

## An EPR Study of 1-Adamantylmethyl Radicals

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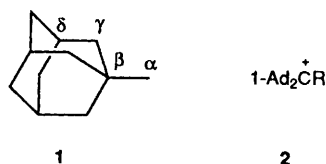
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The 1-adamantylmethyl, di(1-adamantyl)methyl, and tri(1-adamantyl)methyl radicals have been prepared by photolysis of hexabutylditin in presence of the corresponding bromide, the 1-adamantylhydroxymethyl radical by photolysis of di-*tert*-butyl peroxide in presence of 1-adamantylmethanol, and the di-1-adamantylketyl radical anion by photolysis of di-1-adamantyl ketone in presence of sodium-potassium alloy. The EPR  $^1\text{H}$  and  $^{13}\text{C}$  hyperfine coupling constants which are observed in these radicals and in the tetra-1-adamantylcyclobutadiene radical cation are discussed in terms of the structures of the radicals.

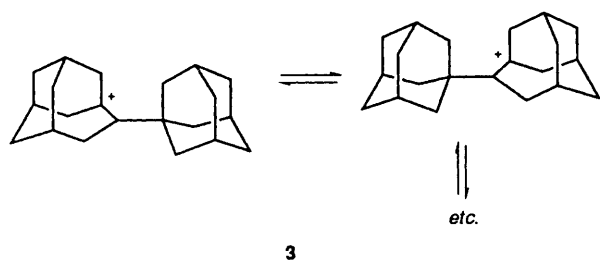
The di-1-adamantylmethyl radical decays in cyclopentane at 310 K and in toluene at 180–240 K by clean pseudo first-order kinetics. The reaction is much faster in the latter solvent, implying that it involves abstraction of benzylic hydrogen. At 190 K in pentane, the decay shows second-order kinetics. The decay of the tri-1-adamantylmethyl radical shows more complicated behaviour.

A common technique for increasing the lifetime of reactive intermediates such as alkyl cations<sup>1</sup> or radicals<sup>2</sup> is to protect the reactive centre with bulky substituents which slow down bimolecular reactions. Tertiary alkyl groups are often used for this purpose, and 1-adamantyl groups (1-Ad;  $\mathbf{1} = \text{1-Ad-C}$ ) are particularly useful because they have a rigid, stable, framework, and have no hydrogen on the  $\beta$ -position which could be involved in an elimination process.

Olah, Schleyer and Prakash and their collaborators<sup>3,4</sup> have generated the 1-adamantylalkyl cations ( $\mathbf{2}$ ;  $\text{R} = \text{Me, Et, Ph, OH,}^3 \text{ 1-Ad}^4$ ) from solutions of the appropriate precursors 1- $\text{Ad}_2\text{CRX}$  ( $\text{X} = \text{OH or halogen}$ ) in  $\text{SO}_2\text{ClF}$  containing  $\text{SbF}_3$ ,  $\text{FSO}_3\text{H}$ , or  $\text{SbF}_5/\text{FSO}_3\text{H}$  at *ca* 195 or 143 K.

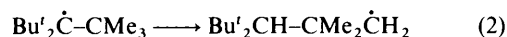
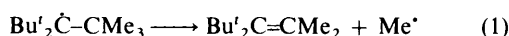


The secondary alkyl derivatives 1- $\text{Ad}_2\text{CHX}$  under similar conditions yielded not the cation ( $\mathbf{2}$ ;  $\text{R} = \text{H}$ ) but an equilibrium mixture of six ring-expanded cations ( $\mathbf{3}$ ).<sup>3</sup>



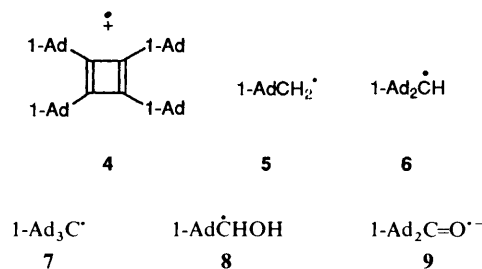
These 1-adamantylmethyl cations  $\mathbf{2}$  and  $\mathbf{3}$  were characterised by  $^1\text{H}$  and, particularly,  $^{13}\text{C}$  NMR spectroscopy.

Tertiary alkyl substituents sterically retard the bimolecular decay of alkyl radicals. For example, the radicals  $\text{Bu}'_2\text{CH}^\bullet$  and  $\text{Bu}'_3\text{C}^\bullet$  are long-lived at 243 K;<sup>5</sup> decay instead is principally by unimolecular  $\beta$ -scission to give a methyl radical and an alkene [e.g. eqn. (1)], or by 1,3-intramolecular hydrogen atom transfer [e.g. eqn. (2)].<sup>5</sup>



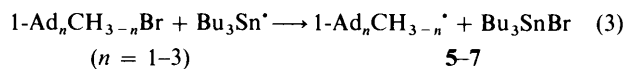
1-Adamantyl substituents would be expected to minimise reactions of this type because the cage would be resistant to the formation of a double bond at a bridgehead, or of a planar ( $\pi$ ) radical at an apex. EPR spectra of the adamantylmethyl radicals should be specially informative because the high concentrations which should be achievable, combined with the presence of a number of equivalent carbon atoms, should make it possible to investigate the  $^{13}\text{C}$  hyperfine coupling in natural abundance. Further, the cage structure should enhance long-range coupling.

Very little use seems to have been made of this potential. We<sup>6</sup> and Hogeveen<sup>7</sup> have described the EPR spectrum of the tetra-1-adamantylcyclobutadiene radical cation ( $\mathbf{4}$ ) and have identified the characteristics noted above. We now report an EPR study of the generation, the nuclear and electronic structure, and the decay of the neutral 1-adamantylmethyl radicals ( $\mathbf{5-8}$ ), and of the di-1-adamantylketyl radical anion ( $\mathbf{9}$ ) in fluid solution.



### Results

The radicals  $\mathbf{5-8}$  were prepared by abstraction of bromine from the corresponding bromides by tributyltin radicals which were generated photolytically within the EPR cavity from hexabutylditin [eqn. (3)].



The 1-adamantylhydroxymethyl radical ( $\mathbf{8}$ ) was obtained by abstraction of hydrogen from the corresponding alcohol with photolytically generated *tert*-butoxyl radicals [eqn. (4)].

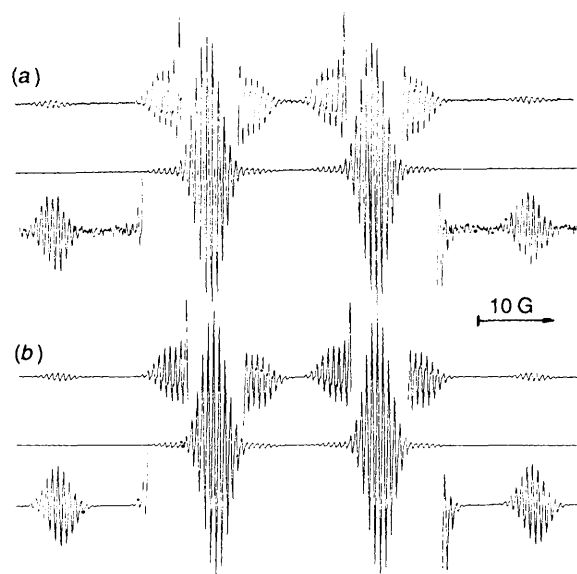
**Table 1** EPS parameters for 1-adamantyl substituted radicals

Radical	T/K	<sup>1</sup> H Hyperfine coupling constants/G			g	Solvent
		<i>a</i> ( <i>n</i> H <sub>α</sub> ) <sup>a</sup>	<i>a</i> ( <i>n</i> H <sub>γ</sub> )	<i>a</i> ( <i>n</i> H <sub>δ</sub> )		
Ad $\dot{C}$ H(OH)	300	14.33(1)	0.76(6)	0.70(3)	2.003 12	Bu'OH–Bu' <sub>2</sub> O <sub>2</sub>
Ad <sub>2</sub> CO <sup>•-</sup>	250	—	0.49(12)	0.49(6)	2.003 77	THF <sup>b</sup>
AdCH <sub>2</sub> <sup>•</sup>	234	21.63(2)	0.78(6)	0.78(3)	2.002 55	Cyclopropane
Ad <sub>2</sub> CH <sup>•</sup>	215	21.57(1)	0.73(12)	0.73(6)	2.002 62	Cyclopentane
Ad <sub>3</sub> C <sup>•</sup>	243	—	0.46(18)	0.58(9)	2.002 67	Cyclopentane
Ad <sub>4</sub> C <sub>4</sub> <sup>•+</sup>	255	—	-0.14(24)	+0.28(12)	2 002 12	Dichloromethane

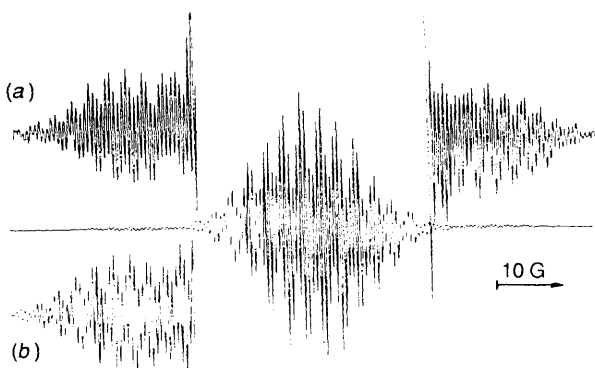
  

Radical	T/K	<sup>13</sup> C Hyperfine coupling constants/G			Solvent
		<i>a</i> ( <sup>13</sup> C <sub>α</sub> )( <i>n</i> C) <sup>a</sup>	<i>a</i> ( <sup>13</sup> C <sub>β</sub> )( <i>n</i> C)	<i>a</i> ( <sup>13</sup> C <sub>γ</sub> )( <i>n</i> C)	
(1-Ad) <sub>2</sub> $\dot{C}$ H	193	40.7(1)	—	—	Cyclopropane
	215	41.0(1)	10.96(2)	11.55(6)	
	308	41.4(1)	—	—	
(1-Ad) <sub>3</sub> $\dot{C}$	203	51.8(1)	8.08(3)	8.90(9)	Cyclopentane
	243	51.8(1)	9.09(9)	9.77(9)	
	284	51.8(1)	9.84(9)	10.64(9)	
(1-Ad) <sub>4</sub> C <sub>4</sub> <sup>•+</sup>	200	11.8(4)	3.07(4)	3.07(12)	Dichloromethane
	255	11.0(4)	3.04(4)	3.04(12)	

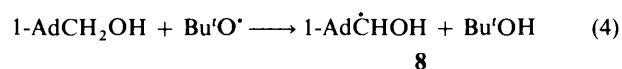
<sup>a</sup> The value of *n* is given in parentheses. <sup>b</sup> Tetrahydrofuran.



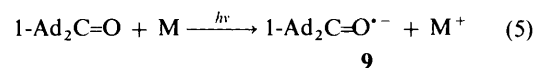
**Fig. 1** (a) EPR Spectrum of the di-1-adamantylmethyl radical **6** in cyclopentane at 215 K; the <sup>13</sup>C satellites are shown at increased gain; (b) computer simulation



**Fig. 2** EPR spectrum of the tri-1-adamantylmethyl radical **7** in cyclopentane at 243 K. (a) <sup>13</sup>C Satellites at increased gain; (b) computer simulation of <sup>13</sup>C hyperfine coupling.



We were unable to observe the spectrum of the radical 1-Ad<sub>2</sub> $\dot{\text{C}}$ OH (or of any other radical) when di-*tert*-butyl peroxide was photolysed in the presence of di-1-adamantylmethanol in various solvents, but the deprotonated species, the di-1-adamantylketyl radical anion **9** was obtained by photoassisted reduction of di-1-adamantyl ketone with sodium–potassium alloy [eqn. (5)].



All the radicals **4–9** showed strong, well-resolved EPR spectra. The <sup>1</sup>H hyperfine coupling was analysed by computer simulation; the assignment to the various types of hydrogen is unambiguous because there are different number of protons on the  $\alpha$ ,  $\gamma$  and  $\delta$  positions.

The radicals **6** and **7**, and the radical cation **4** which we described earlier,<sup>6</sup> which contain more than one adamantyl group, gave spectra strong enough for the <sup>13</sup>C hyperfine coupling to be observed. This coupling was analysed by computer simulation, using the probability relationship outlined by Davies *et al.*<sup>4</sup>

The experimental spectra, and the computer simulations, for the radicals **6** and **7** are shown in Figs. 1 and 2. The EPR parameters for radicals **4–9** are listed in Table 1.

The spectra of the 1-adamantylmethyl (**5**) and 1-adamantylhydroxymethyl (**8**) radicals were lost within the time constant of the spectrometer when the light was shuttered, but the di-1-adamantylmethyl (**6**) and tri-1-adamantylmethyl (**7**) radicals were much more persistent.

In cyclopentane at 310 K, the di-1-adamantylmethyl radical (**6**), prepared by reaction (3), decayed by clean first-order kinetics, with a rate constant of *ca.* 0.52 s<sup>-1</sup>, and a half-life of *ca.* 1.3 s. Between 290 and 210 K, the decay was neither first nor second order, but by 190 K, the decay was so slow that clean second-order kinetics were obtained.

In toluene, the first-order decay was much faster, and it could

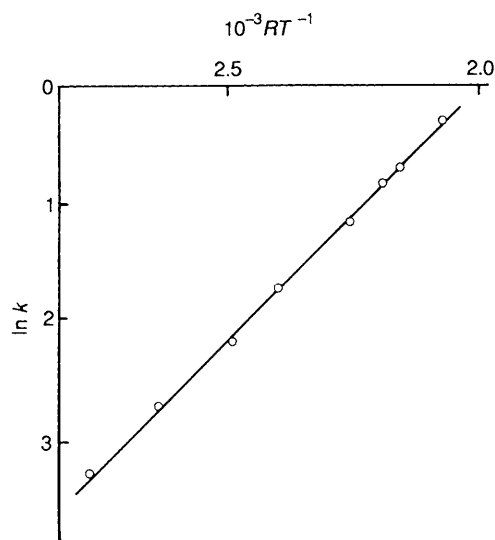


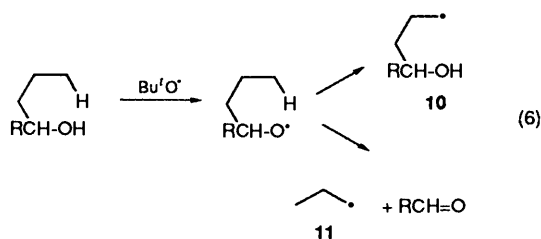
Fig. 3 Arrhenius plot for the decay of 1-Ad<sub>2</sub>CH• in toluene

be studied conveniently only below 250 K. Even at 182 K, the reaction showed only a small deviation from first-order kinetics. The Arrhenius plot (Fig. 3) over a 60 K range of temperature gave an activation energy of 4.82 kcal mol<sup>-1</sup> and pre-exponential factor of  $6 \times 10^3$ .

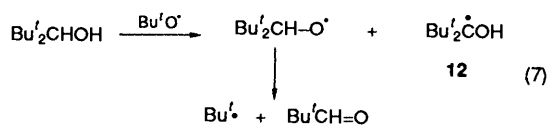
The decay of the tri-1-adamantylmethyl radical **7** showed more complicated behaviour. When the light was shuttered, the EPR signal rapidly decayed, but after *ca.* 30 s it increased again, before decaying more smoothly to zero during *ca.* 8 min with some relatively small further perturbations after *ca.* 1 and 2 min.

## Discussion

*Generation of the Radicals.*—The generation of the radicals **5–7** and **9** follows standard procedures and requires no further comment, but our inability to observe the radical 1-Ad<sub>2</sub>ĈOH is interesting. *tert*-Butoxyl radicals usually react with primary and secondary alcohols by abstracting hydrogen from an  $\alpha$ -CH group, but if steric hindrance at this centre is increased, the attack may be directed to the hydrogen of the OH group.<sup>8,9</sup> The alkoxy radicals which are formed cannot be observed directly by EPR spectroscopy, but the spectra of the radicals **10** from intramolecular transfer of hydrogen, or of **11** from  $\beta$ -scission can often be detected.

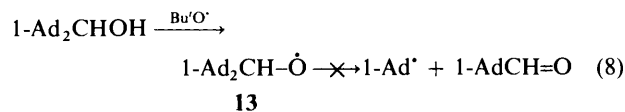


For example, Griller and Ingold<sup>8</sup> photolysed di-*tert*-butyl peroxide in presence of di-*tert*-butylmethanol at 298 K and observed the spectra of the hydroxyalkyl radical (**12**) and of the *tert*-butyl radical in a ratio of 1:4.



It appears that in the corresponding reaction with di-1-

adamantylmethanol, the attack of the *tert*-butoxyl radical is directed exclusively to the OH group to give **13**, either because steric hindrance by 1-adamantyl is greater than by *tert*-butyl, or because the di-1-adamantylhydroxymethyl radical is less thermodynamically stable than **12**.



Intramolecular abstraction of the hydrogen of the  $\delta$ -CH group is sterically impossible, and the alkoxy radical **13** apparently does not undergo  $\beta$ -scission to give the 1-adamantyl radical. Self-reaction may give the corresponding peroxide, or the ketone and alcohol.

*EPR Spectra.*—A great deal of work has been carried out on the systematics of hyperfine coupling to hydrogen in alkyl radicals.<sup>9</sup>

Simple primary and secondary alkyl radicals are planar at the radical centre with the electron located in a 2p orbital. Hyperfine coupling to H <sub>$\alpha$</sub>  is by spin polarisation, and has a value of *ca.* (–)23 G. Coupling to H <sub>$\beta$</sub>  is described by the Heller–McConnell equation [eqn. (9)] where  $A = \text{ca.} (+)1$  G, and  $B = \text{ca.} (+)56$  G. The first term arises from spin polarisation, and the second from hyperconjugation,  $\theta$  being the dihedral angle between the C <sub>$\beta$</sub> –H <sub>$\beta$</sub>  bond and the axis of the singly occupied 2p orbital.

$$a(\text{H}_\beta) = \rho_{C_\alpha}(A + B\cos^2\theta) \quad (9)$$

Coupling to H <sub>$\gamma$</sub>  is dependent on two dihedral angles, namely that which the C <sub>$\beta$</sub> –C <sub>$\gamma$</sub>  bond and the axis of the 2p orbital make about the C <sub>$\alpha$</sub> –C <sub>$\beta$</sub>  bond, and that which the C <sub>$\alpha$</sub> –C <sub>$\beta$</sub>  bond and the C <sub>$\gamma$</sub> –H <sub>$\gamma$</sub>  bond make about the C <sub>$\beta$</sub> –C <sub>$\gamma$</sub>  bond.<sup>10</sup> In neopentyl and isobutyl radicals at low temperatures, values of  $a(\text{H}_\gamma)$  from +4.04 to –0.72 G have been observed, but at higher temperature rotational averaging of these values results in observed values of  $a(\text{H}_\gamma)$  of 0.27 G in the propyl, 0.96 G in neopentyl, and <0.01 G in the isobutyl radical. Hyperfine coupling to more distant hydrogen is not normally detectable in alkyl radicals.

Relatively few data are available on hyperfine coupling to <sup>13</sup>C in alkyl radicals, because isotopic labelling would usually be necessary for the satellite signals to be detected. The methyl radical shows  $a(^{13}\text{C}_\alpha)$  38.3 G,<sup>11</sup> but the *tert*-butyl radical shows a value of *ca.* 45 G,<sup>12</sup> implying that the radical is distorted from planar at the centre, giving an appreciable amount of s-character to the singly-occupied orbital. In the ethyl radical,  $a(^{13}\text{C}_\beta)$  is 13.57 G,<sup>11</sup> and presumably arises from spin polarisation.

One of the few acyclic radicals in which  $a(^{13}\text{C}_\gamma)$  has been detected is the sterically hindered trineopentylmethyl radical (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>C•,<sup>13</sup> which shows  $a(^{13}\text{C}_\alpha)$  40.0 G,  $a(^{13}\text{C}_\beta)$  12.4 G,  $a(^{13}\text{C}; 2\text{C})$  22.6 G at 145 K, and  $a(^{13}\text{C}_\gamma; 3\text{C})$  17.5 G at 363 K. It is assumed that at low temperature two of the C <sub>$\beta$</sub> –C <sub>$\gamma$</sub>  bonds in the three neopentyl groups lie parallel to the axis of the 2p orbital, and the third lies close to the nodal plane. At higher temperatures, all three are in rapid positional exchange. This would be consistent with <sup>13</sup>C <sub>$\gamma$</sub>  hyperfine coupling, like <sup>1</sup>H <sub>$\beta$</sub>  coupling, being largely hyperconjugative in origin, and described by eqn. (10) where  $B = \text{ca.} 22.6$  G, and  $\theta$  is the dihedral angle between the C <sub>$\beta$</sub> –C <sub>$\gamma$</sub>  bond and the axis of the singly occupied 2p orbital.

$$a(^{13}\text{C}_\gamma) = \rho_{C_\alpha}(A + B\cos^2\theta) \quad (10)$$

The first notable point about the hyperfine coupling con-

stants listed for the adamantylmethyl radicals in Table 1 is the large values of  $a(\text{H}_\gamma)$  and  $a(\text{H}_\delta)$ . This property is familiar in adamantyl-containing radicals,<sup>14</sup> and can be ascribed to the fact that the rigid cage structure of the adamantyl group facilitates 'through-space' interaction of the back lobes of the  $\text{C}_\alpha\text{-C}_\beta$  bond and of the  $\text{C}_\gamma\text{-H}_\gamma$  and  $\text{C}_\delta\text{-H}_\delta$  bonds; the latter interaction involves transmission of spin over a W-conformation of bonds.

The second notable feature is the large value of  $a(\text{C}_\alpha)$ . In 1- $\text{Ad}_2\text{CH}^\bullet$  (6) it has a value of ca 41 G, not much larger than that of ca 38 G which is observed for the methyl radical and other simple n-alkyl radicals, but in 1- $\text{Ad}_3\text{C}^\bullet$  (7) it is 51.8 G, substantially larger than it is in the *tert*-butyl radical.<sup>12</sup> This implies severe distortion from a planar structure (see below) despite the increase in steric hindrance which this would appear to involve. It has been suggested that hyperconjugation by the three alkyl groups is more effective, and that torsional interactions are minimised, in a pyramidal radical.<sup>15</sup>

The third point of note is that in the radicals 6 and 7 we can observe  $a(^{13}\text{C}_\gamma)$  in natural abundance and the value of 10.5–11.5 G is as would be predicted from eqn. (10) where the average value of the angle  $\theta$  would be 45°.

We have carried out UMINDO/3-INDO calculations of the values of the hyperfine coupling constants of the radical 1- $\text{AdCH}_2^\bullet$  (5) as the  $\text{C}_\alpha\text{-1-Ad}$  bond is bent out of the plane containing the  $\text{CH}_2$  group,<sup>6</sup> and we find that the observed values for 7 correspond to an out-of-plane distortion of ca. 14°, for which we calculate  $a(^{13}\text{C}_\alpha)$  50.07 G,  $a(^{13}\text{C}_\beta)$  -9.99 G,  $a(^{13}\text{C}_\gamma)$  9.89,  $a(^1\text{H}_\gamma)$  -1.39, and  $a(^1\text{H}_\delta)$  1.72 G. The general agreement between observed and calculated values is encouraging. The absence of any observable temperature dependence of  $a(^{13}\text{C}_\alpha)$  implies that the amplitude of vibration at the radical centre is not sensitive to temperature.

The rapid decay of the 1-adamantylmethyl (5) and 1-adamantylhydroxymethyl (8) radical, and the second-order slower decay of the di-1-adamantylmethyl radical (6) below 190 K in cyclopentane presumably occurs by bimolecular dimerisation as decay by bimolecular hydrogen transfer is precluded by the absence of hydrogen on  $\text{C}_\beta$ .

The unimolecular decay of the diadamantyl radical 6 in cyclopentane at higher temperature could involve abstraction of hydrogen from the hexabutyliditin, or from the solvent, but the much faster decay in toluene suggests that the reaction now involves the transfer of benzylic hydrogen. A similar conclusion was reached recently by Myers and Jones<sup>16</sup> who showed that di-1-adamantylmethyl chloride in cyclohexane reacts with *tert*-butyllithium, then with  $\text{D}_2\text{O}$  to give 1- $\text{Ad}_2\text{CH}_2$  and not 1- $\text{Ad}_2\text{CHD}$ . They interpreted this to imply the formation of the 1- $\text{Ad}_2\text{CH}^\bullet$  radical which abstracts hydrogen from cyclohexane.

The curve of the decay of the tri-1-adamantylmethyl radical (7) when the UV light is shuttered appears to imply that after ca. 30 s, a reaction occurs in the dark to regenerate the radical, and that this process repeats after about 1 and 2 min. This curve was reproducible, but we can offer no satisfactory explanation of this behaviour.

## Experimental

1-Adamantylmethanol<sup>17</sup> was treated with 47% hydrobromic acid giving 1-adamantylmethyl bromide in 78% yield.<sup>18</sup> Di-1-adamantyl ketone,<sup>3</sup> di-1-adamantylmethanol,<sup>3</sup> di-1-adamantyl-

methyl bromide,<sup>3</sup> and tri-1-adamantylmethanol<sup>19</sup> were prepared by literature methods. Tri-1-adamantylmethyl bromide was obtained by treating the alcohol with oxalyl bromide by the method described by Crich and Fortt for preparing the corresponding chloride;<sup>20</sup>  $m/z$  (70 eV) 417 (0.07%;  $M^+ - \text{Br}$ ), 416 (0.1;  $M^+ - \text{HBr}$ ), 361 (0.07,  $M^+ - \text{Ad}$ ) and 135 (100,  $\text{Ad}^+$ ) (Found: C, 75.0; H, 9.2.  $\text{C}_{31}\text{H}_{45}\text{Br}$  requires C, 74.83; H, 9.21%).

EPR spectra were recorded on a Varian E-109 spectrometer fitted with a 500 W high pressure mercury arc (Osram HBO-500W/2) for photolysis in the cavity. Spectra were simulated using a modified version of the ESRSPEC2 program.

## Acknowledgements

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