Photochemically Induced Hydrogen Abstraction by Carbon Radicals in an Adamantane Matrix: Generation and Photochemical Cleavage of 2-Adamantyl Radicals

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Matrix-isolated cyclic allylic and 1-adamantyl radicals are activated by u.v. radiation to abstract hydrogen or deuterium atoms from the matrix material adamantane and $[^2H_{16}]$adamantane, as is observed by e.s.r. spectroscopy. The 2-adamantyl or 2-$[^2H_{15}]$adamantyl radicals thus formed, undergo a further photochemically induced cleavage reaction, interpreted in terms of a β-CC scission to the (7-bicyclo[3.3.1]non-2-enyl)methyl or (7-$[^2H_{15}]$bicyclo[3.3.1]non-2-enyl)methyl radicals, respectively. From the latter radicals, the 2-adamantyl (2-$^2[H_{15}]$adamantyl) radicals are regenerated in the dark, presumably by both intramolecular addition and intermolecular hydrogen (deuterium) abstraction from the matrix.

Adamantane and $[^2H_{16}]$adamantane have been established as useful matrix materials for the generation and e.s.r. spectroscopic investigation of free radicals.[1-3] Radicals of relatively small size are sufficiently free to rotate in those matrices, producing almost isotropic e.s.r. spectra. Furthermore, the e.s.r. hyperfine lines are considerably narrowed in $[^2H_{16}]$adamantane matrix and often approach the linewidth of solution e.s.r. spectra.

We have demonstrated the advantages of adamantane matrices for the study of thermally and/or photochemically initiated free-radical rearrangement reactions, not observable in solution.[1c,3] In the course of these investigations we occasionally observed that different types of matrix-isolated carbon-centred radicals yield the same e.s.r. spectrum on exposure to u.v. light, preferentially at low temperatures. On shutting off the illumination, the e.s.r. spectra related to the enclosed substrates were regenerated thermally.

Here we report on a detailed investigation concerning the origin and structure of the common e.s.r. spectrum and some of the reactions which occur on u.v. irradiation of carbon-centred radicals isolated in adamantane matrices.

Results

Our basic observations which led to the present study are pictorially displayed in Scheme 1, where the dotted arrows denote the observed spectral changes rather than true chemical transformations. As reported earlier,[2] X-irradiation of adamantane matrices containing a few percent of bicyclo[3.1.0]hex-2-ene (1) at 77 K generates the bicyclo[3.1.0]hexenyl radical (2), identified by its e.s.r. spectrum. Above 240 K (2) rearranges thermally to the cyclohexadienyl radical (3) which also has been produced independently from cyclohexa-1,4-diene (4). U.v. photolysis induces ring closure of (3) back to the bicyclic system (2). However, on continuous exposure of the matrix to u.v. light at temperatures below 210 K, the e.s.r. signals of (2) disappeared and a new five-line spectrum $(X_H^{\cdot})$ of approximate intensity ratio 1:2:2:2:1 with a line separation of ca. 2.1 mT emerged. On starting from (1) as the source for (2) the original e.s.r. spectrum of (2) was regenerated slowly after the u.v. light was switched off, superimposed by a broad doublet spectrum, compatible with the 2-adamantyl radical (5),[1a,3,4] With increasing temperature the broad-doublet spectrum also disappeared completely and again a clean spectrum of (2) was observed. Taking cyclohexa-
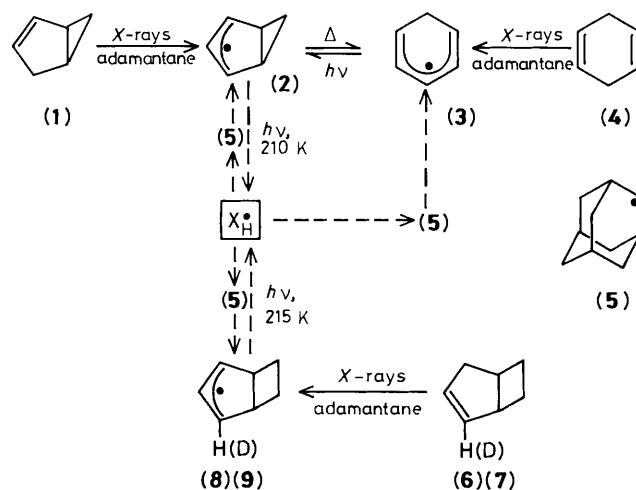

Scheme 1.

1,4-diene (4) as the source for (2), only the cyclohexadienyl radical (3) was regenerated from the unknown radical $X_H^{\cdot}$; no trace of (2) was apparent in the spectrum.

The same radical $(X_H^{\cdot})$ also appeared during photolysis of the matrix-isolated bicyclo[3.2.0]heptenyl radicals (8) and (9) at temperatures below 220 K. Here, we observed a clear build-up of the 2-adamantyl radical (5) at the cost of $X_H^{\cdot}$ after interruption of the u.v. irradiation. The starting radicals (8) and (9) were regenerated within one hour at 240 K with concomitant disappearance of (5).

The intermediate appearance of the 2-adamantyl radical (5) and the specific regeneration of the deuteriated radical (9) gave strong evidence that $X_H^{\cdot}$ could not be a common rearrangement product of the bicyclic radicals themselves. If this conclusion were correct then radical $X_H^{\cdot}$ should be a species produced from the matrix material upon photolysis, most likely *via* the 2-adamantyl radical. In order to prove this proposal we generated (5) by X-irradiation of pure adamantane at 77 K [Figure 1(a)]. Indeed, on u.v. irradiation at 190 K the broad doublet of (5) disappeared, largely, within a few minutes and the expected five-line spectrum of $X_H^{\cdot}$ emerged [Figure 1(b)]. The latter spectrum could be simulated satisfactorily using the set of

Table. E.s.r. hyperfine splittings (mT).

Radical	T/K	a_α	a_β	a_{γ^1}	a_{γ^2}	a_{δ^1}	a_{δ^2}	a_ε
(5)[3]	136	2.073 (1 H)	0.193 (2 H)	0.406 (4 H)	0.098 (4 H)	0.278 (2 H)	—	0.012 (2 H)
(10)[a]	188	0.353 (1 D)	0.033 (2 D)	0.069 (4 D)	—	0.047 (2 D)	—	—
(14a) (X_H)[a]	200	2.12 (2 H)	4.17 (1 H)	0.22 (2 H)	0.14 (2 H)	—	—	—
(X_D)[a]	188	0.325 (2 D)	0.640 (1 D)	0.034 (2 D)	0.021 (2 D)	—	—	—
(11)[5,a]	200	—	0.658 (6 H)	0.466 (3 H)	—	0.308 (3 H)	0.080 (3 H)	—
(15a)[18]	184	2.15 (2 H)	4.12 (1 H)	0.075 (2 H)	0.075 (2 H)	—	—	—
(15b)[18]	140	2.15 (2 H)	3.04 (1 H)	0.096 (2 H)	0.096 (2 H)	—	—	—

[a] This work.
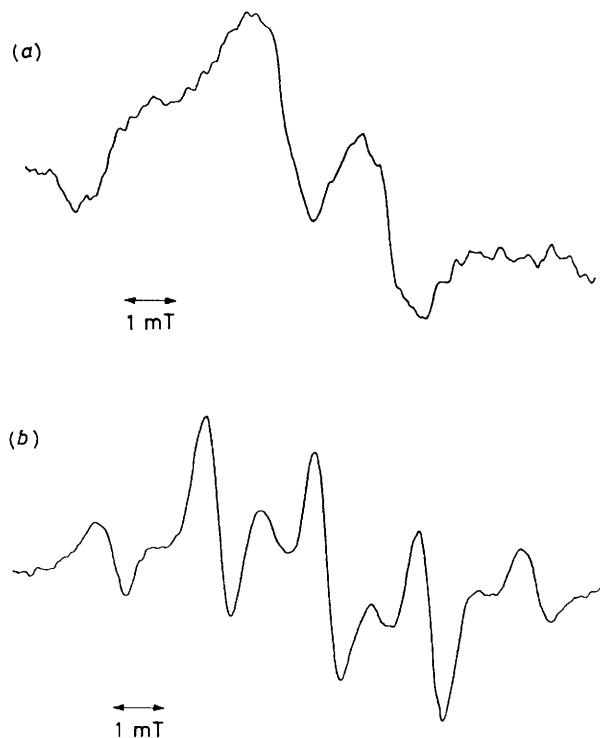
Figure 1. (a) E.s.r. spectrum of the 2-adamantyl radical (5) from X-ray irradiation of adamantane at 77 K, recorded at 190 K; (b) e.s.r. spectrum obtained from the spectrum (a) on continuous u.v. irradiation at 190 K.

coupling constants given in the Table. As observed before, the e.s.r. signals of $X_H^\bullet$ were slowly reconverted (ca. 2 h at 220 K) into the doublet of the 2-adamantyl radical in the dark. The procedure of photolytic transformation and thermal reconversion could be repeated several times. The extent to which $X_H^\bullet$ was formed by photolysis decreases with increasing temperature. At 300 K the formation of $X_H^\bullet$ could be no longer detected.

The foregoing experiment was also carried out taking [$^2H_{16}$]-adamantane as matrix material. The e.s.r. spectrum obtained on X-irradiation of the pellet at 77 K (Figure 2) was virtually identical with a computer simulation with deuterium coupling constants calculated from the hydrogen couplings[3] by the theoretical ratio of the magnetic moments (Table). The ten-line spectrum of $X_D^\bullet$, produced on photolysis at 190 K (Figure 2), similarly, could be simulated using the set of deuterium couplings calculated from the hydrogen couplings of $X_H^\bullet$ (Table). As expected, radical $X_D^\bullet$ was also slowly reconverted into the 2-[$^2H_{15}$]adamantyl radical (10) in the dark.

The foregoing experiments clearly demonstrate that under our conditions only one product radical is formed photolytically from matrix-isolated 2-adamantyl radicals.

The question remained as to whether the transformation of $X_H^\bullet$ or $X_D^\bullet$ into (5) or (10), respectively, occurs by a reversible intramolecular reaction or via an intermolecular hydrogen-/deuterium-transfer reaction. To answer this question we generated regiospecifically 2-adamantyl radicals (5) by gas-phase reaction of 2-bromoadamantane with sodium vapour, trapping them at 15 K by cocondensation with [$^2H_{16}$]adamantane. An unperturbed e.s.r. spectrum of (5) showing partially resolved hyperfine structure [Figure 3(a)] was obtained, virtually identical with the solution e.s.r. spectrum.[3] U.v. photolysis at 180 K produced superposable e.s.r. spectra of (5) and radical $X_H^\bullet$ [Figure 3(b)], proving that the photochemical transformation is an intramolecular process and no participation of the matrix material takes place.

An almost complete conversion of (5) into $X_H^\bullet$ could not be achieved with the arrangement used in this experiment (see the Experimental section), because parts of the matrix layer were not accessible to the u.v. irradiation. This drawback unfortunately avoids the unambiguous verification of the reaction path for the thermal reconversion of $X_D^\bullet$ into (5). With increasing temperature, the signal intensity of both radicals decreased to approximately the same extent. No clear decrease of $X_H^\bullet$ in favour of (5) could be observed. However, at temperatures above 220 K an additional broad singlet emerged in the central region of the e.s.r. spectrum [Figure 3(c)], the shape and width of which was compatible with the e.s.r. spectrum of the 2-[$^2H_{15}$]adamantyl radical (10). The latter only, could have been produced by deuterium abstraction from the matrix. Without preceding photolysis no noticeable amount of (10) was produced by the 2-adamantyl radical over 2 h at 180 K; we thus believe that radical $X_H^\bullet$ is the reactive species in the hydrogen-/ deuterium-abstraction reaction. Hence, the regeneration of the 2-adamantyl radicals from radicals $X_{H(D)}^\bullet$ occurs at least in part by an intermolecular process, however, the intramolecular addition should give a larger contribution to the back reaction (Scheme 2).
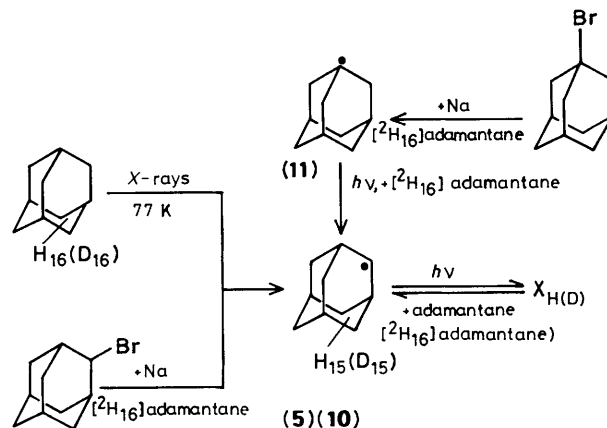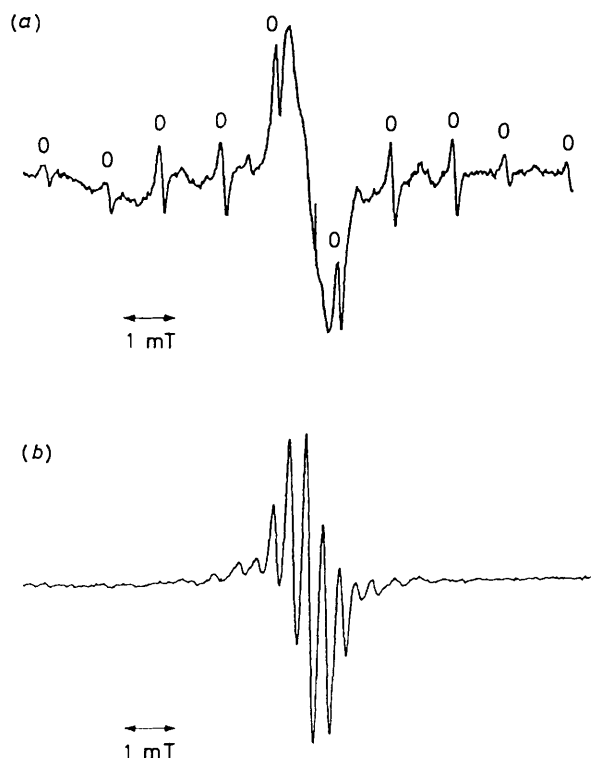

Scheme 2.

Figure 2. (a) E.s.r. spectrum of the 2-[$^2H_{15}$]adamantyl radical (10) from X-irradiation of [$^2H_{16}$]adamantane at 77 K, recorded at 188 K; the marked lines are due to unknown hydrogen-containing impurities; (b) Spectrum obtained from the spectrum (a) on continuous u.v. irradiation of the matrix at 188 K.

It is interesting to compare the photolytic behaviour of the π-type 2-adamantyl radical, possessing a more or less planar radical centre,[3,4] with that of the 1-adamantyl radical (11), regarded to be a prototypal σ-type radical with a pyramidalised radical centre.[5] Radical (11) was generated regiospecifically by gas-phase reaction of 1-bromoadamantane and sodium vapour and trapped in a matrix of [$^2H_{16}$]adamantane by simultaneous deposition at 15 K (Scheme 2). E.s.r. spectra of (11) were recorded in the temperature range 15–220 K, showing a well-resolved hyperfine structure above 180 K. The coupling constants were in excellent agreement with the literature data[5] for the solution spectrum. After 3 h at 180 K, no indication of the thermal formation of the 2-[$^2H_{15}$]adamantyl radical (10) was detected. However, u.v. photolysis of the matrix at 180 K results in the rapid appearance of the spectrum of radical $X_D^\bullet$, which in turn is reconverted into (10) in the dark. Thus, on photochemical excitation, the 1-adamantyl radical (11) is also able to abstract hydrogen or deuterium atoms almost selectively from the 2-position of adamantane or [$^2H_{16}$]adamantane, respectively.

Discussion

The mechanisms for reactions of photochemically excited states of radicals in solid matrices are not very well established.[6,7] The observed reactions appear to depend strongly on the nature of the matrix. To our knowledge, only Dismukes and Willard[7] reported the u.v. photolysis of radicals derived from adamantane. The formation of a five-line e.s.r. spectrum on photolysis of the 2-adamantyl radical has already been observed by these authors, but they did not assign it to a specific structure.

The formation of the 2-adamantyl radicals (5) and (10), and

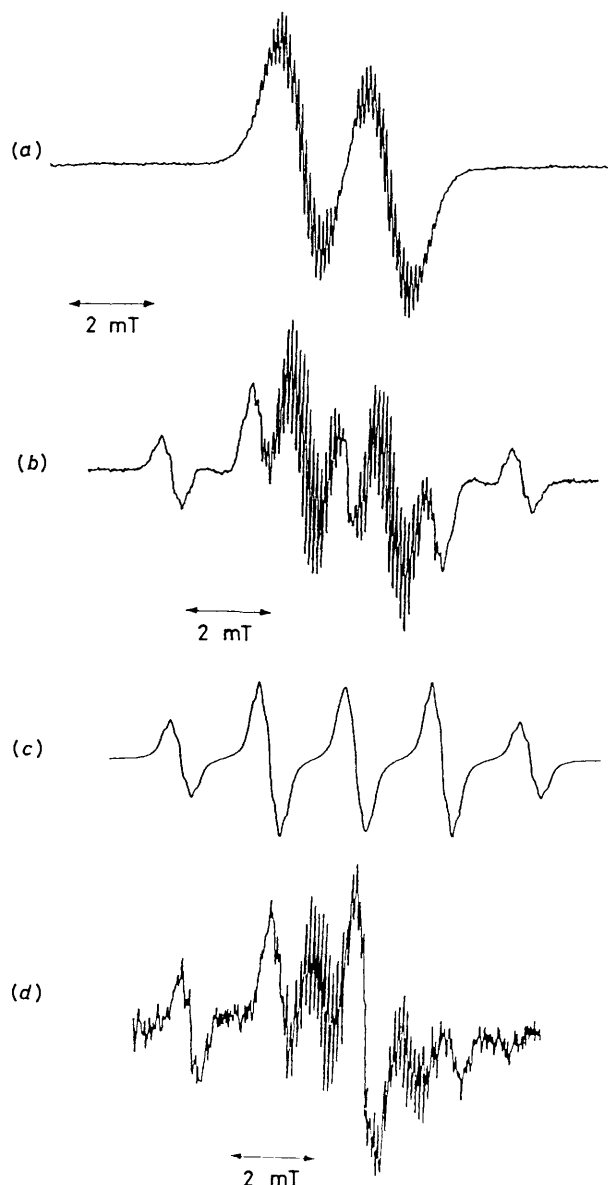Figure 3. (a) E.s.r. spectrum at 190 K of the 2-adamantyl radical (5) in [$^2H_{16}$]adamantane matrix, generated by reaction of 2-bromo-adamantane with sodium; (b) Spectrum recorded at 200 K one hour after 30 min u.v. photolysis at 190 K; (c) Computer simulation of the photolytically generated radical (14a); (d) Spectrum recorded at 220 K, two hours after 30 min photolysis; the decrease of the signal intensity with increasing field strength is due to partial evaporation of the matrix.

their respective photoproducts $X_H^\bullet$ and $X_D^\bullet$, indicates that electronically excited states of the starting radicals (2), (8), (9), and (11) should be the reactive species which abstract hydrogen atoms from the matrix material upon u.v. irradiation. Alkyl-type radicals absorb light in the wavelength region $\lambda \leqslant 350$ nm with fairly high extinction coefficients.[6,8] In the case of allylic radicals these short-wavelength absorptions are assigned to allowed $^2A_2 \longrightarrow {}^2B_1$ transitions.[3,8d,9,10] Alkyl substitution shifts the absorption maxima to somewhat higher wavelengths.[8a,d] Excitation of these transitions should be the initial steps in our experiments as the maximum output of our u.v. source covers the range of 210–360 nm. Accordingly, no formation of (5) or $X_H^\bullet$ has been observed on irradiation at wavelength >450 nm.[11]

In a simple MO description, the $^2A_2 \longrightarrow {}^2B_1$ transition in
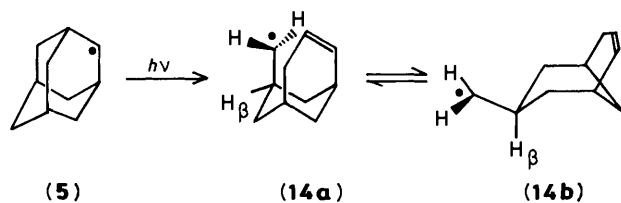
Scheme 3.
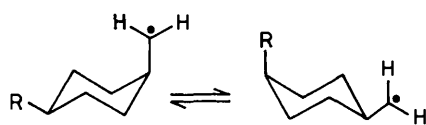
R = H , Me, and Bu^t

Scheme 4.

allylic radicals corresponds to the excitation of the unpaired electron from the non-bonding n_π orbital (SOMO) into the π^* orbital (LUMO),[10] which becomes the new SOMO. The new SOMO now can undergo an energetically more favourable interaction with an empty σ^* orbital of the reactant molecule. The transition state for hydrogen abstraction can be described by 'end-on' overlap of the π^* SOMO with the σ^* orbital of the C–H bond to be broken.[12] This qualitatively explains why electronically excited allylic radicals are able to cleave unactivated C–H bonds, in contrast with ground-state allylic radicals.

Similar arguments can be applied to the hydrogen abstraction reaction by the excited 1-adamantyl radical (11). Here, one might expect the reactive intermediate to be generated by an electronic transition from the singly occupied sp^3 orbital into a σ^* orbital. However, in recent u.v.[8a] and ab-initio[13] studies it has been stated that absorption maxima of 200–350 nm in the u.v. spectra of primary, secondary, and tertiary alkyl radicals should correspond to 3s–3d Rydberg states, σ^* valence states appear to be considerably higher in energy. Our observations indicate that the first Rydberg states of carbon-centred radicals are also suitable for the cleavage of external C–H bonds. Additionally, the abstraction of a secondary hydrogen from adamantane by the 1-adamantyl radical is slightly favoured thermochemically.[14]

The thermal regeneration of the starting radicals (2), (3), (8), and (9) after shutting off the photolysis can be reasonably explained by reaction of the matrix radicals (5) and (10) with excess parent molecules (1), (4), (6), and (7). The matrix molecules are essentially free to rotate,[3] hence there is a good chance for a number of matrix radicals to come into contact with more than one of the enclosed molecules, as the latter are present in a fairly high concentration.

The second topic which has to be discussed is the photochemical rearrangement of the 2-adamantyl radicals (5) and (10). A value of 260 nm has been reported for the absorption maximum of the 2-adamantyl radical (5). As stated before, the excitation of alkyl radicals by short-wavelength radiation most likely produces 3s–3d Rydberg states. These states are not only favourable for hydrogen abstraction, but also are believed to exhibit some predissociative character,[8a,13,15] leading to the

fission of adjacent C–H or C–C bonds. Fragmentation reactions of that kind have been observed several times and seem to be common photochemical reactions of alkyl-type radicals in inert solid matrices.[6a,16] In the case of the 2-adamantyl radicals the primary chemical process following electronic excitation could be reasonably assumed to be the scission of a C–C-bond in β-position to the radical centre, producing the axial conformer (14a) of the (7-bicyclo[3.3.1]non-2-enyl)methyl radical (Scheme 3). Such a ring opening has also been described to occur thermally at 820 K.[14]

The e.s.r. data for the photochemically generated radical $X_H^•$ (Figures 1 and 3; Table) are in good correspondence with structure (14a): the 2.1 mT triplet splitting accounts for the two equivalent α-hydrogens in primary alkyl radicals, the 4.2 mT doublet splitting can be attributed to the β-hydrogen atom, and the two sets of the small triplet couplings are in accord with the presence of equivalent equatorial and axial γ-hydrogens, respectively. The β-H coupling of about 4.2 mT indicates that the singly occupied p-orbital and the β-CH bond adopt a more or less eclipsed conformation.[17] Thus, the rotation about the C_α–C_β bond should be restricted, the most populated conformation being as depicted in Scheme 3.

Recently, Ingold and Walton[18] reported the e.s.r. spectroscopic determination of the conformational dynamics of cyclohexylmethyl radicals (15), which comprises the essential structural features of radicals (14) (Scheme 4). Their e.s.r. data for the axial conformation (15a) (R = H; see Table) are indeed almost identical with our data for (14a). The β-H coupling assumes high values of 4.2–3.7 mT in the temperature range of 180 to 300 K because of a fairly high rotational barrier (V_0 = 1.6 kcal mol^{-1}) about C_α–C_β in the axial orientation. In (14a) steric interactions of the α-hydrogens with the axially fused unsaturated ring imply an even more restricted rotation of the exocyclic methylene group. Hence, the β-hydrogen coupling in (14a) is expected to show a much smaller decrease on increasing temperature than in (15a). So far, the excellent agreement of our e.s.r. data with the data for (15a) strongly favours the cyclohexylmethyl structure (14a) for radical $X_H^•$. Accordingly, an e.s.r. spectrum of the same 1:2:2:2:1 intensity ratio with approximately 2.1 mT line spacing has been observed for the structurally related isobutyl radical at 77 K.[19]

The alternative equatorial conformation (14b) (Scheme 3) is unlikely for radical $X_H^•$ as Ingold and Walton[18] observed significantly reduced β-H couplings for the equatorial conformation (15b) of the structurally related cyclohexylmethyl radicals (Table). Although (14b) represents a boat conformation in the cyclohexylmethyl sub-unit we should expect coupling constants for the α- and β-hydrogens comparable to (15b). With regard to this assumption, the e.s.r. spectra [see e.g. Figure 3(b)] do not indicate the presence of conformation (14b).

Radical (14a) also represents a very reasonable structure for the reverse reaction to the 2-adamantyl radical on interruption of the u.v. light. It can undergo ring closure at C-1 of the double bond and, as it is a primary alkyl radical, abstraction of a secondary hydrogen atom from the adamantane matrix should also be thermodynamically favourable.† The hydrogen abstraction has been proved at least at temperatures above 220 K.

As mentioned above, Dismukes and Willard[7] first reported on the solid-phase photolysis of the 2-adamantyl radical, generated by γ-irradiation of adamantane at 77 K. Upon photolysis at 254 nm and 77 K they observed the formation of an unassigned five-line e.s.r. spectrum with approximately 2.12 mT line separation. Whereas the line spacing agrees very well with our data for $X_H^•$ (14a), they found an unusual intensity distribution of 0.6:4.9:8.7:4.6:1.0. On warming the sample to 206 K, the lines became narrowed and a superposition with the signals of the 2-adamantyl radical (5) was recorded, similar to our spectra at the same temperature. A steady decrease of

† Besides the higher statistical probability, the abstraction of a secondary hydrogen atom from adamantane is favoured by a ca. 1.5 kcal mol^{-1} lower bond energy.[14]

the five-line spectrum with concomitant increase of the 2-adamantyl signals at higher temperature was observed. Most surprising, however, is their statement that the same five-line spectrum was also produced from an unphotolysed sample when it was simply left to stand for 2 h at 77 K. A thermal ring opening of the 2-adamantyl radical at this temperature seems very unlikely to us, so we believe that the thermally produced e.s.r. signals are due to impurity radicals and/or radicals derived from products of γ-ray damage of the matrix. It is known from several investigations (see refs. 1 and 4) that—depending on sample preparation and irradiation conditions—different cleavage products are formed by γ-irradiation of solid adamantane. Coupling constants of *ca.* 2.1 mT are very common values for alkyl radicals, so a similar five-line spectrum might coincidently have been produced by such products. This would account for the unusual intensity distribution of the e.s.r. lines and is indicated by the changes of the e.s.r. spectrum on duration of γ-irradiation, noticed by these authors.

Experimental

Adamantane (Aldrich Gold Label), [^{2}H$_{16}$]adamantane (MSD-Isototopes), 2-bromoadamantane, and 1-bromoadamantane (Aldrich) were purified by vacuum sublimation. E.s.r. measurements were performed on a Bruker ER-420 X-band spectrometer, equipped with a variable temperature unit.

Radical Generation by X-Ray Irradiation.—Pellets of the matrix materials (adamantane, [^{2}H$_{16}$]adamantane) were pressed with a standard 5 cm IR pressing tool without exclusion of air. Matrices were prepared by cosublimation of adamantane (50–70 mg) or [^{2}H$_{16}$]adamantane and the substrate (*ca.* 5 mm^3) in evacuated and sealed glass tubes at 360 K. The matrix pellets were exposed to X-rays in test tubes, sealed with Parafilm and immersed in liquid nitrogen. The Parafilm sealing excludes humidity but allows condensation of oxygen onto the pellets for efficient trappings of hydrogen atoms, produced by the X-rays. X-Irradiation was carried out with a Siemens Stabiliplan instrument (Cu anode; 3 600 W at 240 kV and 15 mA; 240 R min⁻¹; 0.5 mm Cu filter) for 35 min at a distance of approximately 10 cm. For the recording of the e.s.r. spectra the matrix pellets were transferred at 77 K into 6 mm quartz tubes which were inserted into the variable-temperature cell of the spectrometer. U.v. photolysis was done with the filtered light (6 cm water filter and 3 mm UG-5 filter; Schott) of a 1 kW Hg/Xe high-pressure lamp (Hanovia 977-B1).

Radical Generation of Sodium/Alkyl Halide Reaction.—These experiments were carried out using an Air Products closed-cycle helium cryostat CW 202. Most of the experimental details have been described elsewhere.[1c] The matrices were prepared by slow condensation of a 10:1 mixture of [^{2}H$_{16}$]adamantane and the adamantyl bromide (20 mg) from one arm of a Y-shaped reaction cell onto the 15 K cold sapphire rod of the cryostat, with the simultaneous introduction of a stream of sodium vapour, produced at 500 K from purified sodium in the other arm of the cell. The cold finger was then introduced into the cavity of the e.s.r. spectrometer. Excess sodium atoms in the matrix were carefully bleached out at 30 K by illumination with light of wavelength 360 nm.

References
1 (a) R. V. Lloyd, S. DiGregorio, L. DiMauro, and D. E. Wood, *J. Phys. Chem.*, 1980, **84**, 2891; (b) M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, 1976, **98**, 2053; (c) R. Sustmann, D. Brandes, F. Lange, and U. Nüchter, *Chem. Ber.*, 1985, **118**, 3500; and references cited therein.
2 (a) R. Sustmann and F. Lübbe, *J. Am. Chem. Soc.*, 1976, **98**, 6037; (b) D. Brandes, F. Lange, and R. Sustmann, *Tetrahedron Lett.*, 1980, **21**, 261.
3 (a) R. J. Waltmann, A. C. Ling, and J. Bargon, *J. Phys. Chem.*, 1982, **86**, 325; (b) M. Kira, M. Watanabe, M. Ichinose, and H. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 3762.
4 T. Migita and M. Iwaizumi, *Chem. Phys. Lett.*, 1980, **71**, 322.
5 P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1972, **94**, 995.
6 (a) M. Ya. Mel'nikov and N. V. Fok, *Russ. Chem. Rev.*, 1980, **49**, 252; (b) J. C. Scaiano and L. J. Johnston, *Pure Appl. Chem.*, 1986, **58**, 1273; J. C. Scaiano, L. J. Johnston, W. G. McGimpsey, and D. Weir, *Acc. Chem. Res.*, 1988, **21**, 22.
7 G. C. Dismukes and J. E. Willard, *J. Phys. Chem.*, 1976, **80**, 1435.
8 (a) H. R. Wendt and H. E. Hunziker, *J. Chem. Phys.*, 1984, **81**, 717; (b) C. Huggenberger and H. Fischer, *Helv. Chim. Acta*, 1981, **64**, 338; (c) D. A. Parkes and C. P. Quinn, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 1952; (d) A. B. Callear and H. K. Lee, *Trans. Faraday Soc.*, 1968, **64**, 308; (e) H. E. Van den Bergh and A. B. Callear, *Trans. Faraday Soc.*, 1970, 2681.
9 G. Maier, H. P. Reisenauer, B. Rohde, and K. Dehnicke, *Chem. Ber.*, 1983, **116**, 732.
10 P. Carsky and R. Zahradnik, *J. Phys. Chem.*, 1970, **74**, 1249.
11 V. V. Vikulin, E. R. Klinshpont, and A. T. Podkhalyuzin, *Khim. Vys. Energ.*, 1978, **12**, 85.
12 C. Wentrup, 'The Neutral Reactive Intermediates in Organic Chemistry,' Wiley, New York, 1985, p. 90.
13 B. H. Lengsfield III, P. E. M. Siegbahn, and B. Liu, *J. Chem. Phys.*, 1984, **81**, 710.
14 G. H. Kruppa and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1986, **108**, 2162.
15 H. T. Yu, A. Sevin, E. Kassab, and E. M. Evleth, *J. Chem. Phys.*, 1984, **80**, 2049.
16 (a) J. Pacansky and H. Coufal, *J. Chem. Phys.*, 1979, **71**, 2811; (b) J. Pacansky, J. S. Chang, and D. W. Brown, *Tetrahedron*, 1982, **38**, 257; (c) C. F. Adrian, V. A. Bowers, and E. L. Cochran, *J. Chem. Phys.*, 1975, **63**, 919.
17 J. K. Kochi, *Adv. Free-Radical Chem.*, 1975, **55**, 189; P. D. Sullivan and E. M. Menger, *Adv. Magn. Reson.*, 1977, **9**, 1.
18 K. U. Ingold and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1337; *J. Am. Chem. Soc.*, 1985, **107**, 6315.
19 M. Iwasaki and K. Toriyama, *J. Chem. Phys.*, 1967, **46**, 2852.