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

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The title rearrangements occur by hydrogen abstraction from the 3- and 4-positions of homoadamantane, rearrangement by elimination–addition in the radicals formed, and chain transfer through hydrogen abstraction by the 1- and 2-adamantylmethyl radicals.

Several rearrangements which might occur by simple unimolecular concerted or biradical processes have been shown to proceed instead by radical-induced mechanisms in which the actual rearrangement steps occur in radicals.[1–3] We report the simplest case discovered so far, the rearrangement of homoadamantane (**1**) to 1- and 2-methyladamantane, (**2**) and (**3**). The evidence outlined below is consistent with the mechanisms shown in Scheme 1.

Thermolysis of homoadamantane (20 mg) in a Pyrex ampoule (37 ml capacity) for 40 h at 400 °C gave a mixture of 56.8% (**1**), 28.7% (**2**), and 11.6% (**3**).† An identical thermolysis, but with azobisisobutyronitrile (AIBN) (3 mg) added, gave a much greater conversion, 17.1% (**1**), 63.4% (**2**), and 19.5% (**3**). The apparent $\Delta G^{\ddagger}$ (*ca.* 240 kJ mol^{-1}) is so much less than the dissociation energy of any C–C bond in homoadamantane (>330 kJ mol^{-1}) that biradical formation can be discounted. The accelerating effect of AIBN is consistent with the involvement of radicals, the only plausible initiation process being hydrogen abstraction. When thermolyses are conducted with ampoules pretreated with D_2O or [$^2H_8$]toluene, the products contain deuterium.

The rearrangement products from [4-^{13}C]homoadamantane‡ are entirely consistent with Scheme 1. In the 1-methyladmantane formed, the ^{13}C label is equally distributed between the methyl group and a methylene adjacent to the methyl-substituted bridgehead. The 2-methyladamantane product consists of equal amounts of [2-^{13}C-methyl]- and 2-methyl[2-^{13}C]-adamantane.

The most convincing evidence for the mechanisms in Scheme 1 comes from the thermolyses of deuteriated homoadamantanes (Table 1). Thus in the thermolysis of [3,6-$^2H_2$]homoadamantane most of the 1-methyladamantane product is monodeuteriated, indicating that this compound results from abstraction from the bridgehead position as in Scheme 1. The 2-methyladamantane product and recovered homoadamantane are mainly dideuteriated, as expected. In the thermolysis of [4,4-$^2H_2$]homoadamantane, it is the 2-methyladamantane which shows substantial loss of deuterium. This product, according to Scheme 1, derives from competing deuterium abstraction from C(4) and hydrogen

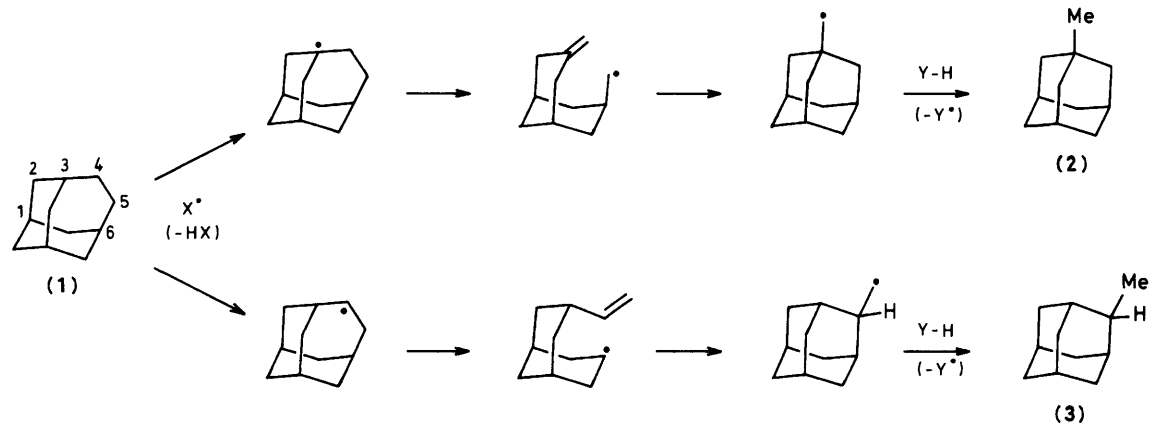
† Capillary g.c. showed the presence of *ca.* 2.5% of a third product eluting with (**2**) in packed column g.c. G.c.–mass spectroscopy showed this product to be another $C_{11}H_{18}$ isomer; its nature will be discussed in the full paper. Apart from this, the thermolyses were very clean, with essentially no formation of involatile products. Both (**2**) and (**3**) are completely stable in the thermolysis conditions.

‡ Prepared by Wolff–Kishner reduction of [5-^{13}C]homoadamantan-4-one (ref. 4).

Table 1. Thermolysis of the deuteriated homoadamantanes.[a]

Starting compound	Product ratio and deuterium distribution (all %)		
	1-Methyladamantane	2-Methyladamantane	Homoadamantane
[3,6-$^2H_2$]Homoadamantane;[b]	15.2	12.1	72.7
93.6% $^2H_2$, 6.4% $^2H_1$	0.9 $^2H_3$, 14.2 $^2H_2$, 80.4 $^2H_1$, 4.5 $^2H_0$	8.9 $^2H_3$, 79.7 $^2H_2$, 10 $^2H_1$, 1.4 $^2H_0$	7.3 $^2H_3$, 81.0 $^2H_2$, 9.4 $^2H_1$, 2.3 $^2H_0$
[4,4-$^2H_2$]Homoadamantane;[c]	14.9	11.6	73.5
98.1% $^2H_2$, 1.9% $^2H_1$	4 $^2H_3$, 89.6 $^2H_2$, 4.5 $^2H_1$, 1.9 $^2H_0$	2.7 $^2H_3$, 75.3 $^2H_2$, 20.8 $^2H_1$, 1.2 $^2H_0$	0.2 $^2H_3$, 96.2 $^2H_2$, 3.1 $^2H_1$, 0.6 $^2H_0$

[a] Thermolyses were conducted by sealing the compound (10 mg) in Pyrex ampoules (37 ml capacity) and heating at 410 °C for 10 h. [b] Prepared from dimethyl 2,7-dioxo-homoadamantane-3,6-dicarboxylate (ref. 5) by hydrolysis–decarboxylation in DCl–D_2O, followed by Wolff–Kishner reduction. [c] Prepared by the method of Rüchardt *et al.* (ref. 6) from 3-(dideuteriohydroxymethyl)adamantane by ring enlargement *via* Koch–Haaf synthesis and subsequent decarboxylation of the t-butyl perester.



Scheme 1

abstraction from C(5). The ratio of $^2H_2$ to $^2H_1$ product can be used to derive an approximate value for k_H/k_D *ca.* 3.5, close to the maximum value expected at 400 °C and consistent with nearly thermoneutral hydrogen transfers between YH and X•, where X• and Y• are similar radicals.[7] This, and the occurrence of some degree of general deuterium scrambling (Table 1), points to chain transfer as in Scheme 1 with YH often being homoadamantane. Although initiation may be a heterogeneous wall reaction, most of the products are probably formed by purely gas-phase processes.

The radical-to-radical rearrangements in Scheme 1 are shown as elimination (β-scission)–addition processes. Our results do not require this, but it is in accord with the lack of simple 1,2-shifts in radicals[8,9] and the easy reversibility of radical addition to alkenes at high temperatures.[10,11]

We believe that many clean, radical-induced, rearrangements may await discovery. They may be expected (a) when no good unimolecular mechanisms are available for achieving a thermodynamically-favourable rearrangement, and (b) when radicals can be generated by addition or abstraction processes which can then rearrange by low activation energy pathways such as β-scission–readdition (*e.g.* the present example) or the homoallyl–cyclopropylmethyl rearrangement (as in the azulene–naphthalene case).§

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§ Under flash thermolysis conditions, it has been shown that the azulene–naphthalene rearrangement occurs mainly *via* non-radical intermediates (ref. 12).

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