little of the dideuteriated product will be (**16**) which abstracted deuterium in the final step. A kinetic isotope effect of *ca.* 3.5 at 400 °C is close to the maximum value expected at this temperature. This is in agreement with literature data for known radical hydrogen abstractions, which leads one to expect maximal k_H/k_D values for nearly thermoneutral hydrogen transfers.[21]

In the thermolysis of [3,6-D_2]homoadamantane (**6**) (Scheme 4) the 1-methyladamantane should be derived from (**17**) and should be mainly monodeuteriated, as observed, whereas the 2-methyladamantane, deriving from (**18**), should be mainly dideuteriated. As before the chain transfer step may involve deuterium abstraction, leading to some redistribution of the label in both the products and in reisolated homoadamantane.

In Schemes 1—4, hydrogen abstraction occurs from the 3-(bridgehead) and 4-(CH_2CH_2 bridge) position of homoadamantane. Hydrogen abstraction must occur at the remaining positions of homoadamantane under the reaction conditions. The radicals formed could undergo β-scission and readdition

giving, after hydrogen transfer, new $C_{11}H_{18}$ isomers. One of these could be the minor product observed by capillary g.c.—m.s. As pointed out in the Results section this unknown does not possess a methyl group and so it cannot be derived from a bridgehead homoadamantyl radical. There are five other non-methylated $C_{11}H_{18}$ isomers which can be derived from homoadamantane by a single rearrangement; all are less stable than homoadamantane according to force field calculations.[22]

In summary we have observed quite clean thermal isomerisation of homoadamantane to its stabilomers, 1- and 2-methyladamantane, by a radical-induced mechanism. The reaction is important as one of the simplest of a growing class of radical-induced thermal rearrangements. As in the present instance, rearrangements by this type of mechanism are observed (a) when there are no good unimolecular mechanisms available, and (b) when the necessary rearrangement of the intervening radicals can occur by a low activation energy pathway such as β-scission–readdition[17-19] or homallyl–cyclopropylcarbinyl rearrangement.[16,23,24]

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