Structure of 2-Alkanonyl Radicals. III. Electron Paramagnetic Resonance Study of Radicals Produced by X-Irradiation of Aliphatic Ketones in Adamantane[1,2]

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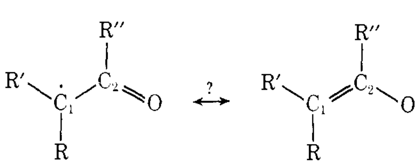
Abstract: A quantitative assessment of the role of spin delocalization in 2-alkanonyl radicals (RR′ĊCOR″) is provided by the measurement of the ^{1}H and ^{13}C hyperfine splitting constants (hfs), *g* values, and optical spectra of 19 radicals of this type (as well as several deuterated species) which are produced by X-irradiation of adamantane containing small amounts of the precursor ketones. The ^{17}O hfs of the 2-cyclohexanonyl radical has been determined and the results of INDO calculations on several model compounds are reported. Based on a comparison of the "experimental" π-orbital spin densities with those previously determined for alkyl and allyl free radicals, it is concluded that 2-alkanonyl radicals are approximately 30% allylic in character. Thus, a typical radical of this type is a resonance hybrid of two allylic structures (RR′ĊCOR″, I, and RR′C=CȮR″, II) with structure II contributing about 15%. This conclusion is supported by the observation of effects due to restricted rotation about the Ċ–CO bond in the epr spectra of several open-chain 2-alkanonyl radicals including (1) symmetrically substituted radicals (*i.e.*, R = R′) which exhibit inequivalent α- or β-proton hfs at relatively high temperatures and (2) unsymmetrically substituted radicals (*i.e.*, R ≠ R′) which exist in two conformations of different energy whose relative populations are temperature dependent. An analysis of the spectra of both types of radicals yields estimates of the order of 9 kcal/mol for the barriers to restricted rotation about the Ċ–CO bond in symmetrically substituted radicals and makes possible a determination of the structures and relative stabilities of the two conformations of unsymmetrically substituted radicals. Finally, the hfs of some of the β protons in several of the open-chain radicals with γ-alkyl groups are unusually small and show a marked temperature dependence. These results are taken as evidence for an additional barrier hindering rotation about the C_α–C_β bond of the radicals and provide information about the structures of the preferred conformations of radicals with intrinsically small rotational barriers.

Free radicals of the type RR′ĊCOR″ have π-electron systems which are isoelectronic with that of the allyl radical and are therefore of considerable interest because of the possibility of spin delocalization, *i.e.*



I II

However, only a few studies of the properties of 2-alkanonyl radicals have been made and these have led to ambiguous conclusions regarding the relative importance of structures I and II in radicals of this type. These studies include measurements of the *g* values and proton hyperfine splitting constants (hfs) of some 2-alkanonyl radicals by epr spectroscopy[3–9] and determinations of the heats of formation of the acetonyl and 1-methylacetonyl radicals using kinetic methods.[10–12] On the basis of these results, it has been suggested that 2-alkanonyl radicals are largely alkyl in character and that the contribution of a structure analogous to II is small in radicals of this type.[4,7,10–12] However, an examination of the temperature dependence of the epr spectrum of the acetonyl radical showed that the two α protons of this radical are inequivalent[6,8] at low temperatures and that there is an unusually high barrier to rotation about the C_1–C_2 bond.[8] As similar results are observed for allylic systems,[13–15] this suggests that there is a significant contribution of II to the structure of the acetonyl radical.[16]

In view of the importance of 2-alkanonyl radicals in organic chemistry, a quantitative assessment of the role of spin delocalization in this class of radicals obviously would be desirable. Therefore, we have carried out an extensive study of the spectroscopic properties of a wide variety of 2-alkanonyl radicals which are produced in high yield by X-irradiation of aliphatic ketones in adamantane. The use of this technique[17] has made possible the determination of the

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(1) Part I: D. M. Camaioni and D. W. Pratt, *J. Amer. Chem. Soc.*, **94**, 9258 (1972).

(2) Part II: D. M. Camaioni, H. F. Walter, and D. W. Pratt, *ibid.*, **95**, 4057 (1973).

(3) W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 3625 (1964).

(4) O. H. Griffith, *J. Chem. Phys.*, **42**, 2644 (1965).

(5) H. Fischer, *Z. Naturforsch. A*, **20**, 428 (1965).

(6) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **45**, 1946 (1966).

(7) G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, **89**, 5059 (1967).

(8) G. Golde, K. Möbius, and W. Kaminski, *Z. Naturforsch. A*, **24**, 1214 (1969).

(9) H. Paul and H. Fischer, *Chem. Commun.*, 1038 (1971).

(10) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 11 (1970).

(11) K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **92**, 5541 (1970).

(12) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).

(13) R. W. Fessenden and R. H. Schuler, *J. Chem. Pyhs.*, **39**, 2147 (1963).

(14) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

(15) The α protons in allyl radical itself are inequivalent at temperatures as high as 475°K: P. J. Krusic, private communication.

(16) The epr spectrum of a radical believed to be $\dot{C}H_2CHO$ also shows inequivalent α protons at 260°K. See R. Livingston and H. Zeldes, *J. Amer. Chem. Soc.*, **88**, 4333 (1966).

(17) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970); **53**, 3932 (1970).

^1H and ^{13}C hfs, g values, and optical spectra of primary, secondary, and tertiary radicals of this type over wide temperature ranges. In addition, we have measured the ^{17}O hfs in the 2-cyclohexanonyl radical and carried out INDO calculations on several model compounds. The results of this study indicate that although 2-alkanonyl radicals are largely alkyl in character, they are stabilized by resonance to a small but chemically significant extent.

As a consequence of this spin delocalization, effects due to restricted rotation about the C_1–C_2 bond have been observed in the epr spectra of several open-chain 2-alkanonyl radicals. These effects include the observation of an inequivalence in the α- and β-proton hfs of several symmetrically substituted radicals at temperatures considerably above room temperature and the finding that unsymmetrically substituted radicals exist in two conformations of different energy whose relative populations are temperature dependent. An analysis of the spectra of both types of radicals yields estimates of the barriers to restricted rotation about the C_1–C_2 bond in the 3,3,3-trimethylacetonyl and 1,1-dimethylacetonyl radicals and makes possible a determination of the structures and relative stabilities of the two conformations of unsymmetrically substituted radicals. Finally, the proton hfs of some of the β protons in several of the open-chain radicals with γ-alkyl groups are unusually small and show a marked temperature dependence. These results are interpreted in terms of preferred conformations of the radicals in the adamantane matrix and hindered rotation about the C_α–C_β bond. Preliminary accounts of some aspects of this work have appeared.[1,2]

Experimental Section

A. Sample Preparation. Puriss grade adamantane was obtained from the Aldrich Chemical Co. and further purified before use by treatment with Nuchar-C190-N activated carbon in reagent grade *n*-heptane followed by recrystallization and removal of the solvent by pumping on a high vacuum line. Adamantane-d_{16} (97.7 atom % D) was a gift from Merck Sharp and Dohme of Canada, Ltd., and was used as received. Incorporation of the ketones was accomplished either by recrystallizing adamantane from the parent ketone or by subliming adamantane in a sealed tube which contained a small amount of ketone. The white powder so obtained was pressed into a small cylindrical or disk-shaped pellet and X-irradiated in air at either room temperature or ~100°K for 5–10 min using an XRD-1 X-ray generator with a Cu-target tube.

All ketones were supplied by Aldrich or Chemical Samples Co. and were used as received or purified by distillation. 3-Methyl-2-butanone-d_4, 3-methyl-2-pentanone-d_4, cyclopentanone-d_4, and cyclohexanone-d_4 were prepared by 3 to 4 exchanges of the parent compound with excess D_2O in the presence of K_2CO_3. Samples of $CH_3COC(CD_3)_3$ were synthesized by using modified versions of the preparation of pinacol hydrate and pinacolone which are described in the literature.[18] Acetone-d_6, obtained from Stohler Isotope Chemical Co., was used as the starting material and the resulting pinacolone-d_{12} was exchanged with H_2O to make the d_9-species. The degree of deuteration of all compounds was checked by nmr.

^{17}O-enriched cyclohexanone was prepared by two exchanges with normalized H_2O containing 4 atom % ^{17}O which was obtained from Stohler. The first exchange was carried out by agitating 0.5 ml of cyclohexanone and 0.25 ml of $H_2{}^{17}O$ in a centrifuge tube topped with a serum cap. After 12 hr, the water layer was removed with a syringe, a second aliquot of 0.25 ml of $H_2{}^{17}O$ was added, and the tube was shaken for an additional 12-hr period. Following removal of the water layer, a small amount of cyclohexanone-^{17}O was removed and used to prepare a sample using the sealed tube method. Analysis of the ketone by mass spectrometry showed an enrichment of 2.5 atom % ^{17}O which is in agreement with the epr results.

Several 2-alkanonyl radicals were also prepared by photolysis of a degassed cyclopropane solution containing small amounts of di-*tert*-butyl peroxide and the precursor ketone.[19] An Osram 500-W medium pressure mercury lamp with quartz optics was used to generate the radical by *in situ* irradiation of the sample which was held in a sealed quartz tube at ~200°K. Because of uv absorption due to the carbonyl group, radical yields were low and best results were obtained using a 3:2:1 volume ratio of cyclopropane, peroxide, and ketone.

B. Epr and Optical Spectra. Epr spectra were obtained with a Varian E-4 epr spectrometer system which is equipped with an E-204 low frequency modulation module and E-257 variable temperature accessory. First and second derivative signal presentations were employed. The temperature controller was calibrated by a thermocouple and temperatures reported over the range of 100–400°K are believed to be accurate to ±2°K. Care was taken to avoid both modulation broadening and power saturation of the spectra; typically, epr spectra of 2-alkanonyl radicals in adamantane could be recorded at power levels as high as 10 mW without noticeable saturation effects. Magnetic field sweep calibration was checked with an aqueous solution of Fremy's salt, and g values were determined by comparison with an internal sample of DPPH. The microwave frequency was measured with a Hewlett-Packard Model 5246L electronic counter and Model 5257A transfer oscillator plug-in.

Optical absorption spectra of 2-alkanonyl radicals were obtained using methods recently developed in this laboratory.[20] Briefly, the procedure consisted of comparing the optical transmission characteristics of two pressed disks of adamantane (10-mm o.d., ~1 mm thick) containing a low concentration of ketone in the sample and reference beams of a Cary 14 spectrophotometer. After a suitable base line was obtained with a pair of disks, one disk was X-irradiated at room temperature and placed in a specially designed low temperature cell. The cell was then evacuated and placed in the sample beam and its transmission characteristics were compared to those of the unirradiated disk in the reference beam. The spectrum was recorded in the usual way with the sample at or below ambient temperature. Wavelength measurements were made following calibration of the instrument with a mercury pen lamp and are thought to be accurate to ±50 Å.

C. Computer Calculations. Isotropic epr spectra of samples which contained only one detectable radical were computer simulated by ISOEPR[17] on an XDS Sigma-5 computer and Calcomp plotter, compared with experimental spectra, and then recomputed if necessary until the best fit was obtained. ISOEPR is a first-order program which can handle ten $I = {}^1/_2$ and two $I = 1$ nuclei with Gaussian line shapes in absorption, first derivative, or second derivative presentation. For samples which contained more than one radical, a modified version of ISOEPR was written. This program (BLEND), also first order, permits the addition of up to ten spectra with different g values, hfs parameters, and relative intensities. It therefore makes possible an estimate of the relative radical concentrations in a single spectrum.

Epr line shapes in the presence of exchange were calculated using the program MEAKIN[21] which assumes a first-order spin Hamiltonian and employs the density matrix approach. The original version of this program included up to six exchanging spins with $I = {}^1/_2$, six nonexchanging spins with $I = {}^1/_2$, six rate constants, and the capability of adding Gaussian character to the line shape function. It has been modified by us to permit hyperfine effects for up to five sets of nine equivalent nuclei with no restriction on I and therefore allows inclusion of hfs due to ^2H, ^{13}C, and ^{17}O which are present either in natural abundance or in enriched samples. In addition, the peak-to-peak line width and per cent Gaussian character in the line are input and the program computes the Lorentzian and Gaussian parameters needed to reproduce the observed line shape. These spectra were simulated on a PDP-10 computer and Calcomp plotter.

Since the ^{13}C satellites in several of the spectra appeared on the wings of the more intense main lines, reliable ^{13}C hfs could be determined in these cases only by varying the per cent Gaussian

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[18] H. Gilman, *et al.*, Ed., "Organic Synthesis," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 459.

[19] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968).

[20] J. E. Jordan, D. W. Pratt, and D. E. Wood, submitted for publication.

[21] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

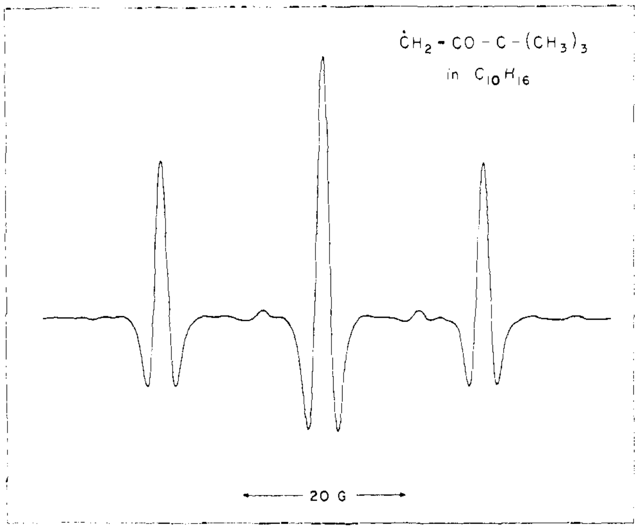

Figure 1. Second-derivative epr spectrum of the 3,3,3-trimethylacetonyl radical in adamantane-h_{16} at 220°K. Weak lines in the spectrum are due to an impurity alkyl radical with a significantly lower *g* value.

character in the line shape. Therefore, these spectra were computer simulated using MEAKIN (without exchange) and adjusting the per cent Gaussian character until a best fit of the main lines was obtained. The ^{13}C lines were then added with the correct relative intensity and the ^{13}C hfs were adjusted until the high gain spectrum was satisfactorily reproduced. This was done for both the low and high field ^{13}C patterns and the values obtained were averaged to correct for second-order effects.

INDO calculations were carried out in single precision on a PDP-10 computer using a modified version of the program which is in the literature.[22] The principal change was the incorporation of the VGEOM subroutine which makes possible energy minimization with respect to each of the bond distances and angles of the radical in a systematic way. Comparison calculations for some structures were also carried out in double precision. The results agreed to seven significant figures for total energy and no difference could be detected in computer values for spin densities or coupling constants.

Results

A. Epr Spectra and Radical Stability. The epr spectra of 2-alkanonyl radicals having eight or less heavy atoms and trapped in the polycrystalline adamantane matrix are "isotropic" and exhibit line shapes which are symmetric over a wide temperature range because of the motional averaging of intramolecular hyperfine and *g*-tensor anisotropies. However, this averaging is not sufficiently fast (or isotropic) to eliminate inhomogeneous broadening owing to intermolecular dipolar interactions between the radical and the magnetic nuclei of the "nonreorienting" matrix.[17] As a result, the line shape of a single hyperfine component is considerably broader (1–2 G) than normally observed in solution and contains a significant amount of Gaussian character which depends on the size and shape of the radical and on temperature. Some improvement in spectral resolution can be obtained by using adamantane-d_{16} as a host material, but even with this matrix all spectra were computer simulated in order to verify assignment.

Formally, 2-alkanonyl radicals are produced by removal of a hydrogen atom from the carbon α to the carbonyl group; for example, X-irradiation of 2-butanone in adamantane leads to the formation of the 1-methylacetonyl radical, $CH_3\dot{C}HCOCH_3$. In most cases where more than one type of radical might be formed, only one is observed and it is always the one which results from damaging the more highly substituted carbon (*e.g.*, the 3-methylacetonyl radical, $\dot{C}H_2COCH_2CH_3$, is not observed by X-irradiation of 2-butanone in adamantane). Thus, the stability of the radicals with respect to carbon substitution is $RR'\dot{C}COR'' > R\dot{C}HCOR' \gg \dot{C}H_2COR$, which is the same ordering as is commonly observed for alkyl radicals. In some cases half-lives of up to 2 days at room temperature have been measured for highly substituted tertiary radicals in adamantane.

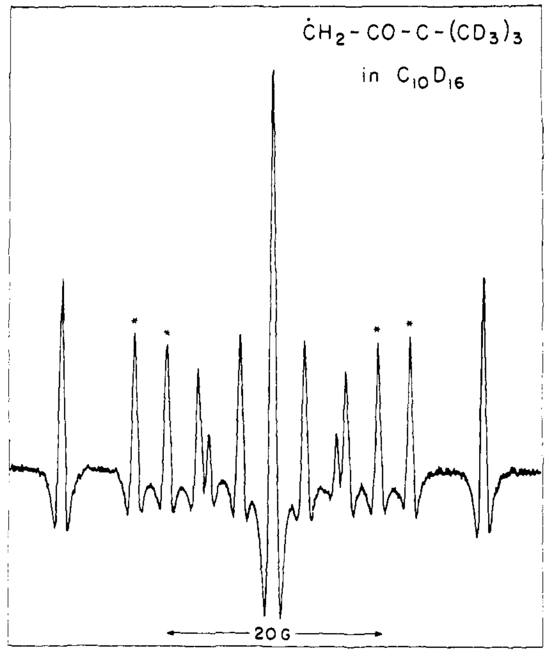

Figure 2. Second-derivative epr spectrum of $\dot{C}H_2COC(CD_3)_3$ in $C_{10}D_{16}$ at 220°K. Lines due to the $\dot{C}HDCOC(CD_3)_3$ and $\dot{C}D_2CO$-$C(CD_3)_3$ radicals, which result from exchange between the parent radical ($\dot{C}H_2$–) and the matrix, are also present. Those marked with an asterisk are lines due to the $\dot{C}HD$– radical and are not affected by overlap from the $\dot{C}D_2$– radical.

1. Primary Radicals. Because of the radiation chemistry of aliphatic ketones in adamantane, the only primary 2-alkanonyl radical which was studied in detail is the 3,3,3-trimethylacetonyl radical ($\dot{C}H_2COC(CH_3)_3$) which is obtained by X-irradiation of 3,3-dimethyl-2-butanone in adamantane-h_{16}. The epr spectrum of this radical at 220°K is shown in Figure 1 and exhibits the three lines expected for two equivalent α protons. However, the relative intensities of the lines are in the ratio 1:1.68:1 at this temperature rather than the expected ratio of 1:2:1 which indicates a small inequivalence of the two α protons. Furthermore, a careful temperature study showed that the relative intensity of the center line is temperature dependent, varying from 1.65 at 211°K (significant anisotropy is exhibited below this temperature) to 1.95 at 303°K.

Several attempts were made to resolve this inequivalence by using different sample preparation techniques. For example, use of adamantane-d_{16} as a host results in somewhat smaller line widths (1.5 G), but no splitting of the center line in Figure 1 is observed at low temperatures. The spectrum in $C_{10}D_{16}$ is further complicated by lines from the $\dot{C}HDCOC(CH_3)_3$ and

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[22] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

Table I. Epr Spectral Parameters of 2-Alkanonyl Radicals in Adamantane

Radical	T, °K	Hyperfine splitting constants, G^a a_α^H	a_β^H	Other	g value^b
$\dot{C}H_2COC(CH_3)_3$	255	19.7 20.2		a_1^C = 28.5^c a_2^C = 14.3	2.0046
$CH_3\dot{C}HCOCH_3$	294	19.0	23.0 (3)^d	a_3^H = 0.8 (3)	2.0045
$CH_3\dot{C}HCOCH_2CH_3$	220	18.6	23.4 (3)	a_1^C = 27.4^c a_2^C = 13.8 a_β^C = 10.1	2.0047
$CH_3\dot{C}HCO(CH_2)_2CH_3$	255	18.2	23.2 (3)		2.0047
$CH_3\dot{C}HCOCH(CH_3)_2$	255	18.8	23.3 (3)		2.0047
$CH_3\dot{C}HCOCH(CH_3)CH_2CH_3$	220	18.5	23.4 (3)		2.0048
$CH_3CH_2\dot{C}HCOCH_3$	328	18.9	13.7 (2)^e	a_3^H = 0.9 (3)	2.0045
$CH_3(CH_2)_2\dot{C}HCOCH_3$^{f}	328	18.3	13.2 (2)^e		2.0045
$CH_2\dot{C}HCOCH_2$	220	19.0	35.6 (2)		2.0047
$CH_2\dot{C}HCO(CH_2)_2$	255	18.7	36.1 (2)	a_1^C = 26.7^c a_3^H = 1.9 (2)	2.0047
$CH_2\dot{C}HCO(CH_2)_3$^{f}	255	18.0	33.0 (2)^e	a_1^C = 26.6^c a_2^C = 14.0^c a_β^C = 10.7^c a^O = 9.3^c	2.0048
$CH_2\dot{C}HCOCH(CH_3)(CH_2)_3$^{f}	294	18.0^g	29.8^{e,g} 37.0^{e,g}		2.0041
$(CH_3)_2\dot{C}COCH_3$	220		19.5 (3) 20.6 (3)	a_1^C = 26.8^c a_2^C = 12.5^c a_β^C = 10.4 (2)^c	2.0043
$(CH_3)_2\dot{C}COCH_2CH_3$	255		19.4 (3) 20.5 (3)		2.0044
$(CH_3)_2\dot{C}CO(CH_2)_2CH_3$	255		19.5 (3) 20.6 (3)		2.0045
$(CH_3)_2\dot{C}COCH(CH_3)_2$	255		19.4 (3) 20.5 (3)		2.0045
$CH_3CH_2\dot{C}(CH_3)COCH_3$	220		9.5 (2)^e 19.7 (3)	a_γ^H = 0.70 (3)	2.0042
$CH_3(CH_2)_2\dot{C}(CH_3)COCH_3$^{f}	220		4.3^g 19.0 (4)^g		2.0043
$CH_2\dot{C}(CH_3)COCH(CH_3)CH_2$	248		19.8 (3) 27.5^e 36.8^e	a_1^C = 25.5^g a_2^C = 11.5^g a_β^C = 9.5 (2)^g a_3^H = 2.5^e a_γ^H = 0.6^e	2.0045

[a] Accuracy ±0.1 G except as noted. [b] Based on g_{DPPH} = 2.0036, accuracy ±0.0002. [c] Corrected for second-order effects. [d] Numbers in parentheses refer to the number of equivalent nuclei with hfs shown. [e] Hfs temperature dependent. See text. [f] Radical exhibits alternating line width effect. [g] Accuracy ±0.5 G.

$\dot{C}D_2COC(CH_3)_3$ radicals which result from exchange between the parent radical ($\dot{C}H_2COC(CH_3)_3$) and the matrix. Therefore, a sample of $CH_3COC(CD_3)_3$ was prepared and X-irradiated in $C_{10}D_{16}$ in order to reduce the contribution to the line width from unresolved δ-proton hfs. The resulting spectrum has line widths of 0.75 G at 220°K and is shown in Figure 2. Careful examination of this spectrum reveals that the lines due to the $\dot{C}HDCOC(CD_3)_3$ radical which are not affected by overlap with lines from the $\dot{C}D_2COC(CD_3)_3$ radical are not equally intense as would be expected if the two (proton) sites were equivalent. Since the $\dot{C}HDCOC(CD_3)_3$ radical can exist in two different conformations (*i.e.*, with the α hydrogen cis or trans to the oxygen of the carbonyl group, *vide infra*), its spectrum was fit using BLEND by assuming that the conformations are equally populated at 220°K but have slightly different (H and D) hfs in the low temperature limit. In this way average values of $\bar{a}_\alpha^D = 3.035 \pm 0.010$ and $\bar{a}_\alpha^H = 19.93 \pm 0.01$ G were determined[23] and the inequivalence in the proton hfs which is necessary to fit the spectrum in Figure 2 is 0.45 ± 0.02 G (*i.e.*, $a_\alpha^H = 19.71$, $a_{\alpha'}^H = 20.16$ G). Unfortunately, high concentrations of this and other primary radicals could not be generated in a static solution using the photolysis method; in the case of 3,3-dimethyl-2-butanone, the spectrum consists mainly of lines due to the *tert*-butyl radical which is produced by Norrish Type I cleavage of the excited n,π* state ketone.[9,25]

2. Secondary Radicals. The epr spectrum of the 1-methylacetonyl radical in adamantane-h_{16} clearly displays the 1:1 doublet of 1:3:3:1 quartets expected for a single α-proton split by three equivalent β protons. In addition, each of the eight lines in the spectrum of $CH_3\dot{C}HCOCH_3$ is further split into a small 1:3:3:1 quartet in $C_{10}D_{16}$. The protons hfs are a_α^H = 19.0 (1 proton), a_β^H = 23.0 (3), and a_3^H = 0.8 (3) G and show no temperature dependence from 170 to 295°K. These values are in reasonable agreement with those obtained by us and by Fischer[5] for this radical in solution (19.0, 22.2, and 0.9 G, respectively). Similar results were obtained by us for the 1,3-dimethyl-, 1-methyl-3-ethyl-, 1,3,3-trimethyl-, and 1,3-dimethyl-3-ethylace-

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(23) It is interesting to note that the ratio of the average α-hydrogen and α-deuterium hfs of the $\dot{C}HDCOC(CD_3)_3$ radical at 220°K ($\bar{a}_\alpha^H/\bar{a}_\alpha^D$ = 6.57 ± 0.03) deviates from the expected ratio of 6.51. Similar effects have been observed in the spectra of the $\dot{C}H_2D$ and $\dot{C}HD_2$ radicals.[24]

(24) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(25) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966.

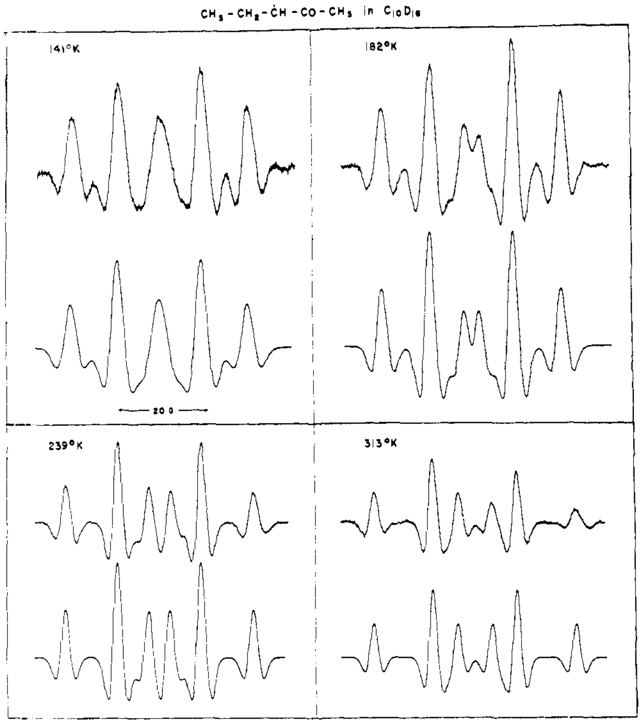

Figure 3. Experimental (top) and computed (bottom) second-derivative epr spectra of the 1-ethylacetonyl radical in adamantane-d_{16} at various temperatures.

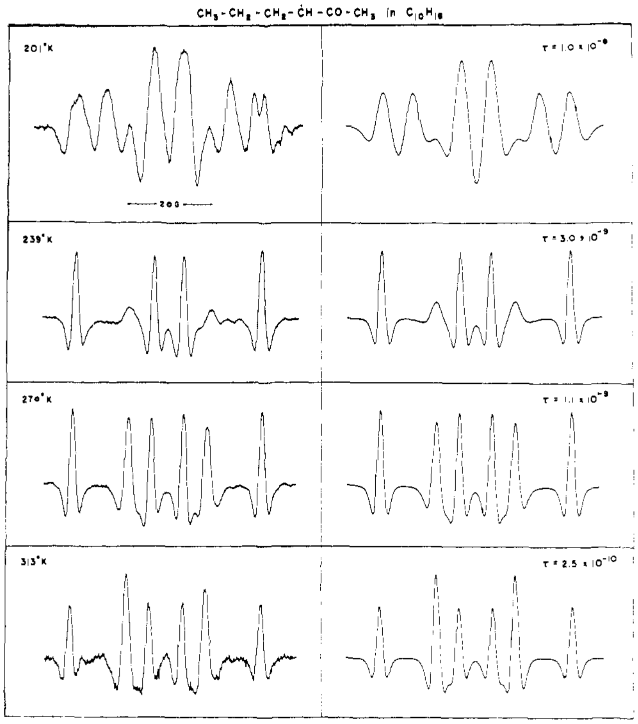

Figure 5. Experimental (left) and computed (right) second-derivative epr spectra of the 1-propylacetonyl radical in adamantane-h_{16} at various temperatures.

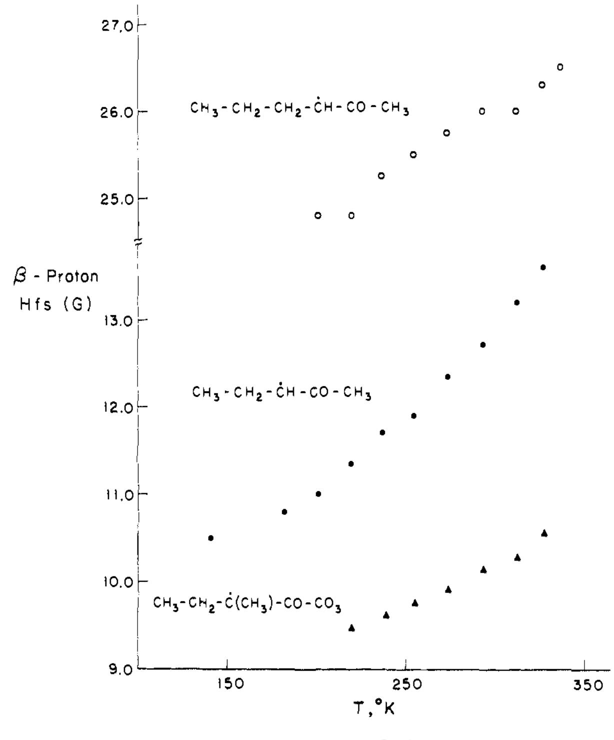

Figure 4. Temperature dependence of the β-methylene proton hyperfine splittings in the 1-methyl-1-ethylacetonyl, 1-ethylacetonyl, and 1-propylacetonyl radicals in an adamantane matrix. Values shown for $CH_3CH_2CH_2\dot{C}HCOCH_3$ are the sum of the two β-proton hfs.

tonyl radicals in adamantane, and values of the parameters determined by computer simulation of the observed spectra are listed in Table I.

Replacement of the methyl group in the 1-methylacetonyl radical with an ethyl group produces a dramatic change in the magnitude of the β-proton hfs observed in adamantane and in the behavior of the spectrum with changes in temperature as can be seen in Figure 3. The spectrum of the 1-ethylacetonyl radical at 141°K has hfs of a_α^H = 18.9 (1) and a_β^H = 10.5 (2) G; in addition, a small C_3-proton hfs of 0.9 (3) G is observed in the spectrum of this radical in $C_{10}D_{16}$. As the temperature is increased, the α- and C_3-proton hfs remain constant but the β-proton hfs increases rapidly to a value of 13.7 G at 328°K. This temperature dependence is summarized in Figure 4 which also contains data for other radicals which show similar effects. The magnitude of the β-proton hfs of the 1-ethylacetonyl radical in adamantane is significantly different from that reported by Paul and Fischer,[9] who found a_α^H = 18.8 (1), a_β^H = 19.2 (2), and a_3^H = 0.9 (3) G for this radical in liquid CCl_3F at 269°K. Therefore, the $CH_3CH_2\dot{C}HCOCH_3$ radical was also prepared in solution by *in situ* photolysis of a mixture of 2-pentanone, di-*tert*-butyl peroxide, and cyclopropane, and the β-proton hfs observed in this experiment at 200°K is essentially identical with the earlier solution value.[9]

Anomalous β-proton hfs were observed in the epr spectra of other secondary radicals as well. For example, Figure 5 shows a series of spectra which were obtained for the 1-propylacetonyl radical over the temperature range 201–313°K. At 201°K, the spectrum can be fit with hfs of 18.3 (1), 18.0 (1), and 6.8 (1) G whereas at 313°K the radical has hfs of 18.3 (1) and 13.2 (2) G. At intermediate temperatures, the spectra show pronounced alternating line width effects. These were fit using MEAKIN by assuming a temperature-independent α-proton hfs of 18.3 and two β protons (at 18.0 and 6.8 G in the low temperature limit) which exchange positions at a temperature-dependent rate. The fact that the sum of the two β-proton hfs increases

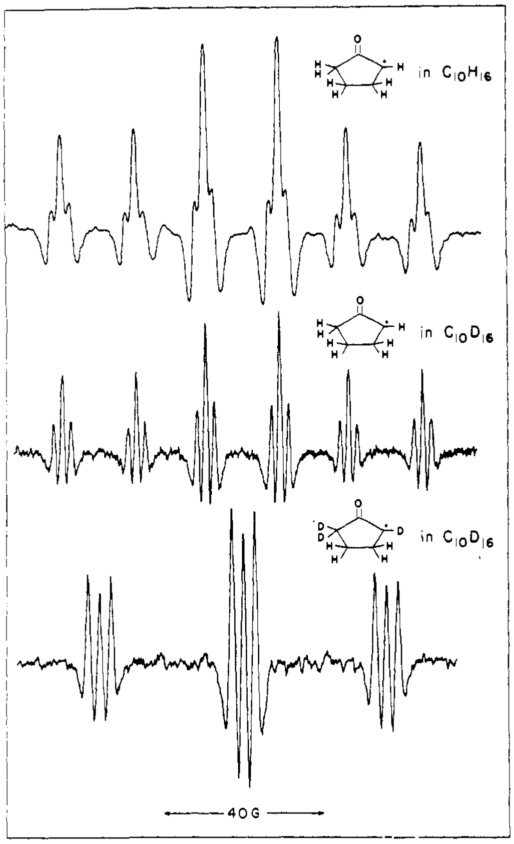

Figure 6. Second-derivative epr spectra of the 2-cyclopentanonyl radical in adamantane-h_{16} and adamantane-d_{16} and of the 2-cyclopentanonyl-*1,3,3*-d_3 radical in adamantane-d_{16}; recorded at 294, 220, and 239 °K, respectively.

with increasing temperature (from 24.8 G at 201 °K to 26.4 G at 328 °K, *cf.* Figure 4) made it necessary to adjust the low temperature values slightly in order to obtain satisfactory fits at the intermediate temperatures.

Epr parameters also were obtained for several cyclic secondary 2-alkanonyl radicals. For example, the 2-cyclobutanonyl radical has a single α proton with $a_\alpha{}^H$ = 19.0 G, two equivalent β protons with $a_\beta{}^H$ = 35.6 G, and line widths of nearly 2.0 G in $C_{10}H_{16}$ which are presumably the result of unresolved C_3-proton hfs. The spectrum of the 2-cyclopentanonyl radical, which is shown in Figure 6, is similar to that obtained for the four-membered ring radical except that each of the six main lines is split into a small 1:2:1 triplet which is completely resolved in $C_{10}D_{16}$. The proton hfs of the 2-cyclopentanonyl radical are $a_\alpha{}^H$ = 18.7 (1), $a_\beta{}^H$ = 36.1 (2), and $a_3{}^H$ = 1.9 (2) G; deuteration of the parent molecule at the 2 and 5 positions results in a spectrum which shows a single deuterium splitting of 2.83 G, two β protons at 36.1 G, and no C_3-proton hfs. Thus, the small splitting which is observed in the spectrum of the undeuterated species can be assigned to the two protons in the 3 position of the radical. In support of this assignment, a single C_3-proton hfs is observed in the spectrum of the 1,3-dimethylcyclopentanonyl radical (*cf.* Table I).

The proton hfs of the unsubstituted four- and five-membered ring radicals are independent of temperature from 182 to 328 °K. In contrast, radicals containing a six-membered ring have temperature-dependent β-proton hfs, and their epr spectra show pronounced

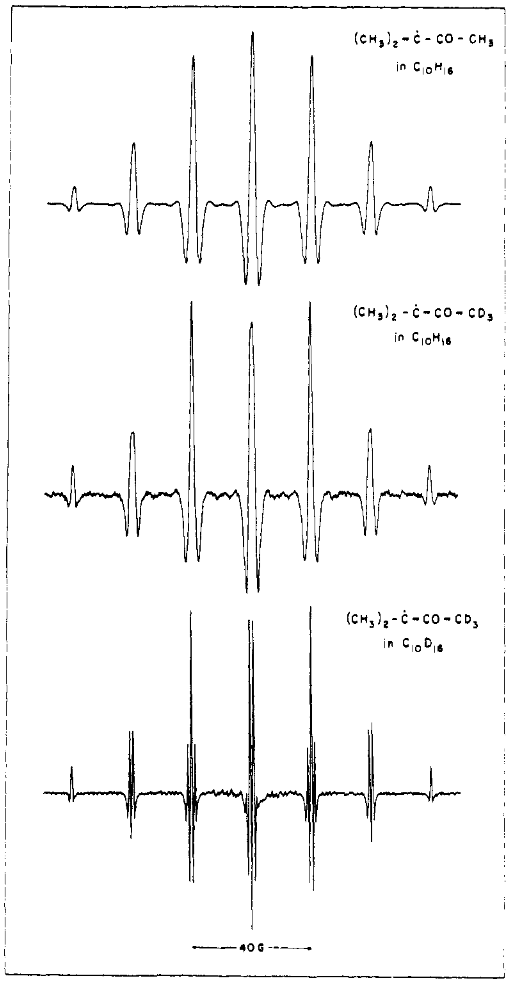

Figure 7. Second-derivative epr spectra of the 1,1-dimethylacetonyl radical in adamantane-h_{16} and of the 1,1-dimethylacetonyl-*3,3,3*-d_3 radical in adamantane-h_{16} and adamantane-d_{16}; recorded at 255 °K.

alternating line width effects at intermediate temperatures.[1,26,27] Similar behavior has been discovered in the spectra of substituted five- and seven-membered ring radicals and a detailed analysis of these will be presented elsewhere.[27]

3. Tertiary Radicals. As an example of the results obtained for tertiary 2-alkanonyl radicals, Figure 7 shows a series of spectra of the 1,1-dimethylacetonyl radical in adamantane. The spectrum of $(CH_3)_2\dot{C}COCH_3$ in $C_{10}H_{16}$ exhibits seven equally spaced lines as expected for six equivalent β protons, but the experimental relative intensities depart considerably from the theoretical 1:6:15:20:15:6:1 ratio. Replacing the C_3 hydrogens with deuterium considerably enhances the anomalous intensity ratio of the lines in the $C_{10}H_{16}$ matrix, and when this experiment is repeated in $C_{10}D_{16}$, each of the inner five lines of the spectrum is observed to be split into two or more components. Examination of this spectrum reveals that the origin of the anomalous intensities noted above is a slight inequivalence of the two β-methyl groups; the spectrum of the $(CH_3)_2\dot{C}COCD_3$ radical in $C_{10}D_{16}$ is clearly a 1:3:3:1 quartet of 1:3:3:1 quartets and has proton hfs of $a_\beta{}^H$ = 19.48 (3) and $a_{\beta'}{}^H$ = 20.58 (3) G.

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[26] See also C. Corvaja, G. Giacometti, and M. Brustolon, *Z. Phys. Chem.*, **82**, 272 (1972).

[27] D. W. Pratt, *et al.*, submitted for publication.

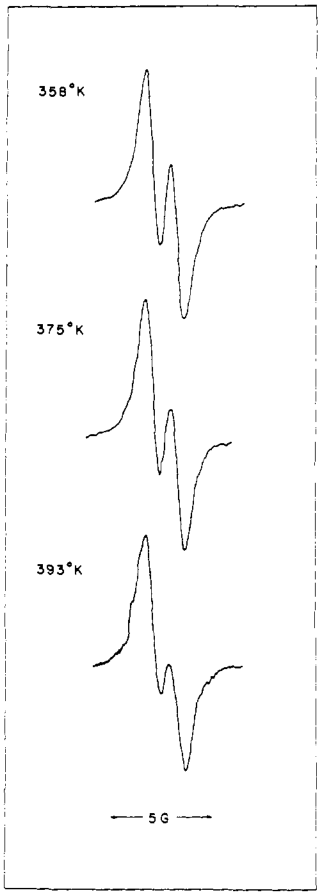

Figure 8. First-derivative high resolution scans of the low field doublet in the epr spectrum of the 1,1-dimethylacetonyl-*3,3,3-d*$_3$ radical in adamantane-*d*$_{16}$ at elevated temperatures.

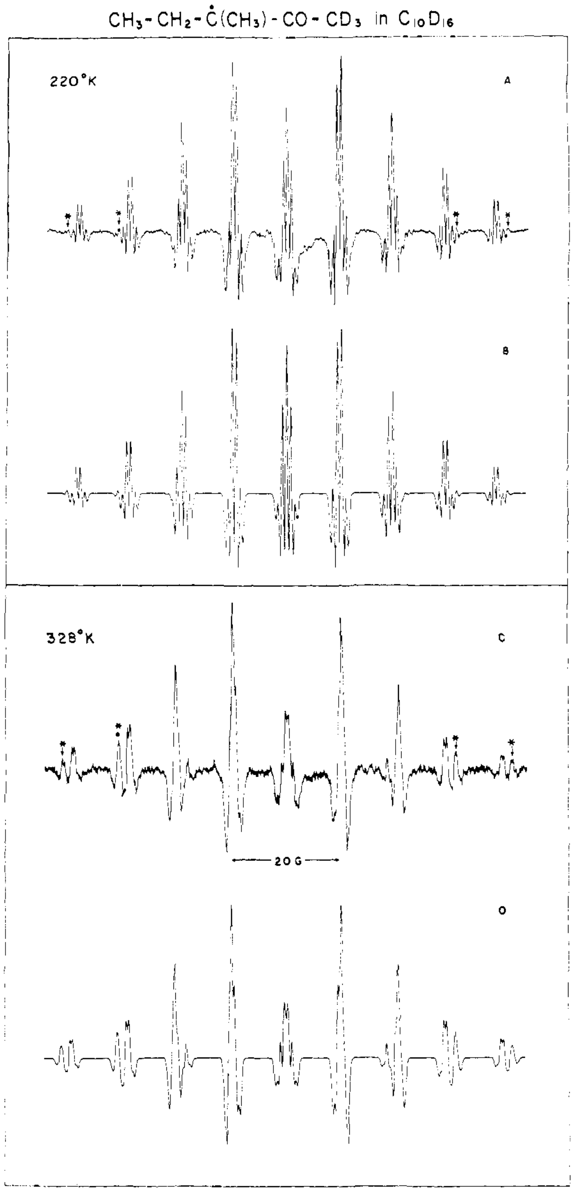

Figure 9. Second-derivative epr spectra of the 1-methyl-1-ethylacetonyl-*3,3,3-d*$_3$ radical in adamantane-*d*$_{16}$ at 220°K (A) and at 328°K (C) together with their respective computer simulations (B and D). Asterisks denote lines due to a second conformation of the radical whose relative concentration depends on temperature.

This inequivalence is also present in the spectrum of this radical in cyclopropane at 200°K.

The spectrum of the $(CH_3)_2\dot{C}COCD_3$ radical in $C_{10}D_{16}$ was carefully examined over the temperature range 182–393°K in order to determine whether the two methyl groups become equivalent at elevated temperatures. No change in either the positions or widths of the lines was observed up to 358°K; however, above this temperature some of the lines broaden noticeably. Figure 8 shows some high resolution scans of the low field doublet in the spectrum of $(CH_3)_2\dot{C}COCD_3$ in $C_{10}D_{16}$ recorded at 358, 375, and 393°K which illustrate this effect. Inequivalent β-proton hfs are also observed in the epr spectra of the 1,1,3-trimethyl-, 1,1-dimethyl-3-ethyl-, and 1,1,3,3-tetramethylacetonyl radicals in adamantane-*h*$_{16}$ and the hfs and *g* values of these radicals are listed in Table I. Detailed studies of the spectra of these radicals at elevated temperatures were not carried out.

The unsymmetrically substituted tertiary radical 1-methyl-1-ethylacetonyl has hfs of $a_\beta{}^H = 19.8$ (3) and $a_{\beta'}{}^H = 9.5$ (2) G at 239°K, but the small β-proton hfs is observed to be temperature dependent as in the case of secondary 2-alkanonyl radicals with β-methylene groups. This temperature dependence is summarized in Figure 4. Furthermore, at high temperatures (358°K and above), the wing lines in the epr spectrum of the $CH_3CH_2\dot{C}(CH_3)COCH_3$ radical in $C_{10}H_{16}$ show additional structure. In order to examine this effect in more detail a sample of $CH_3CH_2CD(CH_3)COCD_3$ was prepared and X-irradiated in $C_{10}D_{16}$. The resulting spectra are shown in Figure 9. In addition to the small γ-proton splittings which appear in *each* of the main lines of the spectrum in this matrix, other weak lines (denoted by asterisks) are observed in the wings of *some* of the main lines and the relative intensities of these weak lines increase with increasing temperature. This effect was found to be completely reversible and can be attributed to the appearance of a second conformation of the 1-methyl-1-ethylacetonyl radical at higher temperatures (*vide infra*). Similar observations were made in the case of other radicals in this study including the secondary radical 1-methylacetonyl in adamantane-*d*$_{16}$ and the tertiary radical 1-methyl-1-propylacetonyl in adamantane-*h*$_{16}$, but these were not examined in detail because of low radical concentrations at the temperatures required for accurate measurements.

4. **^{13}C and ^{17}O Hfs.** Several of the radicals examined in this work were obtained in sufficiently high yield to enable measurements of ^{13}C hfs in natural abundance. For example, under high gain conditions the spectrum of the $\dot{C}H_2COC(CD_3)_3$ radical in $C_{10}D_{16}$ (*cf.* Figure 2) shows a number of weak lines which can be assigned to the radicals having ^{13}C at either the C_1 or C_2 positions. The intensities of these lines are, as expected from the natural abundance of ^{13}C, 0.55% of the intensity of the main ^{12}C spectrum and the observed ^{13}C hfs (corrected for second-order shifts) are 28.5 and 14.3 G. The assignment of these splittings to respectively the C_1 and C_2 positions of the 3,3,3-trimethylacetonyl radical which is given in Table I is based on a comparison of these values with those observed for the ethyl radical ($a_\alpha{}^C = 39.07$, $a_\beta{}^C = 13.57$ G).[24] The spectrum of the secondary radical $CH_3\dot{C}HCOCH_2CH_3$ also shows hfs caused by ^{13}C in the C_1, C_2, and C_β positions; in this case, the hyperfine parameters are 27.4, 13.8, and 10.1 G at 220°K. An unequivocal assignment of the two smaller ^{13}C splittings in this radical is not possible without specific ^{13}C labeling studies. However, the tertiary radical $(CH_3)_2\dot{C}COCH_3$ has ^{13}C hfs of 26.8, 12.5, and 10.4 G at 255°K and the corresponding ^{13}C lines have intensities of 0.55, 0.55, and 1.1% relative to the main ^{12}C spectrum. The fact that the 10.4 G carbon-13 satellite shows an intensity which is twice as large as the intensities of the other ^{13}C lines in the spectrum of the 1,1-dimethylacetonyl radical suggests that the smallest ^{13}C splitting in secondary and tertiary radicals should be assigned to the β carbon(s) and that the intermediate ^{13}C hfs in these radicals belongs to the carbonyl carbon (C_2).

Carbon-13 hfs also were observed in the epr spectra of some cyclic 2-alkanonyl radicals and Figure 10 shows the results obtained for the 2-cyclohexanonyl radical in adamantane-d_{16}. At temperatures above 200°K this radical has $a_\alpha{}^H = 18.0$ (1) and $a_\beta{}^H = 33.0$ (2) G and exhibits a six-line epr spectrum.[1] At high gain each of the six lines shows three pairs of ^{13}C satellites which are most clearly resolved on the wings of the spectrum. These are shown in Figure 10 together with the computer-simulated spectra calculated using the procedure described in the Experimental Section. The "best-fit" ^{13}C hfs are 26.6, 14.0, and 10.7 G at 255°K and, based on a comparison of these parameters with those obtained for the noncyclic radicals, these can be assigned to the C_1, C_2, and C_β (*i.e.*, C_6) positions, respectively, of the 2-cyclohexanonyl radical. This assignment is confirmed by the ^{13}C data for other cyclic radicals which are given in Table I.

Because of the well-known sensitivity of α-carbon-13 splittings in hydrocarbon radicals to the detailed geometry at the radical site,[24,28] careful measurements of the large ^{13}C hfs in both open-chain and cyclic radicals were made over a restricted temperature range. Some changes in this parameter with temperature are observed. Thus, the value of $a_1{}^C$ in $CH_3\dot{C}HCOCH_2CH_3$ increases from 27.4 G at 220°K to 27.7 G at 255°K and the corresponding ^{13}C hfs in $(CH_3)_2\dot{C}COCH_3$ increases from 26.8 G at 220°K to 27.4 G at 294°K. A positive temperature coefficient is also observed for the α-carbon-13 hfs in cyclic radicals except that in these cases the magnitude of the coefficient is somewhat less. For example, the value of $a_1{}^C$ in the 2-cyclohexanonyl radical increases from 26.5 at 220°K to 26.8 G at 294°K. No dependence of the smaller ^{13}C hfs on temperature is observed for either the open-chain or cyclic radicals. However, it should be noted that small changes in these parameters are difficult to detect because of the high degree of overlap in these regions of the spectrum.

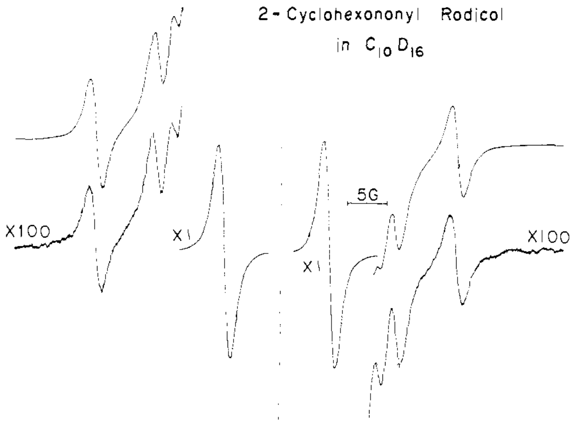

Figure 10. High resolution scans of the two wing lines in the first-derivative epr spectrum of the 2-cyclohexanonyl radical at 255°K showing the three ^{13}C satellites observed in natural abundance at high gain. Above the experimental traces are the computer fits which were used to obtain values of the ^{13}C hyperfine splittings in this radical. The computed line shapes contain 30% Gaussian character.

As previously reported,[2] a sample of ^{17}O-enriched cyclohexanone was prepared by exchange with $H_2{}^{17}O$ and X-irradiated in adamantane-h_{16}. The resulting spectrum contained lines from the 2-cyclohexanonyl-^{17}O radical which were about as intense as the ^{13}C lines in natural abundance, and an analysis of these yielded an ^{17}O hfs of 9.3 G. Unfortunately, the sign[29] of the ^{17}O splitting constant could not be determined because the large ^{13}C hfs in this radical is approximately three times the ^{17}O hfs causing severe overlap with some of the ^{17}O lines.

B. **Optical Spectra.** Using methods which are described in the Experimental Section, the optical absorption spectra of several 2-alkanonyl radicals were also examined using the adamantane matrix technique. Typical of the results obtained are those shown in Figure 11, which illustrates the room temperature absorption spectrum of the 2-cyclohexanonyl radical in the ultraviolet region together with the spectrum of an unirradiated pellet of adamantane containing a small amount of cyclohexanone. In all cases examined, the parent molecule exhibits a moderately intense transition with λ_{max} 2850 Å, which compares favorably with the solution values for aliphatic ketones (*e.g.*, cyclohexanone has λ_{max} 2900 Å in cyclohexane at room temperature). This transition has been assigned[25] as an $n \rightarrow \pi^*$ transition involving a lone pair electron in the $n_O \sim 2p_x{}^O$ orbital on oxygen. The spectra of X-irradiated samples show a similar feature at approximately the same wavelength, and since the parent molecule absorption in this region is largely eliminated by the use of a reference sample, we believe that the band at 2850 Å in the irradiated sample is the corresponding $n_O \rightarrow \pi^*$

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[28] D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972); D. E. Wood and R. F. Sprecher, *Mol. Phys.*, submitted for publication.

[29] B. L. Silver, Z. Luz, and C. Eden, *J. Chem. Phys.*, **44**, 4258 (1966).

Table II. INDO Energies and Hyperfine Splitting Constants of 2-Alkanonyl Radicals[a]

		Hyperfine splitting constants, G							
Radical	Energy, au	a_α^H	a_β^H	a_3^H	a_1^C	a_2^C	a_β^C	a_3^C	a^O
$\dot{C}H_2COCH_3$	−41.69966	−16.2 (cis)[b] −17.5 (trans)		−8.7	33.8	−18.0		3.6	−11.0
$\dot{C}H_2COCH_3$[c]	−41.75298	−8.9 (cis) −10.3 (trans)		−6.7	16.8	−14.3		2.8	−14.0
$CH_3\dot{C}HCOCH_3$[d]	−50.15919	−16.2 (trans)	22.3 (cis)	−8.2	30.4	−17.2	−9.7 (cis)	3.3	−10.9
$CH_3\dot{C}HCOCH_3$[e]	−50.15721	−15.6 (cis)	22.5 (trans)	−8.4	30.3	−17.4	−10.0 (trans)	3.4	−11.0
$(CH_3)_2\dot{C}COCH_3$	−58.61172		20.4 (cis) 20.6 (trans)	−7.9	27.2	−16.6	−9.0 (cis) −9.3 (trans)	3.2	−10.5

[a] Standard bond lengths and angles[32] were used except as noted. [b] Cis or trans to the oxygen of the carbonyl group. [c] Energy minimized with respect to C_1–C_2 and C_2–O bond distances. Initial values of these parameters were 1.46 and 1.22 Å, respectively; final values were 1.35 Å in both cases. [d] β-Methyl group cis to carbonyl oxygen. [e] β-Methyl group trans to carbonyl oxygen.

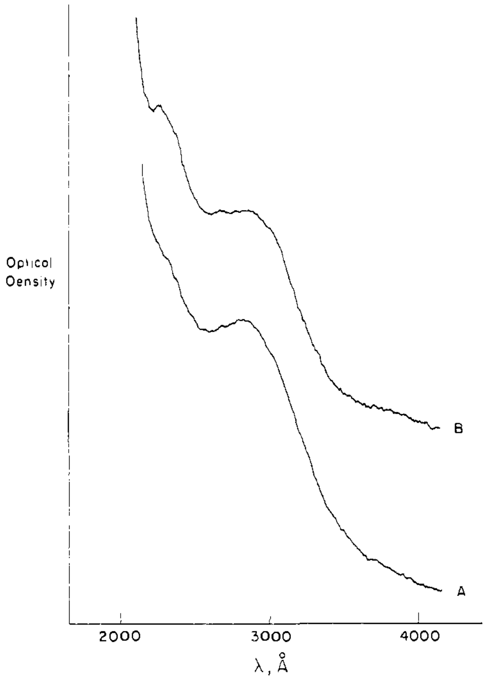

Figure 11. Room temperature optical absorption spectra of cyclohexanone (A) and the 2-cyclohexanonyl radical (B) in adamantane.

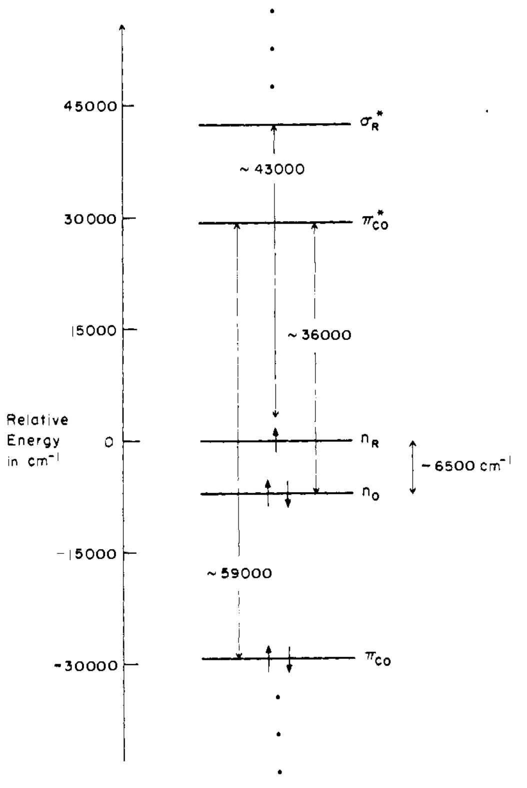

Figure 12. Molecular orbital diagram for 2-alkanonyl radicals showing the electronic configuration of the ground state and the approximate energies of the $\pi \rightarrow \pi^*$ transition in the parent molecule and the $n_O \rightarrow \pi^*$ and $n_R \rightarrow \sigma_R^*$ transitions in the radical.

transition of the radical. In addition to this band, a second feature having λ_{max} 2250 Å is also observed in the absorption spectra of 2-alkanonyl radicals. This band is believed to be analogous to similar bands which are observed in alkyl radicals (*e.g.*, methyl radical has λ_{max} 2150 Å)[30] and therefore can be assigned to a transition which involves the promotion of the unpaired electron at the radical site from a nonbonding orbital (n_R) to a σ_R^* orbital of the radical fragment. These results are summarized in the form of a schematic molecular orbital diagram for 2-alkanonyl radicals which is shown in Figure 12.

C. INDO Calculations. Molecular orbital calculations on the intermediate neglect of differential overlap (INDO) level of approximation have been shown to be extremely useful for estimating electron spin density distributions and hfs in paramagnetic species.[31] Therefore, we have carried out a number of INDO calculations on model radicals of the 2-alkanonyl type and the results obtained are summarized in Table II.

Generally, the proton hfs predicted by INDO are in satisfactory agreement with experiment. For example, the calculations on the acetonyl radical assuming standard bond lengths and angles[32] reproduce the observed inequivalence in the α-proton hfs of this radical (a_α^H = 19.48 and $a_{\alpha'}^H$ = 19.95 G at 223°K)[6] and predict that it is the hydrogen atom cis to the carbonyl oxygen which shows the smaller hfs. A significant improvement in the total INDO energy is obtained when the energy of this radical is minimized with respect to the C_1–C_2 and C_2–O bond distances, but the agreement between the observed hfs and that of the optimized structure is poor. The calculations also show that the cis form of the 1-methylacetonyl radical is somewhat more stable than the trans form when standard geometries are used and that the β-proton hfs of the 1-methyl- and 1,1-dimethylacetonyl radicals is slightly smaller

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(30) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

(31) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(32) Reference 22, Table 4.16.

when the β-methyl group is in the cis position. Finally, the INDO values for the C$_3$-proton hfs (a_3^{H}) are considerably larger in magnitude than those observed experimentally.

Of particular importance in this work are the carbon-13 hyperfine parameters calculated by INDO. Examination of Table II shows that the large ^{13}C hfs observed in primary, secondary, and tertiary 2-alkanonyl radicals should be assigned to C$_1$ and that the value of a_1^{C} decreases as the α carbon is more highly substituted, in agreement with experiment. The ^{13}C hfs of the carbonyl carbon (a_2^{C}) is predicted to be larger than that of the β carbon(s) (a_β^{C}) in secondary and tertiary radicals, which is in complete accord with the ^{13}C assignments made previously on the basis of the observed relative intensities of the ^{13}C satellites. Thus, although the calculated values of a_1^{C} and a_2^{C} are somewhat higher than observed, we believe that the INDO results obtained using standard geometries together with the experimental relative intensities are reliable enough to permit the ^{13}C assignments to C$_1$, C$_2$, and C$_\beta$ which are given in Table I.

Discussion

A. Electronic Structure of 2-Alkanonyl Radicals. It is apparent from the data of Table I that 2-alkanonyl radicals are largely alkyl in character and that structure I makes the principal contribution to the ground state wave function of radicals of this type. For example, the α- and β-proton hfs of the 1-methylacetonyl radical (19.0 and 23.0 G, respectively) are considerably larger than the corresponding values for similar allyl radicals (*e.g.*, the *trans*-1-methylallyl radical has $a_\alpha^{\mathrm{H}} = 13.8$ and $a_\beta^{\mathrm{CH_3}} = 16.4$ G).[14] A comparison of the average α-proton hfs of primary radicals of this type (*e.g.*, $\dot{\mathrm{C}}\mathrm{H_2COCH_3}$ has $\bar{a}_\alpha^{\mathrm{H}} = 19.7$ G[6] and $\dot{\mathrm{C}}\mathrm{H_2COC(CH_3)_3}$ has $\bar{a}_\alpha^{\mathrm{H}} = 19.9$ G) with those of typical alkyl radicals (*e.g.*, *n*-propyl radical has $\bar{a}_\alpha^{\mathrm{H}} = 22.1$ G)[13] suggests, however, that there is some spin delocalization in 2-alkanonyl radicals. Further evidence for the participation of structure II comes from the observation of an inequivalence in the α- and β-proton hfs of several of the symmetrically substituted radicals listed in Table I and the finding that this inequivalence remains even at relatively high temperatures (*e.g.*, 393°K in the case of the 1,1-dimethylacetonyl radical).

Quantitative estimates of the relative importance of structures I and II in 2-alkanonyl radicals can be obtained by comparing the values of the spin densities at carbons 1 and 2 and the oxygen atom (ρ_1^{C}, ρ_2^{C}, and ρ^{O}, respectively) with those determined previously for alkyl and allyl free radicals. That these are truly π-orbital spin densities is evident from the observation of a small positive temperature coefficient for the α-carbon-13 hfs in both cyclic and noncyclic radicals since a negative temperature coefficient would be expected if the geometry at the radical site were significantly nonplanar.[24,28,33] Therefore, ρ_1^{C} and ρ_2^{C} can be determined from the observed proton hfs using the relationship[35]

$$a_i^{\mathrm{H}} = Q_i \rho_i^{\mathrm{C}} \qquad (1)$$

and similar equations can be used to estimate ρ_1^{C}, ρ_2^{C}, and ρ^{O} from the observed ^{13}C and ^{17}O hfs. The results of these calculations are summarized below.

1. ρ_1^{C}. Values of ρ_1^{C} can be obtained by several independent methods. First, we use eq 1 and $Q_\beta = 29.3$ G[13] to calculate the spin density at C$_1$ from the average β-methyl proton hfs of the noncyclic secondary and tertiary radicals listed in Table I which do not show temperature-dependent β-proton hfs. This gives values of 0.79 and 0.68 for the secondary and tertiary radicals, respectively. Second, following Fischer,[5] we use the value $\rho_1^{\mathrm{C}} = 0.79$, the average α-proton hfs of the noncyclic secondary radicals, and eq 1 to determine the parameter Q_α. The value obtained is 23.5 G which is in substantial agreement with the earlier estimate of 23.9 G.[5] This parameter can then be used to calculate ρ_1^{C} for primary radicals from the average α-proton hfs of the acetonyl and 3,3,3-trimethylacetonyl radicals and eq 1. This gives $\rho_1^{\mathrm{C}} = 0.84$. Third, the equation[36]

$$a_i^{\mathrm{C}} = \left[S^{\mathrm{C}} + \sum_{j=1}^{3} Q_{\mathrm{C}_i\mathrm{X}_j}{}^{\mathrm{C}_i}\right]\rho_i^{\mathrm{C}} \qquad (2)$$

where the atoms X$_j$ are those bonded to the carbon atom *i*, can be used to calculate values of ρ_1^{C} from the α-carbon hfs data. Taking $S^{\mathrm{C}} = -12.7$, $Q_{\mathrm{C_1H}}{}^{\mathrm{C_1}} = +19.5$, and $Q_{\mathrm{C_1C'}}{}^{\mathrm{C_1}} = +14.4$ G[36] (C′ = C$_2$ or C$_\beta$), we obtain respectively $\rho_1^{\mathrm{C}} = 0.70$, 0.74, and 0.86 for the primary, secondary, and tertiary radicals. Fourth, ρ_1^{C} can also be estimated by comparing the values of the β-carbon-13 hfs given in Table I with that for ethyl radical (13.57 G)[24] for which the value of ρ_1^{C} is 0.92.[13] This gives $\rho_1^{\mathrm{C}} = 0.71$ and 0.67 for the secondary and tertiary 2-alkanonyl radicals.

2. ρ_2^{C}. Similar methods can be used for obtaining values of the spin density at the carbonyl carbon. For example, the C$_3$-proton hfs data for the radicals $\dot{\mathrm{C}}\mathrm{H_2COCH_3}$,[6] $\mathrm{CH_3\dot{C}HCOCH_3}$, and $\mathrm{CH_3CH_2\dot{C}HCOCH_3}$ can be used to estimate ρ_2^{C}, since the C$_3$ protons are β to C$_2$ in the epr sense. This method (with $Q_\beta = 29.3$ G) gives $\rho_2^{\mathrm{C}} = \pm 0.01$ and ± 0.03 for the primary and secondary radicals. The values ± 0.04 and ± 0.05 are obtained from the C$_3$-proton hfs in the 2-cyclopentanonyl and 1,3-dimethyl-2-cyclopentanonyl radicals by comparison with the β-proton hfs in these species. Finally, comparison of the ^{13}C hfs of the carbonyl carbon in the 2-cyclohexanonyl radical with that calculated on the basis of spin polarization effects alone[2] gives an indirect estimate of $\rho_2^{\mathrm{C}} = +0.04$ for this radical.

3. ρ^{O}. A direct determination of the π-orbital spin density on oxygen is possible only in the case of the 2-cyclohexanonyl radical, where the value $a^{\mathrm{O}} = 9.3$ G was obtained from the epr spectrum of an ^{17}O-enriched sample. Using the relationship[37,38]

$$a^{\mathrm{O}} = (S^{\mathrm{O}} + Q_{\mathrm{OC_2}}{}^{\mathrm{O}})\rho^{\mathrm{O}} + Q_{\mathrm{C_2O}}{}^{\mathrm{O}}\rho_2^{\mathrm{C}} \qquad (3)$$

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[33] Recent calculations[34] have shown that some care should be exercised in the use of this "rule." For example, in a nonplanar radical with a large inversion barrier, the ^{13}C hfs is predicted to first decrease and then *increase* with increasing temperature (*cf.* ref 28). However, the existence of a similar barrier in the case of 2-alkanonyl radicals seems unlikely in view of the data reported herein.

[34] D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, Abstract No. PHYS-11.

(35) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

(36) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

(37) W. M. Gulick and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 4119 (1966).

(38) P. D. Sullivan, J. R. Bolton, and W. E. Geiger, Jr., *ibid.*, **92**, 4176 (1970).

Table III. Comparison of π-Orbital Spin Densities of 2-Alkanonyl, Alkyl, and Allyl Radicals

Method of determination	ρ_1^C	ρ_2^C	ρ_1^C	ρ_2^C	ρ_1^C	ρ_2^C	Other
	$\dot{C}H_2COR$		$R\dot{C}HCOR'$		$RR'\dot{C}COR''$		$R\dot{C}HCOR'$
a_α^H	+0.84[a]						
a_β^H			+0.79[a]		+0.68		
a_3^H		±0.01		±0.03		±0.05	
a_1^C	+0.70		+0.74		+0.86		
a_2^C				+0.04			
a_β^C			+0.71		+0.67		
a^O							$\rho^O = +0.21$
Hückel[b]			+0.78	+0.03			$\rho^O = +0.18$
INDO[c]	+0.73	−0.30	+0.68	−0.28	+0.64	−0.27	$\rho^O = +0.56$
	$\dot{C}H_2CH_3$		$CH_3\dot{C}HCH_3$		$(CH_3)_3\dot{C}$		$\dot{C}H_2CH_2CH_3$
a_α^H, a_β^H	+0.92	+0.08	+0.84	+0.08	+0.78	+0.08	$\rho_3^C \sim 0$
	$CH_2\dot{C}RCH_2$		$CH_3CH\dot{C}RCH_2$		$(CH_3)_2C\dot{C}RCH_2$		$CH_3CH\dot{C}RCH_2$
a_α^H, a_β^H	+0.59	−0.16	+0.54	−0.16	+0.50	−0.16	$\rho_3^C = +0.59$

[a] Not corrected for conformational effects. See text. [b] Assuming $(\alpha_O - \alpha_C)/\beta_{CC} = 1.0$ and $\beta_{CO}/\beta_{CC} = 2.0$. See ref 4. [c] Assuming standard bond lengths and angles. See Table II.

with $(S^O + Q_{OC_2}^O) = -44.5$ G, $Q_{C_2O}^O = -14.3$ G,[38] and $\rho_2^C = \pm 0.03$, gives a value for ρ^O of 0.21 ± 0.01 with a^O assumed to be negative.[29]

4. Comparison of Spin Densities. Collected in Table III are the values of ρ_1^C, ρ_2^C, and ρ^O determined above together with those calculated using the Hückel[4] and INDO molecular orbital methods. In most cases there is reasonable agreement between the π-orbital spin densities obtained by different methods. For example, in the case of secondary radicals, the three "experimental" values of ρ_1^C are all within 0.04 units of 0.75 and the sum of ρ_1^C, ρ_2^C, and ρ^O is 0.99 (assuming $\rho_2^C = +0.03$). The Hückel spin densities calculated for secondary radicals by Griffith[4] are also in excellent agreement with experiment. However, there are two notable inconsistencies. First, the values of ρ_1^C obtained from the proton and β-carbon-13 hfs and the INDO calculations show the expected decrease with methyl substitution owing to increased hyperconjugation with the radical site whereas the ρ_1^C derived from the α-carbon-13 hfs show the *opposite* trend. This is because the values of a_1^C do not decrease as rapidly with methyl substitution as predicted by eq 2. Thus, a value of $a_1^C \sim 21$ G is calculated for tertiary radicals (assuming $\rho_1^C = 0.68$) from eq 2 which is considerably less than that observed ($a_1^C \sim 26$ G). In view of the experimental evidence for a planar geometry at the radical site, we believe that the origin of this inconsistency lies in the choice of values for S^C, $Q_{C_1H}^{C_1}$, and $Q_{C_1C'}^{C_1}$ for these radicals. That some revision of these parameters might be necessary is not surprising since the same values also yield anomalous results for simple alkyl radicals.[39]

The second major inconsistency in the data of Table III is that the magnitudes of ρ_2^C and ρ^O predicted by INDO are considerably larger than those derived from the observed hyperfine parameters. In particular, the calculations predict a large positive spin density at the oxygen atom and a relatively large negative spin density at the carbonyl carbon. Similar effects have been noted in the INDO results for several related radicals[40,41] and might be interpreted as evidence for a large amount of allylic character. However, it is known from other theoretical results that electronic wave functions based on spin-unrestricted determinants of molecular orbitals are not in general eigenfunctions of S^2 because of contamination with states of higher spin multiplicity.[31,42] In the case of allylic systems, this leads to serious overestimates of the negative central and positive peripheral spin densities.[43] Thus, we believe that reliable INDO results on radicals of this type can only be obtained by using a spin projected ($S = 1/2$) wave function.

Also shown in Table III are the "experimental" spin densities for several alkyl and allyl radicals which have been determined for the most part from proton hfs.[44] These can be used as reference values for estimating the relative importance of structures I and II in 2-alkanonyl radicals. For example, the average value of the "experimental" ρ_1^C for secondary radicals of this class is 0.75, hence the per cent allylic character is $100(0.84 - 0.75)/(0.84 - 0.54) \sim 30\%$. Similarly, the values of ρ_2^C give $100(0.08 - 0.03)/(0.08 + 0.16) \sim 21\%$, and the value of ρ^O gives $100(0.21)/(0.59) \sim 36\%$. Therefore, we conclude on the basis of these comparisons as well as others made possible by the data in Table III that *2-alkanonyl radicals are approximately 30% allylic in character* and that the nonbonding orbital containing the unpaired electron in radicals of this type can be represented approximately as

$$\psi_0(n_R) = c_1(2p_z^{C_1}) + c_2(2p_z^O) \tag{4}$$

with $c_1^2 \sim 0.85$ and $c_2^2 \sim 0.15$. From a valence bond viewpoint, this means that a *typical 2-alkanonyl radical is a resonance hybrid of structures I and II with structure II contributing about 15%*. The fact that both structures do not contribute equally to this hybrid is undoubtedly due to the large difference in energy between I and II (I is more stable by ~20 kcal/mol),[45] and, as

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(39) For example, from the observed α-carbon-13 hfs of methyl and ethyl radicals,[24] we calculate ρ_1^C values of 0.84 and 0.96, respectively, using eq 2, the appropriate spin polarization parameters,[38] and the assumption that $\rho_2^C = 0$ for ethyl radical.

(40) G. P. Laroff and R. W. Fessenden, *J. Chem. Phys.*, **55**, 5000 (1971).

(41) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 7975 (1972).

(42) L. C. Snyder and A. T. Amos, *J. Chem. Phys.*, 42, 3670 (1965).

(43) For example, the calculations on allyl radical[42] yield spin densities of $\rho_{1,3}^C = 0.65$ and $\rho_2^C = -0.30$ using a single determinant unrestricted wave function whereas the $S = 1/2$ projected wave function yields values of 0.55 and −0.09, respectively, which are in much better agreement with experiment (*cf.* Table III).

(44) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972.

(45) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

noted previously by Benson, *et al.*,[10–12] this difference is presumably responsible for the lack of a large amount of resonance (*i.e.*, stabilization) energy in radicals of this type.

5. *g* Values and Optical Spectra. The above conclusion is further substantiated by both the observed *g* values and optical spectra of 2-alkanonyl radicals. The deviation of a principal value of the *g* tensor from the free spin value of 2.0023 can be described by the equation[46]

$$\Delta g_{ii} = -2\sum_{jk}\frac{\xi^j}{E_k - E_0}\langle\psi_0|L_i|\psi_k\rangle\langle\psi_k|L_i|\psi_0\rangle \qquad (5)$$

where ξ^j is the spin–orbit coupling constant of atom j; E_0, E_k and ψ_0, ψ_k are the energies and eigenfunctions of the ground and excited states, respectively; and L_i is the orbital angular momentum operator about the i axis. For 2-alkanonyl radicals, only one term of eq 5 will be important and it can be written as

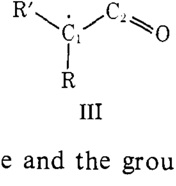
$$\Delta g_{yy} = -\frac{2\xi^{\mathrm{O}}}{E_1 - E_0}\langle\psi_0|L_y|\psi_1\rangle\langle\psi_1|L_y|\psi_0\rangle \qquad (6)$$

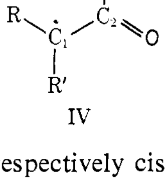
where E_1 and ψ_1 are the energy and eigenfunction of the first excited state of the radical which is obtained by promoting an electron from the lone pair orbital on oxygen ($n_O \sim 2p_z{}^{O}$) to the nonbonding orbital n_R (*cf.* Figure 12). Since the wave functions ψ_0 and ψ_1 are known, the matrix elements are easily calculated and eq 6 becomes

$$\Delta E = E_1 - E_0 = 2c_2{}^2\xi^{\mathrm{O}}/\Delta g_{yy} \qquad (7)$$

Then, using $c_2{}^2 = 0.15$, $\xi^{\mathrm{O}} = 150\ \mathrm{cm}^{-1}$,[46] and $\Delta g_{yy} = 3(2.0045 - 2.0023)$, we calculate from eq 7 that $\Delta E = 6800\ \mathrm{cm}^{-1}$. This should correspond to the energy difference between the orbitals n_R and n_O in Figure 12. From the optical spectra of both the parent aliphatic ketones[25] and the corresponding 2-alkanonyl radicals, we estimate that this difference is about 6500 cm^{-1}, which is in excellent agreement with the value of ΔE calculated above. This result, coupled with the observation that the optical spectra of 2-alkanonyl radicals are significantly different from those of allylic systems[20] and are essentially a superposition of the spectra of an alkyl radical and the parent ketone, provides further evidence for the largely alkyl character of radicals of this type.

B. Restricted Rotation about the C$_1$–C$_2$ Bond. The conclusion that there is some delocalization of the unpaired electron over the C=O π system implies that there is some partial double bond character to the C$_1$–C$_2$ bond in 2-alkanonyl radicals. Therefore, open-chain radicals of this type may exist in two conformations, III and IV, in which the heavy atoms shown lie in a plane and the group R is respectively cis or trans to the oxygen of the carbonyl group. Generally, if the barrier restricting rotation about this bond is sufficiently high so that the radical spends most of the time near one of the two minima of the potential function, then the effect of interconversions between the two conformations on the epr spectrum can be treated as exchange between two magnetic environments. That these environments are inequivalent is apparent from examination of the structures III and IV and of the epr parameters in Table I.


III


IV

1. Symmetrically Substituted Radicals. The effect of restricted rotation about the C$_1$–C$_2$ bond on the temperature dependence of the epr spectrum depends on the nature of the substituents R and R′ which are attached to C$_1$, the magnitude of the inequivalence of the hfs, and the height of the potential barrier. Thus, since conformations III and IV of symmetrically substituted radicals (*i.e.*, R = R′) are degenerate and therefore equally populated at all temperatures, no change in the epr spectrum with temperature should be observed if R and R′ are magnetically equivalent. On the other hand, if R and R′ are magnetically *inequivalent* at low temperature, then restricted rotation about the C$_1$–C$_2$ bond will lead to selective line broadening (and eventual sharpening) in the epr spectra taken at higher temperatures. The rate of this process and its temperature dependence can be determined by comparing the experimental line shape with that calculated using computer techniques and the height of the barrier governing this motion can be obtained in favorable cases.[1,8,27]

As noted previously in the Results section, the epr spectrum of the symmetrically substituted 3,3,3-trimethylacetonyl radical exhibits inequivalent α-proton hfs and a selectively broadened center line (*cf.* Figure 1) whose relative intensity increases with increasing temperature. Since this is the expected behavior for a pair of protons which are exchanging between two inequivalent sites at a rate which is comparable to the difference in hfs, an estimate for the barrier to rotation about the C$_1$–C$_2$ bond could be obtained using MEAKIN. For this calculation, the inequivalence in the proton hfs determined from the spectrum of the $\dot{\mathrm{C}}\mathrm{HDCOC(CD_3)_3}$ radical in $C_{10}D_{16}$ was assumed, and the spectrum of the $\dot{\mathrm{C}}\mathrm{H_2COC(CH_3)_3}$ radical in $C_{10}H_{16}$ at 211°K was fit exactly by adjusting both the line width and the magnitude of the unresolved δ-proton hfs. These parameters were then kept constant and the spectra between 211 and 303°K were fit by varying the characteristic time for exchange (τ) between the two sites. From the resulting linear plot of log τ *vs.* $(1/T)$ the barrier height in this radical was found to be $\Delta H^{\ddagger} = 8.6 \pm 3.0$ kcal/mol.

The 1,1-dimethylacetonyl radical is also symmetrically substituted and shows inequivalent β-proton hfs even at the highest temperature studied (393°K). However, selective broadening of some of the lines in the spectrum of the $\mathrm{(CH_3)_2\dot{C}COCD_3}$ radical in $C_{10}D_{16}$ is observed above 358°K (*cf.* Figure 8), and an analysis of these data using methods similar to those described above provides a value of 9.1 ± 2.0 kcal/mol for the magnitude of the barrier in this radical.

Unfortunately, it was not possible to examine the spectra of either of these two radicals in both the slow and fast exchange regions, and therefore the values of

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[46] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967.

Table IV. Computer-Fit Hyperfine Splittings and Populations of the Two Conformations of the 1-Methyl-1-ethylacetonyl Radical in Adamantane[a]

	Conformation III				Conformation IV[b]			
T, °K	$a_\beta^{\mathrm{CH_3}}$, G	$a_\beta^{\mathrm{CH_2}}$, G	a_γ^{H}, G	Rel pop	$a_\beta^{\mathrm{CH_3}}$, G	$a_\beta^{\mathrm{CH_2}}$, G	Rel pop	K = IV/III
220	19.68	9.47	0.70	0.97	20.95	9.60	0.03	3.1×10^{-2}
239	19.72	9.61	0.65	0.97	20.95	9.65	0.03	3.1×10^{-2}
255	19.66	9.75	0.63	0.96	20.95	9.80	0.04	4.2×10^{-2}
274	19.66	9.90	0.63	0.93	20.95	9.95	0.07	7.5×10^{-2}
294	19.63	10.13	0.60	0.86	20.85	10.12	0.14	1.6×10^{-1}
313	19.64	10.27	0.57	0.84	20.85	10.30	0.16	1.9×10^{-1}
328	19.62	10.55	0.53	0.72	20.85	10.50	0.28	3.8×10^{-1}

[a] Hfs accurate to ±0.02 G. [b] γ-Proton hfs not resolved.

$\Delta H^{\ddagger}$ obtained in the two cases are only approximate.[47] It is also possible that the matrix may affect the barrier estimates although this seems unlikely in view of the small number of heavy atoms in the two radicals and the observation of a similar inequivalence in the β-proton hfs of the 1,1-dimethylacetonyl radical in liquid cyclopropane. However, in spite of these difficulties, the barrier heights obtained in this work compare favorably with the value obtained previously for the acetonyl radical (9.4 ± 0.5 kcal/mol)[8] and are unusually high. In this connection it is interesting to note that a barrier height of 9.6 kcal/mol is calculated by assuming a 15% contribution of structure II and a bond energy difference of 64 kcal/mol between a carbon–carbon single and double bond.[48] Although this agreement with the experimental results may be fortuitous, little steric contribution to the barrier is expected for two adjacent sp^2 carbons with small alkyl groups attached. Thus we conclude that *the magnitude of the barriers to free rotation about the* C_1–C_2 *bond in 2-alkanonyl radicals is largely due to spin delocalization effects.*

2. Unsymmetrically Substituted Radicals. For unsymmetrical radicals (*i.e.*, $R \neq R'$), conformations III and IV have different energies and are unequally populated at temperatures (*i.e.*, kT) small compared to the conformational energy difference. Thus, the effect of temperature on the epr spectra of such systems depends on this energy difference as well as the hfs of two conformations and the height of the C_1–C_2 barrier. Three distinct behavior patterns are possible depending on whether the equilibrium in reaction 8 is fast or slow. If the rates (k_f and k_r) of interconversion are fast, the

$$\mathrm{III} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{IV} \tag{8}$$

$$\Delta H = H_{\mathrm{IV}} - H_{\mathrm{III}}; \; K = k_f/k_r \tag{9}$$

observed hfs of an exchanging nucleus is the time average of the hfs in the two conformations and a change in temperature will result in a shift in the position of the equilibrium and a change in the observed hfs. The conformational energy difference (ΔH) can then be determined from an analysis of the spectra at different temperatures providing the values of the hfs of the two conformations are known. In addition, selective line broadening may be observed if the rates of interconversion are comparable to the difference in hfs in the two conformations, and in such cases information about the barrier ($\Delta H^{\ddagger}$) governing the interconversion process may also be obtained. Both types of behavior have been observed in the case of unsymmetrically substituted 2-cyclohexanonyl radicals.[1,27] On the other hand, if the equilibrium in reaction 8 is slow, the epr spectrum will consist of a mixture of lines due to the two possible conformations of the radical. In this case a change in temperature will result in a change of the relative intensities of the two subspectra. Furthermore, since the hfs of the two conformations can be determined directly from the spectrum, ΔH is easily found from an analysis of the relative populations as a function of temperature.

In view of the magnitude of the C_1–C_2 barrier in 2-alkanonyl radicals, the rates of interconversion of III and IV are expected to be slow and behavior of the last type should be observed providing the spectrum of a suitable radical can be studied at high temperatures. We believe that the 1-methyl-1-ethylacetonyl radical is such a case and that *the weak lines which appear in the epr spectrum of* $CH_3CH_2\dot{C}(CH_3)COCH_3$ *at high temperatures are due to the second conformation of this radical.* Therefore, the spectra at several different temperatures were fit using BLEND (*cf.* Figure 9), and Table IV summarizes the epr parameters and relative populations of the two conformations of the 1-methyl-1-ethylacetonyl radical which were obtained in this way. By assuming that the conformations are in equilibrium at each temperature (no hysteresis effects were observed with rapid changes in temperature), an equilibrium constant for reaction 8 could be defined and a plot of log K *vs.* $(1/T)$ yields a straight line with a slope of 5.0 ± 0.2 kcal/mol. This corresponds to the zero-point energy difference between conformations III and IV of this radical.

Examination of the data in Table IV shows that the principal difference in the hfs of the two conformations of the 1-methyl-1-ethylacetonyl radical is in the magnitudes of $a_\beta^{\mathrm{CH_3}}$, which are 19.67 ± 0.05 and 20.90 ± 0.05 G, respectively. This inequivalence is comparable to that observed for the several 1,1-dimethyl-substituted radicals listed in Table I and can be used to determine which of the two conformations (*i.e.*, R = CH_3 or C_2H_5) is more stable by comparison with the hfs of cyclic 2-alkanonyl radicals. For example, the 1,3-dimethyl-2-cyclopentanonyl radical has a β-methyl proton hfs of 19.8 G. Since the β-methyl group of this radical is constrained to be *cis* to the oxygen of the carbonyl group, we believe that the more stable conformation of the 1-methyl-1-ethylacetonyl radical (with $a_\beta^{\mathrm{CH_3}} = 19.67$ G) is III with R = CH_3 and R′ = C_2H_5. This result is consistent with the finding that the most stable conformation of 2-methylbutanal is the one

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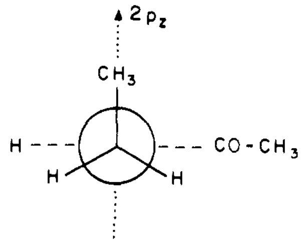
[47] Clearly, more accurate values of the barriers to restricted rotation in 2-alkanonyl radicals can be obtained from solution epr measurements and experiments of this type are in progress.

[48] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

which has the methyl group (rather than the ethyl group) eclipsing the oxygen of the carbonyl group.[49] However, the conformational energy differences in disubstituted acetaldehydes are no larger than 1.1 kcal/mol,[49] and the considerably larger value obtained for the 1-methyl-1-ethylacetonyl radical may reflect in part an influence of the matrix on the magnitude of ΔH in this radical.

Finally, it should be pointed out that the epr parameters of the other unsymmetrically substituted radicals listed in Table I are almost certainly characteristic of one of the two conformations possible in each case. In most instances it is possible to decide to which of the two the data pertain. For example, the 1-methylacetonyl radical has $a_\alpha^H = 19.0$ G and $a_\beta^{CH_3} = 23.0$ G. If we assume that an 8% reduction in the spin density at C_1 would occur upon replacement of the α hydrogen by an ethyl group,[13] the β-methyl hfs in this radical would decrease to 0.92(23.0) = 21.1 G. Since this value is similar to that of the β-methyl group in conformation IV of the 1-methyl-1-ethylacetonyl radical, the more stable conformation of the 1-methylacetonyl radical is the one which has the β-methyl group trans to the oxygen of the carbonyl group.[50] Thus, it appears that *if R and R′ are different, the stable conformation of the radical has the less bulky group cis to the oxygen.* For symmetrically substituted radicals, the data are consistent with there being equal populations of each conformation present and also show that the two groups are magnetically inequivalent with the substituent cis to the oxygen having the smaller hfs. This conclusion is in agreement with the predictions of INDO.

C. Hindered Rotation about the C_α–C_β Bond. As shown in Figure 4, the values of $a_\beta^{CH_2}$ in several of the 2-alkanonyl radicals with γ-alkyl groups are unusually small and increase rapidly with increasing temperature. For example, the $CH_3CH_2\dot{C}HCOCH_3$ radical in adamantane has a β-methylene proton hfs of 10.5 G at 141°K which increases to 13.7 at 328°K. This observation, together with the conclusions of the previous section, suggests that there is also a barrier which hinders rotation about the C_α–C_β bond and that the radical has as its most stable conformation one in which the α hydrogen is cis to the oxygen of the carbonyl group *and* in which the β-methyl group is eclipsed with the π orbital containing the unpaired electron (V).



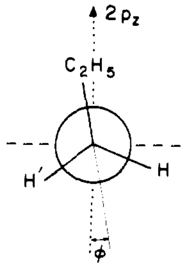
V

Similar effects have been observed in other systems[13,51–55] and it has been found experimentally that the angular dependence of a_β^H can be approximated by[56]

$$a_\beta^H = B_0 + B_2 \cos^2 \theta \tag{10}$$

where B_0 and B_2 are empirical constants and θ is the dihedral angle between the carbon–hydrogen bond and the axis of the π orbital. For alkyl radicals, it is usually assumed that the spin polarization term B_0 is zero and that B_2 is twice the isotropic hfs of a freely rotating β-methyl group. Thus, a similar assumption in the case of 2-alkanonyl radicals leads to values of $B_2 = 46.0$ G (from the value of a_β^H in the $CH_3\dot{C}H$-$COCH_3$ radical which also has the α hydrogen cis to the oxygen atom) and $a_\beta^{CH_2} = 11.5$ G for $\theta = 120°$. This β-methylene proton hfs is in reasonable agreement with the experimental value of a_β^H in the 1-ethylacetonyl radical at 141°K. The increase in $a_\beta^{CH_2}$ which is observed with increasing temperature in adamantane is therefore caused by an increase in the expectation value of $\cos^2 \theta$ which occurs on populating higher torsional states of the periodic potential governing rotational motion about the C_α–C_β bond. This interpretation is supported by the decrease in the γ-CH_3 hfs of conformation III of the 1-methyl-1-ethylacetonyl radical which is observed on increasing the temperature (*cf.* Table IV).

Unlike the β protons in the 1-ethylacetonyl radical, the two β-methylene protons in the 1-propylacetonyl radical are magnetically inequivalent at low temperatures. This indicates that the preferred conformation of this radical in adamantane is one in which the γ-ethyl group is tilted with respect to the π orbital containing the unpaired electron (*e.g.*, VI). Furthermore, the low temperature values of $a_\beta^{CH_2}$ and $a_{\beta'}^{CH_2}$ can be used to determine the dihedral angle ϕ, the angles θ and θ' (which describe the orientation of the protons H and H′ with respect to the π orbital), and the parameters B_0 and B_2 for secondary 2-alkanonyl radicals. With $a_\beta^{CH_2} = 6.8$, $a_{\beta'}^{CH_2} = 18.0$, and the assumption that



VI

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(49) G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965).

(50) This conclusion implies that the values of ρ_1^C which were obtained from average α- and β-proton hfs of primary and secondary radicals (19.8, 18.6, and 23.3 G, respectively, *cf.* section A1 and Table III) are not strictly correct. If we assume that the average values of the α- and β-proton hfs of the less stable conformations of secondary radicals are 19.1 and 22.0 G, respectively, then the spin densities can be corrected for conformational effects by averaging the hfs of both conformations. This calculation yields the values $\rho_1^C = 0.81$ (for primary radicals with $Q_\alpha = 24.5$ G) and $\rho_1^C = 0.77$ (for secondary radicals), which are in better agreement with the values obtained from the ^{13}C hfs.

(51) R. W. Fessenden, *J. Chim. Phys.*, **61**, 1570 (1964).

(52) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

(53) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

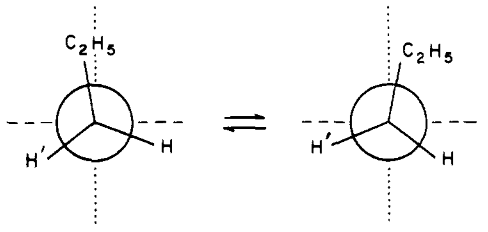
(54) D. J. Edge and J. K. Kochi, *ibid.*, **94**, 6485 (1972).

(55) T. Kawamura, P. Meakin, and J. K. Kochi, *ibid.*, **94**, 8065 (1972).

(56) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

$(B_0 + {}^1/_2B_2) = 23.0$ G, we find $\phi = 8.5°$, $\theta = 111.5°$, $\theta' = 128.5°$, $B_0 = 0.8$ G, and $B_2 = 44.3$ G. As expected, the values of B_0 and B_2 so obtained are somewhat smaller than those estimated for secondary alkyl radicals.[52,53]

Since the two protons attached to the methylene carbon of the 1-propylacetonyl radical are inequivalent at low temperatures, it is obvious from earlier discussion that hindered rotation about the C_α–C_β bond should result in an alternating line width effect in the epr spectra at higher temperatures. Thus, the spectra in Figure 5 are interpreted as arising from an interconversion of the type



VI VII

If we assume that conformations VI and VII are of equal energy, then a plot of the τ values (obtained from computer simulating the spectra over the temperature range 201–328°K, *cf.* Figure 5) *vs.* $(1/T)$ yields an activation energy of 4.9 ± 1.0 kcal/mol for this process. Because this value is considerably higher than the corresponding rotational barriers in simple alkyl radicals (*e.g.*, the *tert*-amyl radical has $\Delta H^{\ddagger} = 0.6$ kcal/mol),[52] we believe that it contains a significant contribution from intermolecular effects. Such effects are undoubtedly responsible for the large difference between the β-proton hfs observed for the 1-ethylacetonyl radical in solution and that observed in adamantane.[57] However, it should be apparent that *the adamantane matrix technique* does offer certain advantages in a problem of this type because it *makes possible a determination of the structures of the preferred conformations of radicals with intrinsically small rotational barriers.*

Summary

Based on a comparison of the experimental and theoretical ^{1}H, ^{13}C, and ^{17}O hyperfine splitting constants, *g* values, and optical spectra of several different 2-alkanonyl radicals with the corresponding properties of alkyl and allyl radicals, it is concluded that a typical 2-alkanonyl radical is a resonance hybrid of two allylic structures with structure II, having the unpaired electron on oxygen, contributing about 15%. The fact that the contributions of the two canonical structures are significantly different suggests that the amount of resonance energy in radicals of this type is small. However, the presence of a carbonyl group in the α position of an alkyl radical may influence the chemistry of such systems in view of the partial double bond character of the $\dot{C}$–CO bond. Thus, 2-alkanonyl radicals have a planar geometry at the radical site, exhibit restricted rotation about the $\dot{C}$–CO bond with barrier heights of the order of 9 kcal/mol, and exist in preferred conformations which may be sufficient to control stereochemistry in reactions involving radicals of this type as intermediates.

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(57) Strong solvent effects on the temperature dependence of the β-proton hfs of other radicals have also been observed: J. K. Kochi, private communication.