Free Radicals in an Adamantane Matrix. XI. Electron Paramagnetic Resonance Study of Conformations in the β-Halo-*tert*-butyl Radicals

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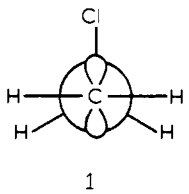
Abstract: The β-halo-*tert*-butyl radicals were prepared by X-irradiation of the corresponding isobutyl halides in an adamantane matrix at 77 K and their conformations were determined by analysis of their EPR spectra. It was concluded that the radicals are nonplanar at the radical site, the fluoro and chloro radicals trans eclipsed and the bromo and iodo radicals gauche staggered with respect to the relative orientation of the carbon halogen bond and the direction of the singly occupied orbital. Vibration-rotation motions about the favored conformation are much larger for the fluoro radical than for the others. The rate of interconversion of the inequivalent methylene protons is $\sim 1.5 \times 10^9$ sec^{-1} for the bromo radical at 202 K while it is too slow to measure for the iodo radical at the same temperature. The barrier to interconversion has a lower limit of 3 kcal/mol for the bromo radical and higher than that for the iodo radical. The halogen and proton hfsc in gauss and the g values for the $XCH_2\dot{C}(CH_3)_2$ radicals are: $^{19}F = 103.7$, $CH_2 = 10.4$, $CH_3 = 23.3$, $g = 2.0030$ at 214 K; $^{35}Cl = 19.5$, $CH_2 = 6.3$, $CH_3 = 21.1$, $g = 2.0042$ at 215 K; $^{81}Br = 6.7$, $CH_2 = 21.4, 42.7$, $CH_3 = 21.4$, $g = 2.0010$ at 202 K; $^{127}I = 7.0$, $CH_2 = 21.9, 43.8$, $CH_3 = 21.9$, $g = 2.0009$ at 208 K. The fluoro radical decays to nonradical products above 318 K, the chloro radical converts to 2-methyl allyl radical above 306 K, the bromo radical converts to *tert*-butyl radical by exchange with a matrix proton (or deuteron) at 209 K as does the iodo radical above 225 K. Photolysis with a Xe lamp converts the bromo and iodo radicals to nonradical products in less than the experimental time constant of 0.3 sec, whereas the other radicals are essentially unaffected. The hypothesis is put forward that the nonplanarity and high barrier to rotation observed explain the retention of stereochemical configuration in reactions involving β-chloro, β-bromo, and β-iodo alkyl radicals.

There is a large body of work which demonstrates that β-halo alkyl radicals are not only intermediates in many free-radical reactions but that chlorine, bromine, and iodine exert stereochemical control in these reactions under certain conditions.[2] This behavior has been interpreted by Skell and others to be a result of bridging of two adjacent carbons by the halogen in the free-radical intermediate. In fact, EPR studies of β-chloro alkyl radicals[3-6] demonstrate that the chlorine is not symmetrically bridged. However, there is a large barrier to rotation about the C_α–C_β bond, and the large chlorine hfsc observed is diagnostic of an eclipsing of the unpaired electron orbital by the chlorine as in **1**. The unusually low β-proton hfsc observed for the chloro and other β-substituted radicals which strongly prefer such eclipsing has been attributed to a *tendency* toward bridging by the substituent, with angles of distortion of up to 30° required to explain the reduction[3b,7] (cf. **2**). On the other hand, β-fluoro alkyl radicals have low barriers to rotation and in particular the β-fluoro ethyl radical[3a,6,8,9] prefers the staggered conformation **3**. The fact that bromine is more effective in stereochemical control than chlorine[2] has led to the expectation that β-bromo alkyl radicals would also be eclipsed and that their tendency toward bridging would be even more pronounced than that of chlorine. Efforts to observe the analogous bromo and iodo radicals in fluid media via EPR have so far met with no success;[6] however, we have recently reported that the β-bromo-*tert*-butyl radical prepared in an adamantane matrix is better described as staggered than as eclipsed.[10]



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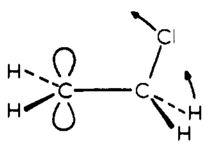

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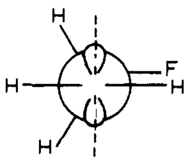

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An empirical rule has been promulgated which catagorizes substituents into a preference for conformation **3** when they are from the first row of the periodic table (B, C, N, O, and F) and a preference for conformation **1** when they are from rows 2, 3, and 4.[11] It has also been found that substitution of the α protons by methyl groups (that is, to form the β-substituted *tert*-butyl radical) creates an apparent tendency to favor conformation **1**, whereas substitution of the β protons by methyl groups has the opposite effect.[4,12,13]

In this paper we report the preparation of the β-fluoro, chloro, bromo, and iodo-*tert*-butyl radicals and the determination of their conformational preferences by EPR. We also suggest alternative explanations for the retention of configuration, the low β-proton hfsc, and the conformational effects of methyl substitution mentioned above.

Experimental Section

The precursors for all of the radicals reported herein were the appropriate 1-substituted 2-methylpropanes. The 1-chloro-2-methylpropane (Eastman) and 1-bromo-2-methylpropane (Matheson Coleman and Bell) were redistilled before use. The 1-iodo-2-methylpropane was prepared from 2-methyl-1-propanol and constant-boiling hydroiodic acid according to the procedure of Vogel.[14] NMR spectra in satisfactory agreement with the literature were obtained for all compounds.

1-Fluoro-2-methylpropane. The tosyl ester was prepared from 2-methyl-1-propanol and p-toluenesulfonyl chloride in pyridine. The tosylate was then heated with potassium fluoride dihydrate in β,β'-dihydroxydiethyl ether. The product was collected in a Dry Ice-acetone trap and the liquid so obtained was redistilled in a cold room (bp 22°C). The 60 MHz proton NMR spectrum (A-60) in ppm downfield from internal TMS is: CH_3 (d, 6, 0.66, $J = 6.5$ Hz), CH (m, 1, 1.62), CH_2 (d of d, 2, 3.82, $J = 6.0, 47.4$ Hz).

1-Bromo-1,1-dideuterio-2-methylpropane. The Grignard reagent from isopropyl bromide was reacted with paraformaldehyde-d_2 (Merck Sharp and Dohme of Canada) and then water to give 1,1-dideuterio-2-methylpropanol. This was converted to the bromide with phosphorus tribromide.[15]

1-Deuterio-2-methylpropane. The Grignard reagent from isobutyl bromide was reacted with D_2O on a vacuum line and the product was trapped at 77 K. It was purified by distillation from a Dry Ice-acetone trap into a liquid-nitrogen trap.

Samples were prepared by cosublimation of the precursor with adamantane-d_{16} (Merck Sharp and Dohme of Canada). The re-

Table I. EPR Parameters of β-Substituted *tert*-Butyl Radicals $XCH_2\dot{C}(CH_3)_2$

X	F	Cl(soln)[a]	Cl	Br	I	D
Temp, °K	214	144	215	202	208	217
$a_X \pm 0.1$, G	103.7	21.24 17.63	19.5 (^{35}Cl) 16.2 (^{37}Cl)	6.7 (^{81}Br) 6.3 (^{79}Br)	7.0	3.25 ± 0.05
$a_H(CH_2) \pm 0.1$, G	10.4[b]	6.18[b]	6.3[b]	21.4 42.7	21.9 43.8	23.2[b] ± 0.05
$a_H(CH_3) \pm 0.1$, G[c]	23.3	21.24	21.1	21.4	21.9	22.6 ± 0.05
$g \pm 0.0002$	2.0030[d]	2.00359	2.0042	2.0010	2.0009	

[a] From ref 4. [b] Values for two equivalent methylene protons. [c] Values for six equivalent protons. [d] Corrected for second-order shift.

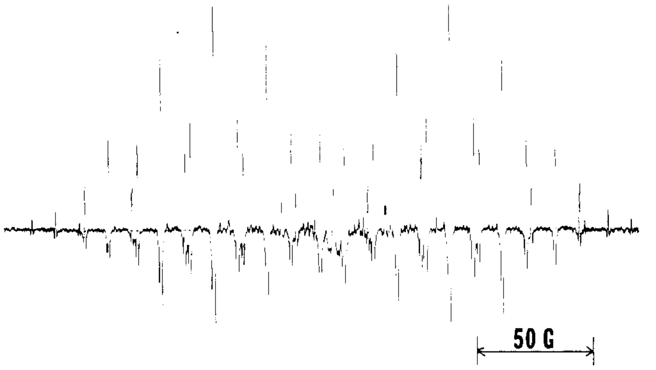


Figure 1. Second-derivative EPR spectrum of the radical from X-irradiated 1-fluoro-2-methylpropane in adamantane-d_{16} at 214 K.

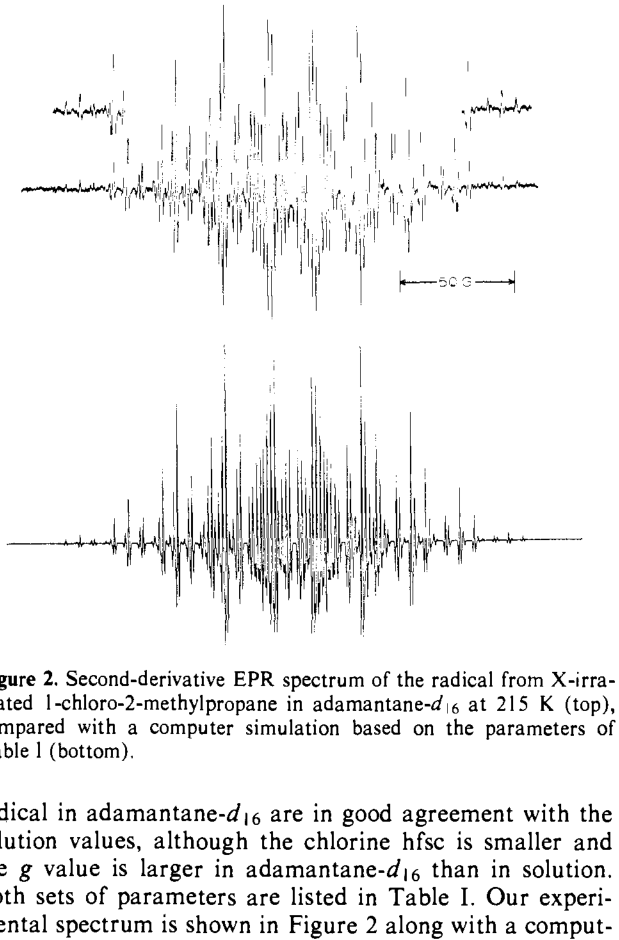


Figure 2. Second-derivative EPR spectrum of the radical from X-irradiated 1-chloro-2-methylpropane in adamantane-d_{16} at 215 K (top), compared with a computer simulation based on the parameters of Table I (bottom).

sulting solid was pressed into a hard pellet and X-irradiated at 77 K for 30-40 min. The X-ray unit and the EPR spectrometer have been previously described.[16] When necessary, computer simulations were obtained by use of DIGTIZE, a first-order EPR spectral fitting program which makes use of an IBM 2250 interactive graphic display attached to an IBM 360/65 computer. The effect of hindered rotation of the XCH_2 groups on the spectrum was studied by means of the line width alternation program described by Krusic, Meakin, and Jesson,[17] which makes use of the density matrix method of calculating line shapes, adapted for our local computer and plotting facilities.

Results

In all cases the radical initially observed after X-irradiation at 77 K was the β-substituted *tert*-butyl radical $XCH_2\text{-}\dot{C}(CH_3)_2$ (X = F, Cl, Br, I, and D) formed by removal of the tertiary proton from the precursor molecule (vide infra). The perdeuterio-2-adamantyl radical was also formed by radiation damaging of the matrix but this could either be partially removed by thermal annealing or discriminated against by the second-derivative EPR presentation (which favors narrow lines over broad ones). The spectra, with computer simulations where necessary, are shown in Figures 1-6 and the EPR parameters are listed in Table I.

EPR Spectral Results. 2-Fluoro-1,1-dimethylethyl Radical (β-Fluoro-*tert*-butyl Radical). The EPR spectrum at 214 K of 1-fluoro-2-methylpropane (isobutyl fluoride) X-irradiated in adamantane-d_{16} (Figure 1) consists of a large doublet (103.7 G) split into binomial septets (23.3 G), with each line finally split into triplets (10.4 G), also with binomial intensity ratios. We attribute this spectrum to interaction of the unpaired electron with a fluorine, six equivalent methyl protons, and two equivalent methylene protons. The methyl proton hfsc has a relatively small temperature dependence while the fluorine hfsc has a large negative, and the methylene hfsc a large positive, temperature dependence. The temperature dependences are plotted in Figure 7.

β-Chloro-*tert*-butyl Radical. This radical has previously been reported in solution and our EPR parameters for the radical in adamantane-d_{16} are in good agreement with the solution values, although the chlorine hfsc is smaller and the g value is larger in adamantane-d_{16} than in solution. Both sets of parameters are listed in Table I. Our experimental spectrum is shown in Figure 2 along with a computer simulation which includes both ^{35}Cl and ^{37}Cl in the ratio of their natural abundances. Also in agreement with the solution results, and in marked contrast to the fluoro radical (vide supra), the chlorine and methylene proton hfsc are nearly temperature independent over the range 210 to 300 K.

β-Bromo-*tert*-butyl Radical. The EPR spectrum to be expected from a bromine-containing radical is complicated by the presence of two almost equally abundant bromine isotopes (^{79}Br and ^{81}Br) with nearly equal magnetic moments and both with $I = \frac{3}{2}$. For a single bromine a pattern of four pairs of lines should be observed, with the splitting between the lines of the outer pairs being $\frac{3}{2}$ (a ^{81}Br − a ^{79}Br) and between the lines of the inner pairs $\frac{1}{2}$ (a ^{81}Br − a ^{79}Br), as shown in the stick diagram below.

Resolution of each pair would depend on the values of the hfsc relative to the line width, and in our experimental spectra (Figures 3 and 4) only the outer pairs are resolved while the inner pairs merge to form lines of double the intensity.

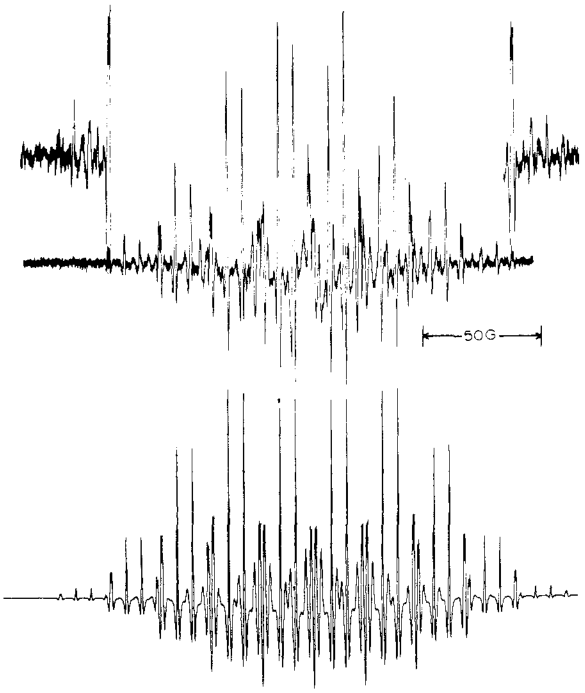


Figure 3. Second-derivative EPR spectrum of the radical from X-irradiated 1-bromo-2-methylpropane in adamantane-d_{16} at 202 K (top), compared with a computer simulation based on the parameters of Table 1 and a methylene proton exchange rate of 1.5×10^9 sec^{-1} (bottom).

Nevertheless, the pattern is certainly diagnostic of the presence of bromine in the radical. Since the original carbon skeleton remains intact as shown by the formation of *tert*-butyl radical upon reaction with the matrix (vide infra), we conclude that the radical originally formed upon X-irradiation of isobutyl bromide in adamantane-d_{16} is the β-bromo-*tert*-butyl radical. There are no 1:2:1 triplets from small equivalent methylene protons as there are in the fluoro and chloro radicals and the overall spectrum is best fitted by a computer simulation which includes, in addition to the bromine, seven equivalent protons with hfsc of 21.4 G and one proton with hfsc twice as large (42.7 G). The structure of the radical thus requires *inequivalent* methylene protons, one with an hfsc accidentally equivalent to six methyl protons and the other twice as large.

The broad, low-intensity lines in the spectrum (crosses in Figure 4) are not yet accounted for; however, hindered rotation of the CH_2Br group involving an intermediate rate of exchange of the two inequivalent methylene protons would produce line-width alternation in the spectrum and would generate broad lines at the observed locations. Computer simulation with the line-width alternation program gave the best fit to the experimental spectrum at 202 K with an assumed rate of exchange of 1.5×10^9 sec^{-1}, while at lower temperatures ($\simeq 150°$ K), where the radical is presumably in the slow-exchange limit, the spectra were best fitted with a rate no faster than 10^8 sec^{-1}. These parameters lead to a *lower* limit (because of uncertainty in the determination of the slow-exchange rate) for the activation energy for methylene group torsion of 3 kcal/mol by use of the Arrhenius equation. From transition state theory the rate and the free energy of activation are related by the expression

$$\text{rate} = (kT/h) \exp(-\Delta F^{\ddagger}/RT)$$

At 202 K this gives $\Delta F^{\ddagger} = 3.2$ kcal/mol. The only remaining difference between the computer simulation and the experimental spectrum is the unusual intensity ratios within the bromine multiplets which will be explained in the Discussion section. Within the resolution of the spectra, which is poorer than the radicals discussed above because of a greater experimental line width, the methyl proton hfsc are independent of temperature while the bromine hfsc has a negative temperature dependence (Figure 7).

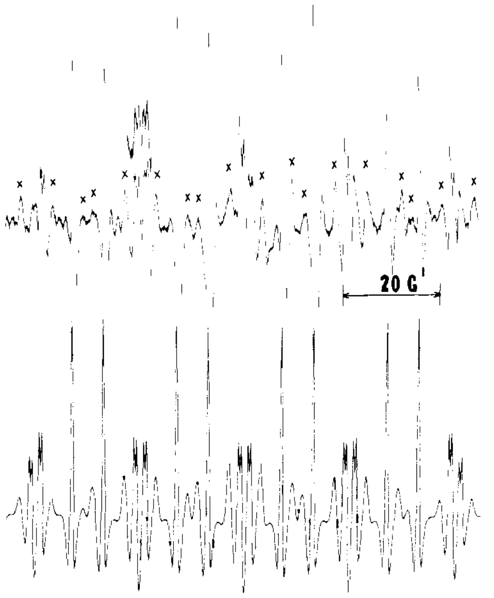


Figure 4. Expanded-scale spectrum of the radical from 1-bromo-2-methylpropane (see caption for Figure 3).

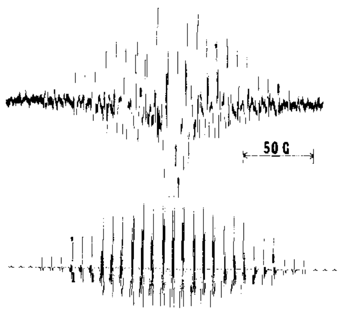


Figure 5. Second-derivative EPR spectrum of the radical from X-irradiated 1-iodo-2-methylpropane in adamantane-d_{16} at 208 K (top), compared with a computer simulation based on the parameters of Table 1 (bottom).

The EPR spectrum of the radical produced from 1-bromo-1,1-dideuterio-2-methylpropane was correctly simulated by replacing the inequivalent methylene proton hfsc by two deuterium hfsc of 3.28 and 6.55 G (also undergoing exchange).

β-Iodo-*tert*-butyl Radical. Iodine has only one naturally occurring isotope (^{127}I, $I = 5/2$), so that the EPR spectrum from a radical containing iodine should show groups of six equally spaced lines. Such patterns can be seen in the experimental spectrum (Figure 5), with the last three lines of each group almost overlapped with the first three lines of the next group. Like the bromo radical, the best computer simulation of the spectrum included seven equivalent protons and one proton with hfsc twice as large. Thus we assume that this radical also has inequivalent methylene protons, with one of them accidentally having the same hfsc as the six methyl protons and the other having twice this hfsc. The iodine hfsc has a negative temperature dependence very similar to that of bromine (Figure 7), while the methyl proton hfsc are independent of temperature within the line width (0.65 G).

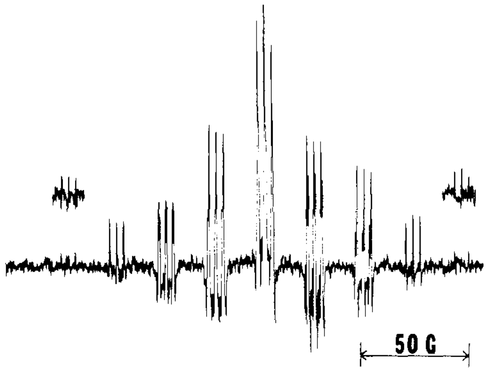
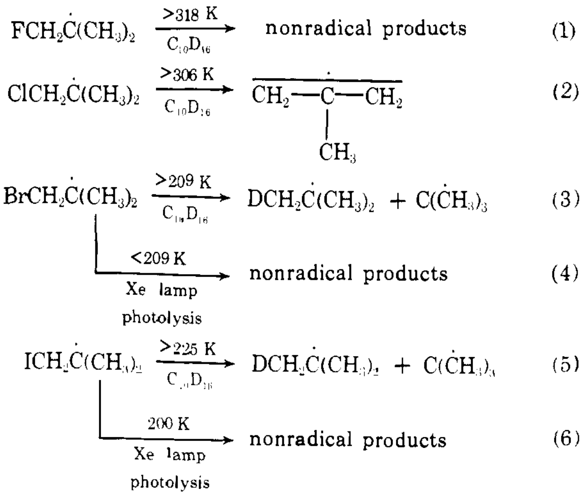


Figure 6. Second-derivative EPR spectrum of the radical from X-irradiated 1-deuterio-2-methylpropane in adamantane-d_{16} at 217 K.

Although line width alternation due to exchange of the two methylene protons could be expected to occur in this radical also, the characteristic broad lines were not observed and the intensity ratios in the iodine multiplet appear to be 1:1:1:1:1:1. Therefore it is likely that this radical is in the slow-exchange region up to the temperature at which it disappears (~225 K).

β-Deuterio-*tert*-butyl Radical. To confirm the identity of the thermal reaction product from the β-bromo-*tert*-butyl and β-iodo-*tert*-butyl radicals (vide infra), the β-deuterio-*tert*-butyl radical was prepared by X-irradiation of β-deuterio-2-methylpropane in adamantane-d_{16}. Close examination of the spectrum (Figure 6) shows that there is some asymmetry, because of partial resolution of the second-order components of the proton hfsc. Also, the methylene proton hfsc is no longer exactly equivalent to the methyl proton hfsc (Table I) at low temperatures, and the deuterium hfsc (3.25 G at 217 K) is considerably less than the value of 3.56 G that would be calculated from the methylene proton hfsc and the (D/H) magnetic moment ratio. At higher temperatures the methyl and methylene proton hfsc approached the same average value (Figure 7), with the former hfsc having a positive temperature dependence and the latter a negative temperature dependence.

Radical Reactions and Stability. Although the radicals initially formed are all of the same type, the subsequent modes of decay differ greatly depending on the particular halogen. Furthermore the stability of the radicals (as shown by the temperature of disappearance or reaction) reaches a minimum with the bromo radical. The results are summarized in eq 1-6.



$$\mathrm{FCH_2\dot{C}(CH_3)_2} \xrightarrow[\mathrm{C_{10}D_{16}}]{>318\ \mathrm{K}} \text{nonradical products} \quad (1)$$

$$\mathrm{ClCH_2\dot{C}(CH_3)_2} \xrightarrow[\mathrm{C_{10}D_{16}}]{>306\ \mathrm{K}} \overline{\mathrm{CH_2{-}\overset{\cdot}{\underset{\displaystyle CH_3}{\underset{|}{C}}}{-}CH_2}} \quad (2)$$

$$\mathrm{BrCH_2\dot{C}(CH_3)_2} \xrightarrow[\mathrm{C_{10}D_{16}}]{>209\ \mathrm{K}} \mathrm{DCH_2\dot{C}(CH_3)_2 + C(\dot{C}H_3)_3} \quad (3)$$

$$\xrightarrow[\text{Xe lamp photolysis}]{<209\ \mathrm{K}} \text{nonradical products} \quad (4)$$

$$\mathrm{ICH_2\dot{C}(CH_3)_2} \xrightarrow[\mathrm{C_{10}D_{16}}]{>225\ \mathrm{K}} \mathrm{DCH_2\dot{C}(CH_3)_2 + C(\dot{C}H_3)_3} \quad (5)$$

$$\xrightarrow[\text{Xe lamp photolysis}]{200\ \mathrm{K}} \text{nonradical products} \quad (6)$$

At sufficiently high temperatures (>306 K) the spectrum of the β-chloro-*tert*-butyl radical disappeared and the spectrum of the 2-methyl allyl radical[18] appeared in its place. Presumably this was formed by the elimination of HCl from the chloro radical. The 2-methyl allyl radical decayed in turn to nonradical products.

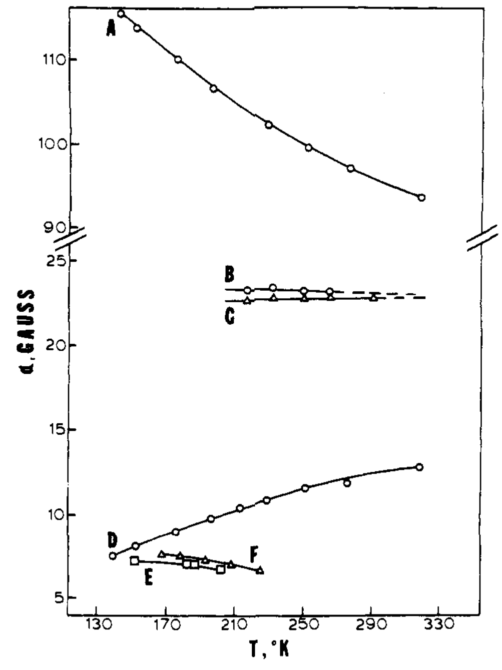


Figure 7. Temperature dependences of nuclear hyperfine splittings (gauss vs. °K). Note the change in the vertical scale for curve A. (A) Fluorine hfsc's in $\mathrm{FCH_2\dot{C}(CH_3)_2}$; (B) methylene proton hfsc's in $\mathrm{DCH_2\dot{C}(CH_3)_2}$; (C) methyl proton hfsc's in $\mathrm{DCH_2\dot{C}(CH_3)_2}$; (D) methylene proton hfsc's in $\mathrm{FCH_2\dot{C}(CH_3)_2}$; (E) bromine hfsc's in $\mathrm{^{81}BrCH_2\dot{C}(CH_3)_2}$; (F) iodine hfsc's in $\mathrm{ICH_2\dot{C}(CH_3)_2}$.

The thermal reaction of the bromo radical (eq. 3) is the only one in this series that occurs almost instantaneously at a specific temperature, 209 K, which is the same as the first-order phase transition temperature of adamantane.[19] We have previously noted sharp effects on the optical spectra of the *p*-fluorobenzyl radical in adamantane caused by the increase in the size of the cavity available in the matrix as it changes from the low-temperature tetragonal lattice to the high-temperature cubic lattice.[20] The spectrum formed upon warming of the sample contained lines from both the monodeuterio-*tert*-butyl radical and ordinary *tert*-butyl radical in about equal abundance. The latter radical is probably formed from the protons present (the adamantane is 97% deuterated according to the manufacturer's analysis) aided by a large isotope effect in the exchange reaction. Hydrogen atom exchange with the adamantane matrix has been observed previously with other radicals.[21,22] The thermal reaction products of the iodo radical are the same as for the bromo, the only difference being that the reaction occurs at higher temperatures and appears to proceed more slowly. In the case that ordinary adamantane is utilized as the matrix the thermal reaction product for both β-bromo- and β-iodo-*tert*-butyl radicals is $\cdot\mathrm{C(CH_3)_3}$.

We have also observed that the in situ photolysis of the bromo and iodo radicals in adamantane-d_{16} with a 1 kW xenon lamp causes rapid disappearance[23] of the radicals (eq 4 and 6) whereas photolysis of the chloro radical only causes a slight decrease in signal intensity. This observed high reactivity of the bromo radical upon photolysis may be the explanation for the failure of previous workers to observe β-bromoethyl radical by uv photolysis in solution.[6]

Discussion

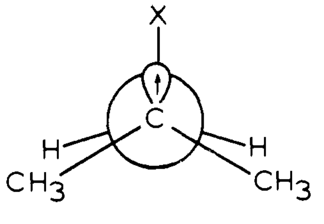
The similarity of the methyl proton hfsc in this series of halogenated radicals and the fact that either large halogen and small β-proton hfsc's or vice versa are observed (Table I) are strong evidence that the species are indeed β-halo-*tert*-butyl radicals. Further evidence for their identity are the identical methods of preparation and the retention of the *tert*-butyl carbon framework in the radicals produced upon thermal reaction for the chloro, bromo, and iodo species. The unexpected aspect of our results is primarily that the β-bromo- and β-iodo-*tert*-butyl radicals do not have the halogen eclipsed with the unpaired electron orbital as is the case for the fluoro and chloro radicals.

In order to discuss the conformational preferences of radicals such as those reported herein one must consider the relevant interactions in the corresponding closed shell species. Barriers to rotation about single bonds in closed shell molecules are attributed primarily to repulsion between electron pairs on the joined atoms.[24] The repulsion is smaller for electron pairs involved in bonding to other atoms than for lone pairs because of the more diffuse nature of the latter, and the repulsion is further reduced as the bond angles are increased. In addition to electronegative and electropositive substituents which affect the barrier through bond polarization, substituents which are sufficiently bulky cause a steric repulsion which must also be taken into account. In the case of free radicals, however, the interaction of the singly occupied orbital with lone-pair orbitals becomes favorable via conjugation and the interaction with electron-pair bonds becomes favorable via hyperconjugation.[25] These latter very specific interactions together with those operative for closed shell molecules will then determine the stable conformations and barriers to rotation of free radicals.

Applying these ideas to the β-fluoroethyl radical which has been shown to prefer conformation **3** slightly to conformation **1**, it can be seen that hyperconjugation with the β hydrogens is slightly more favorable than hyperconjugation with the fluorine.[26] The 1-propyl radical also prefers conformation **3** and thus the hyperconjugation with the methyl group must also be less favorable than with the β hydrogens. The β-chloroethyl radical, on the other hand, prefers conformation **1** so strongly that there is only a small temperature dependence of the β proton and chlorine hfsc's, and therefore hyperconjugation with the chlorine must be considerably more favorable than with the β hydrogens. The effect of the repulsion caused by eclipsing the bonding electron pairs (as in C–F with C–H for **3**) is probably quite small for these ethyl radicals because of the 120° bond angles around the trigonal carbon and because it enters primarily as a sixfold term in the potential.[24]

One would expect that the smaller carbon–halogen bond energies of bromine and iodine compared to that of chlorine would also create a favorable hyperconjugative interaction for them relative to hydrogen,[25] and therefore the β-bromo- and β-iodoethyl radicals should also prefer conformation **1.** Furthermore the effect of substitution of the α protons with methyl groups to form the corresponding β-halo-*tert*-butyl radicals, which causes the fluoro radical to change its preference to the eclipsed conformation and causes the chloro radical to prefer the eclipsed conformation even more strongly as determined by the increased halogen hfsc and the decreased β-proton hfsc, has been attributed to steric effects. This effect would be even more important for the bromo and iodo radicals because of the larger size of the halogens. Our contrary experimental results thus effectively preclude this simple explanation. Since steric repulsion between the halogen and the methyl group obviously cannot be ignored, especially for bromine and iodine, we suggest that nonplanarity at the radical site allows the staggered forms to exist.

The nonplanarity of the *tert*-butyl radical has been suggested by ab initio calculations[27] and the anomalous temperature dependence of the ^{13}C and ^{1}H hfsc.[27,28] Calculations of these hfsc temperature dependences yield a barrier of ~0.5 kcal/mol for inversion.[29] Making the radical site nonplanar for a radical initially in a conformation such as **1** will result in either conformation **4** or **5** depending on the direction of the deformation. Conformation **4** is unfavorable because of the repulsion between bonding electron pairs which are now closer because of the decreased bond angles at the trigonal carbon, although some hyperconjugative stabilization would occur with the C–X bond. Conformation **5** eliminates this repulsion and allows even better hyperconjugative stabilization with the C–X bond so that this should be the favored conformation for nonplanar radicals with eclipsed X substituent.



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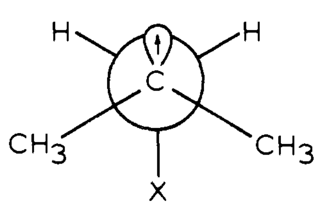

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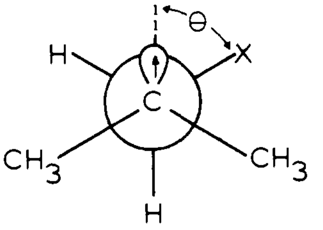

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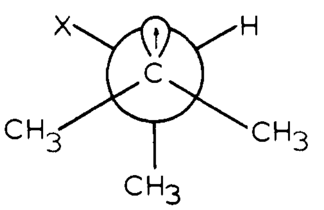

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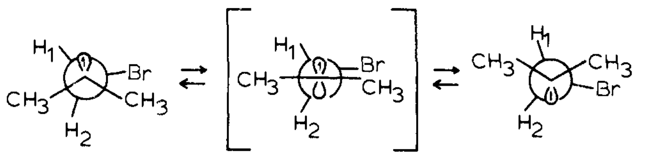
This also offers a ready explanation for the anomalously low β-proton hfsc observed for some β-substituted *tert*-alkyl radicals compared to the corresponding β-substituted ethyl radicals.[12] The results of an INDO calculation of β-proton hfsc as a function of rotation about the C_α–C_β bond for both a planar and a nonplanar ethyl radical are plotted in Figure 8.[30] A reduction of ~50% in the hfsc at $\theta = 60°$ corresponding to the angle of the β protons in conformation **5** is observed upon going from planar to pyramidal (for conformation **4,** $\theta = 120°$, there is actually a slight increase). The minimum β-proton hfsc of ~12 G[7] expected for conformation **1** would therefore be reduced to ~6 G in the nonplanar conformation **5.** Thus the β proton hfsc of β-fluoro-*tert*-butyl radical which appears to have reached a minimum of 5.5 G, at 77 K, and the β-proton hfsc of the β-chloro-*tert*-butyl radical, which is nearly temperature independent at 6.3 G, are actually not anomalous if the radicals prefer the nonplanar conformation **5.**

Conformation **6** will be the only other one which minimizes bonding electron pair repulsions. The local minima would not be expected exactly at $\theta_X = 60°$, however, because of competition between differing steric and conjugative interactions of X and H with the methyl groups and the singly occupied orbital, respectively. There are in fact two values for θ_X which yield the 2:1 ratio for the methylene hydrogen hfsc observed for the β-bromo- and β-iodo-*tert*-butyl radicals (cf. Figure 8). The one with $\theta \simeq 120°$ can be ruled out because this creates maximal interference of the halogen with the methyl group. The one with $\theta_X \simeq 80°$ ($\theta_H = 40$ and 160°, denoted by vertical lines on Figure 8) is therefore predicted by this method. It is interesting to note that utilizing the usual $\cos^2 \theta$ relationship (or the curve for planar ethyl radical in Figure 8) for β-proton hfsc results in $\theta_X \simeq 75°$, which for a planar radical would have the halogen within 15° of eclipsing the methyl group. A possible explanation for the change in conformation observed in the β-halo-*tert*-butyl radicals is that steric repulsion in conformation **5** becomes too large when bromine and iodine are the substituents, because the halogen will be gauche to two methyl groups in **5** but gauche to only one in **6**. In addition the larger halogens may be better able to interact with the singly occupied orbital through lone-pair conjugation in conformation **6** than the smaller ones, thus retaining an effective stabilization.

The previously mentioned β-methyl substitution effect can also be explained on the basis of a nonplanar radical site. Replacing the β protons of the β-X-*tert*-butyl radical with methyl groups will serve to reduce the hfsc of the X substituent if the methyl group prefers to be eclipsed as in **7** to a greater extent than did the proton it replaced. That this is in fact true is substantiated by the β-proton hfsc of the *tert*-amyl radical which is already down to 11.1 G at 114 K in an adamantane matrix.[33]

The motions responsible for the temperature dependences of the nonplanar radicals could be considerably more complicated than for planar ones, since nonplanarity offers the possibility of an umbrella vibration and rotational–vibrational coupling in addition to rotation about the C_α–C_β bond. Coupling can be important as shown by the results for the β-deuterio-*tert*-butyl radical, wherein the deuterium hfsc is less than, and the methylene proton hfsc greater than, the values expected from the methyl proton hfsc. These additional complications together with the fact that the $\cos^2 \theta$ dependence for β-proton hfsc is not applicable to nonplanar radicals could explain the difficulties observed in fitting temperature dependences of substituted alkyl radicals[17] and also the similarity noted[12] for the β-proton hfsc in $CH_3CH_2CCl_2$ and *tert*-amyl radical. It is clear from the hfsc values approached at low temperature that **5** is (slightly) the more stable conformation for the β-fluoro-*tert*-butyl radical but the β-chloro radical, on the other hand, is strongly locked into **5**. Likewise the β-iodo-*tert*-butyl radical strongly prefers **6**.

If it is assumed that the process which causes interconversion of the methylene protons in the β-bromo radical is also responsible for the negative temperature dependence of the bromine hfsc, then the bromine must move through an area of lowered hfsc, during the interconversion process. A simultaneous increase in θ_X of 20° from the previously determined conformation and inversion at the radical center as shown below would accomplish this result.



8 9 10

Conformations **8** and **10** differ only in the interchange of H_1 and H_2 which gives rise to the line-width alternation involving the β-proton multiplet. The planar structure **9** is then identified as the transition state with energy ~3 kcal/mol greater than **8** and **10**. The modulation of the hfsc caused by passing through **9** can cause not only the negative temperature dependences of the Br hfsc but also the progressive broadening observed within each set of Br multiplets as one approaches the center of the spectrum. The mechanism for this latter effect can be explained by a consideration of the schematic correlation diagram for the lines arising from H_1, H_2, and Br as the process **8** ↔ **9** ↔ **10** occurs. The hfsc of H_1 and H_2 would be expected to be equal and ~40 G for geometry **9** (see Figure 8) while the Br hfsc would be smaller than in **8** and **10**.

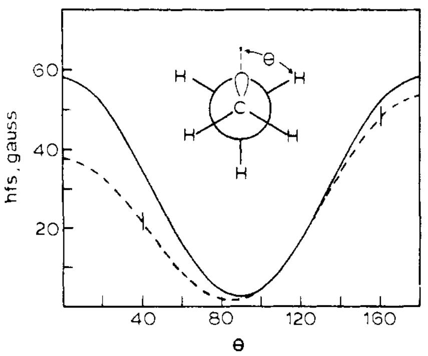
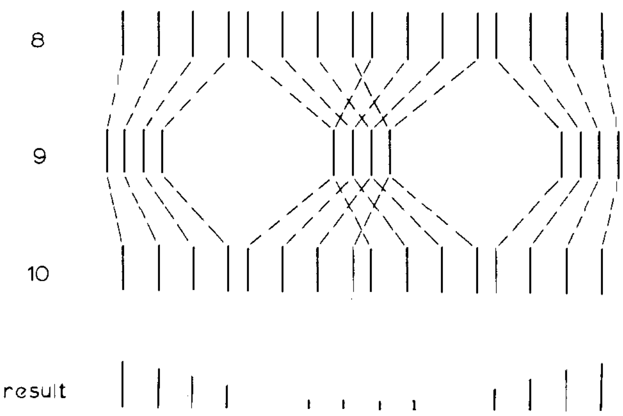


Figure 8. Ethyl radical β-proton hfsc's calculated by INDO as a function of methyl group rotation, where θ is the dihedral angle between the unpaired electron orbital and the C_β–H_β bond: (—) radical planar at C_α; (- - -) radical tetrahedral at C_α.



The resulting peak heights will be smaller according to the spectral distance the line must travel, as is shown in the result. The total spectrum will be a 1:6:15:20:15:6:1 summation of this result with interval $a(CH_3)$ giving the observed intensity modulation within the Br multiplets (Figures 3 and 4). A treatment along these same lines utilizing either **4** or **5** as the transition state results in a similar pattern within the Br multiplets but has the disadvantage of predicting a positive temperature dependence of the Br hfsc.

Such a simultaneous vibration–rotation as suggested above or indeed any process involving inversion at the radical center would result in racemization of an initially optically active radical at a rate equal to the inversion frequency. Thus our model for the bromo and iodo radicals, which involves a nonplanar radical and restricted rotation of the CH_2X group, would be expected to give the same results for hydrogen abstraction as the bridged radical intermediates proposed by Skell and others.[2] The primary difference between the two models is actually a minor detail, namely we propose that the nonplanarity of the radical site allows attack preferentially from the same side from which the hydrogen was removed (until inversion occurs), whereas Skell proposed that one side of a planar radical site is blocked by a bridging halogen. Our proposed structure is indicative of a bridged free radical in the most general sense, that is, of a strong, specific interaction of the halogen with the singly occupied orbital which freezes the nonplanar alkyl radical site in its initial conformation long enough for trapping with retention of configuration to occur. (It must be emphasized that the barrier to inversion of ~0.5 kcal/mol for *tert*-butyl radical in adamantane[29] is increased to ~3 kcal/mol by β-bromine substitution and even greater by β-iodo substitution.) For example, the rate of racemization[2] for the 1-bromo-2-methylbutyl radical is $\sim 10^{10}$ sec^{-1}. We obtain rates of interconversion of $\sim 10^8$ to $\sim 10^9$ sec^{-1} for the β-bromo-*tert*-butyl radical over a range of temperatures, which considering the differences in reaction conditions are obviously in the range that would permit retention of configuration. A stabilization energy of 2.9 kcal/mol was recently reported from the CH_2Br group in a free-radical ring-opening reaction of a substituted bicyclohexane,[34] and Skell found an activation energy of 6 kcal/mol for racemization of the 1-bromo-2-methylbutyl radical.[2] Our lower limit of 3 kcal/mol is in reasonable agreement with these values.

There have been very few bromine- and iodine-containing alkyl radicals studied in solution by EPR. The 2-bromo allyl radical has been tentatively identified with a *g* value of 2.0018 and a bromine hfsc of 1.35 G.[6] The γ-bromopropyl radical and several of its higher homologs have also been reported but the bromine hfsc's were not resolved.[6] A study of irradiated frozen alkyl halides[5] and frozen solutions of ethylene plus bromine or iodine[5,35] have led to the identification of halogen-containing radicals with large halogen hfsc's which were identified as β-halo alkyl radicals. The radical from irradiated *tert*-butyl chloride[5] is certainly the β-chloro-*tert*-butyl radical; however, if the radicals with Br and I hfsc's of 250 and 400 G,[35] respectively, are the corresponding β-halo radicals, then they must have a very different conformation than those measured here. It is actually not unlikely that the most stable conformation of a β-halo alkyl radical could depend upon the solvent or matrix in which it is produced since the order of stability of halogenated alkane conformations is known to change with solvent.[36-40] Therefore, the observed conformations of these radicals in the adamantane matrix may not be the most stable conformations in other solvents.

The trend in the *g* values which we observe (Table I) is indicative of a closer approach of vacant σ^* orbitals to the singly occupied as one goes from the chloro ($+\Delta g$) to the bromo and iodo radicals ($-\Delta g$). This is not unexpected considering the smaller carbon-halogen bond energies of the latter (cf. $g = 2.0018$ for 2-bromo allyl radical).

Detailed calculations on the phenomena qualitatively treated herein will be reported in a following paper.[41]

Conclusions

We conclude that our experimental results and other relevant data in the literature are more nearly consistent with the assumption that tertiary alkyl radicals are more nonplanar than they are planar at the radical site. Specifically we find that the β-chloro-*tert*-butyl radical is strongly locked into the eclipsed conformation **5**, the fluoro radical also prefers conformation **5** but has much larger vibration-rotation motions, while the bromo and iodo radicals prefer the staggered conformation **6** in an adamantane matrix. The different conformational preferences of the radicals are probably the cause of their different modes of decay. Finally our observations offer an alternative explanation to the bridged radical hypothesis for the retention of stereochemical configuration in reactions of β-haloalkyl radicals.

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