

the isotopic isomers were estimated from the dipole moment of normal species by calculating the rotation of the inertial axis with respect to the molecular frame due to the deuterium substitution. The width of the line, $\Delta\nu$, is not so different in the isomers of propene- d_1 ^{3b} or propene- d_2 that $\Delta\nu$ was assumed to be constant within propene- d_1 isomers or propene- d_2 isomers. The effect of power saturation can be safely neglected under the experimental condition described above.

The correction coefficients for all the relevant pairs of various isomers are given in Table VII. The real relative concentration of each species was obtained by dividing the observed intensity ratio by the total correction coefficient listed in Table VII. The

sum of the systematic and random errors was estimated to be several per cent of the relative concentration for each isomer.^{3a}

We can determine the relative concentrations for the isomers of propene- d_1 and propene- d_2 whose partial pressure is as low as 0.1% of the total pressure. This is due to the high sensitivity of our microwave spectrometer, which can detect the line of $\gamma_{\max} = 1 \times 10^{-10} \text{ cm}^{-1}$.²⁹

Acknowledgment. The authors wish to thank Professor Yonezo Morino, the director of Sagami Chemical Research Center, for his helpful discussion.

Benzoylmethyl Radicals. Matrix Isolation Electron Spin Resonance Study¹

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Abstract: Phenacyl (=benzoylmethyl) radicals produced by photolysis and pyrolysis of phenacyl iodide were examined by matrix-isolation esr spectroscopy. While photolysis of the iodide trapped within the matrix produced phenacyl radicals of the normal structure (PhCO $\dot{\text{C}}\text{H}_2$), the pyrolysis at 500° resulted in the formation of benzyl radicals suggesting intricate rearrangement and decomposition processes of the phenacyl radicals at elevated temperatures.

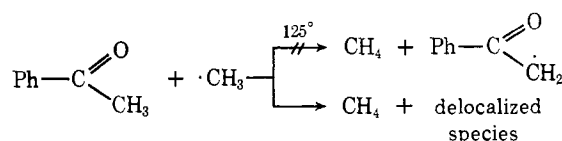
Sometime ago a technique was developed for the synthesis of 1,4-diketones^{3a} *via* free-radical dehydrodimerization. In that work methyl free radicals generated by the thermal decomposition of diacetyl peroxide have been the hydrogen-abstrating agents. This technique has subsequently been used to synthesize several 1,4-diketones which are precursors of materials of possible biomedical interest.^{3b} The technique dimerizes in good yield purely aliphatic ketones which have in their structure at least one hydrogen atom at the position α to the carbonyl group.

All attempts to dimerize by this technique alkyl phenyl ketones with the phenyl group attached directly to the carbonyl group have failed, however. Instead of the expected crystallizable 1,4-diketones, one repeatedly obtained amorphous, reddish-brown, resinous polymeric materials. Despite various attempts at its synthesis, nowhere in the literature has dibenzoyl-ethane been reported as having been synthesized by free-radical coupling of phenacyl (=benzoylmethyl) radicals. These results suggest that the intermediate phenacyl radicals, if they exist, do not have the classical structure which would lead to the expected dimerization. Its real structure must have greatly reduced electron spin density at the α carbon. The attached benzoyl group might well serve as an electron sink enhancing delocalization of the spin density away from the α position.

(1) A part of the present study was done while H. C. McBay was at Tarrytown Technical Center as a Research Fellow during Summer 1968.

(2) Union Carbide Corp.; (b) Morehouse College.

(3) (a) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, **70**, 1269 (1948); (b) H. C. McBay, unpublished results.



Reported in this paper are the results of matrix isolation esr study of phenacyl radicals generated by photolysis and pyrolysis of phenacyl iodide. While the photolysis of the precursor isolated in an argon matrix at $\sim 4^\circ\text{K}$ produced the phenacyl radicals of "normal" structure, the pyrolysis of the iodide at 500° resulted in the formation of the benzyl radicals suggesting intricate rearrangement and decomposition processes of the phenacyl radicals at elevated temperature.

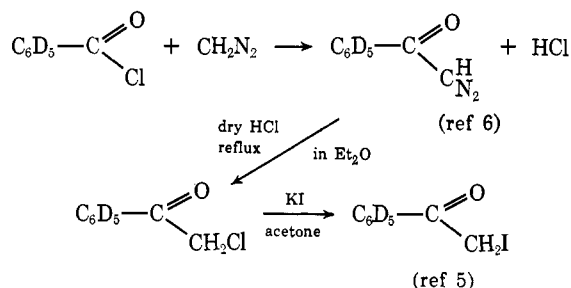
Experimental Section

The descriptions of the liquid-helium cryostat and X-band esr spectrometer system which allow the trapping of transient radicals in an inert gas matrix and the observation of their esr spectra have been reported earlier.⁴ In the case of pyrolysis the precursor (phenacyl iodide) was passed through a resistively heated quartz tube and then trapped in an argon or neon matrix being formed upon a flat spatula-shaped sapphire rod. The sapphire rod is in contact with the liquid-helium reservoir and can be rotated about its long axis so that the direction of the magnetic field relative to the plane of the rod can be varied. In the case of photolysis, an argon matrix containing the precursor was first prepared and then irradiated with uv light through the side quartz window. A high-pressure mercury arc (GE, AH-6) equipped with a Corning 7-54 uv filter was used for this purpose. All the spectra were obtained while the matrix was maintained at liquid helium temperature, and the spectrometer frequency locked to the loaded sample cavity was 9,430 GHz.

(4) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *J. Chem. Phys.*, **44**, 2581 (1966).

Phenacyl iodide was prepared by a modification of the procedure of Conant.⁵ Straw-colored crystals were obtained with mp 34 (lit. 29–30°). This compound showed a sharp single peak in its nmr spectrum with proper integration at δ 4.30 compared with the methylene peak in the nmr spectrum of phenacyl chloride at δ 4.55, while the aromatic hydrogens showed no appreciable change in posture.

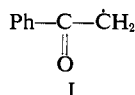
Pentadeuteriophenacyl iodide, $C_6D_5COCH_2I$, was prepared following the scheme outlined below.



It is worth mentioning that the diazoacetophenone requires prolonged digesting in absolute ether with excess dry hydrogen chloride gas to convert it to phenacyl chloride. The product, pentadeuteriophenacyl iodide, showed a single sharp methylene peak in its nmr spectrum at δ 4.30 with no other lines in the spectrum. There were thus no impurities due to any undeuterated aromatic moiety, mp 34°.

Results

Photolysis. Shown in Figure 1 is the spectrum obtained when phenacyl iodide trapped and isolated in an argon matrix was photolyzed. The spectrum is attributed to the phenacyl radical (I). The identical



spectrum was obtained when the experiment was repeated using the pentadeuterio species $C_6D_5COCH_2I$, indicating little delocalization of the spin density into the aromatic ring. This is not surprising since no resonance structure with the unpaired electron in the ring can be drawn without invoking a charge separation. The complex and severely distorted triplet pattern of Figure 1 must therefore be the manifestation of the hyperfine coupling tensors to the two α protons and the g tensor, particularly their anisotropies and the non-coincidence of their principal axes.

The radical I must be planar, the most pertinent resonance structures being Ia and Ib. Let us denote the



direction perpendicular to the molecular plane as the z axis. It is the only direction along which the principal axes of the three tensors are collinear. It is well-known that the anisotropic part of the hyperfine interaction is related to $\langle 1/r^3 \rangle$ where r is the distance between the unpaired electron and the magnetic nucleus of concern. The coupling tensors to the α protons of the phenacyl

(5) J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, **46**, 250 (1924); R. E. Hussey, *ibid.*, **47**, 286 (1925); see also C. Djerassi and C. T. Lenk, *ibid.*, **76**, 1722 (1954).

(6) T. J. De Boer and H. J. Backer, "Organic Synthesis," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 250; see also T. Malkin and M. Nierenstein, *J. Amer. Chem. Soc.*, **52**, 1506 (1930).

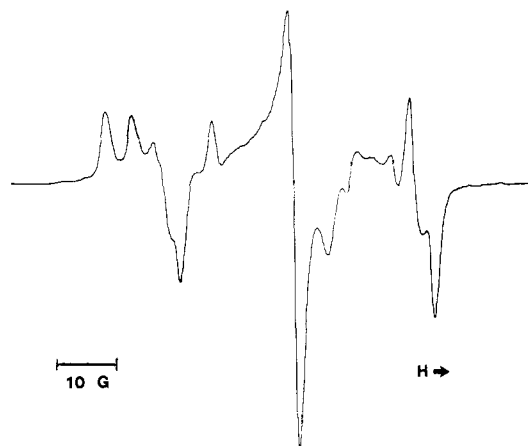


Figure 1. Esr spectrum of phenacyl radicals generated by photolysis of phenacyl iodide trapped in an argon matrix.

radicals are thus determined predominantly by the resonance structure Ia. In fact, it has been shown that the diagonal elements of the coupling tensor to a α proton of a π radical are given approximately by the following.^{7,8}

$$A_x = A(\parallel) = (Q + 11.0)\rho = -12.0\rho \text{ G} \quad (1a)$$

$$A_y = A(\perp, \perp) = (Q - 12.0)\rho = -35.0\rho \text{ G} \quad (1b)$$

$$A_z = A(\perp, \parallel) = (Q + 1.0)\rho = -22.0\rho \text{ G} \quad (1c)$$

Here $A(\perp, \parallel)$, for example, represents the element in the direction perpendicular to the $C_\alpha-H_\alpha$ bond but parallel to the p_π orbital of the α carbon. Q is the proportionality constant relating the isotropic coupling constant A_{iso} of the α proton to the spin density ρ at the p_π orbital. The figures at the end are obtained assuming $Q = -23.0 \text{ G}$, a well-established figure for a sp^2 hybridized carbon.⁹

As for the g tensor, it has been shown that, for a non-degenerate ground state, the deviation of the g value along a given principal axis, say " x ," from that of a free electron (2.0023) can be given by¹⁰

$$\Delta g_x = -2\lambda \sum_{n \neq 0} \frac{\langle 0 | L_x | n \rangle \langle n | L_x | 0 \rangle}{E_n - E_0}$$

Here λ is the spin-orbit coupling constant of the relevant atom, L_x is the usual angular momentum operator, and $E_n - E_0$ is the energy separation between the ground state $|0\rangle$ and the excited state $|n\rangle$. For a hydrocarbon radical, the anisotropy and the deviation from the free spin value of the g tensor are usually very small, $|\Delta g|$ rarely exceeding 0.001. This is due to the fact that the spin-orbit coupling constant of carbon atom is small ($\sim 0.0019 \text{ eV}$) and that the semifilled orbitals of these radicals are well separated from other orbitals which would give nonvanishing $\langle 0 | L_x | n \rangle_{i=x,y,z}$ matrix elements. The spin-orbit coupling constant of oxygen is much larger ($\sim 0.01 \text{ eV}$). Also in the hydrocarboxy radical such as I, there exists a filled nonbonding orbital consisting primarily of the oxygen p orbital perpendicular to the carbonyl bond. We may therefore assume that the g tensor of the phenacyl radical is predomi-

(7) H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).

(8) P. H. Kasai, *J. Amer. Chem. Soc.*, **94**, 5950 (1972).

(9) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(10) M. H. L. Pryce, *Proc. Phys. Soc., London, Sect. A*, **63**, 25 (1950).

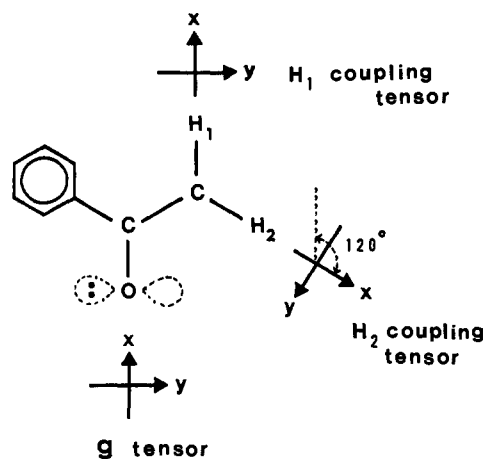


Figure 2. Assumed orientations of the g tensor and the hyperfine coupling tensors to the α protons of phenacyl radical.

nantly determined by the resonance structure Ib and that one of its in-plane principal axes, say the x axis, coincides with the C–O bond. If we further assume that both the carbonyl and the α carbons are exactly sp^2 hybridized, the orientations of the three principal tensors would be as depicted in Figure 2.

The triplet of Figure 1 has an average spacing of ~ 20 G. Let us assume $A_{iso} = Q\rho = -20$ G and $Q = -23.0$ G. We then have $\rho = 0.87$ and, from the eq 1a–c, $A_x = -10.4$ G, $A_y = -30.4$ G, and $A_z = -19.1$ G. A computer program that would simulate the esr spectrum exhibited by an ensemble of randomly oriented but rigidly held radicals, possessing an anisotropic g tensor and anisotropic hyperfine coupling tensor to protons, has been described earlier.⁸ The program takes into account the relative orientations of the g and the coupling tensors, the forbidden transitions ($\Delta M_s = \pm 1$, $\Delta M_I = \pm 1$), as well as the orientation dependence of the transition probability. Figure 3a shows a simulated spectrum of phenacyl radical based upon (1) the coupling tensors computed above, (2) the orientations of the tensors given in Figure 2, and (3) an isotropic g tensor with $g_x = g_y = g_z = 2.0023$. In variance with the observed, the simulated spectrum lacks prominence in the central part and the unusual doublet like pattern of the lowest field component. These features must result from the anisotropy of the g tensor.

The filled nonbonding orbital discussed earlier consists mainly of the p_y orbital of the oxygen, while in the resonance structure Ib, the unpaired electron resides in its p_z orbital. A large positive shift is, therefore, expected in the x direction of the g tensor. Figures 3b and 3c show the effect upon the simulated spectrum of increasing g_x to 2.0053 and to 2.0083, respectively, keeping all other parameters constant. Both the prominence in the central region and the doublet like pattern of the lowest field component are apparent in Figure 3c. The simulated spectrum obtained by adjusting g_x and g_y as well as the elements of the coupling tensors for the best fit is shown in Figure 4a. Table I shows the final set of parameters used. The agreement between the observed and the simulated spectra should be considered excellent in view of the assumptions maintained regarding the orientations of the tensors. Figure 4b is the spectrum simulated using the same set

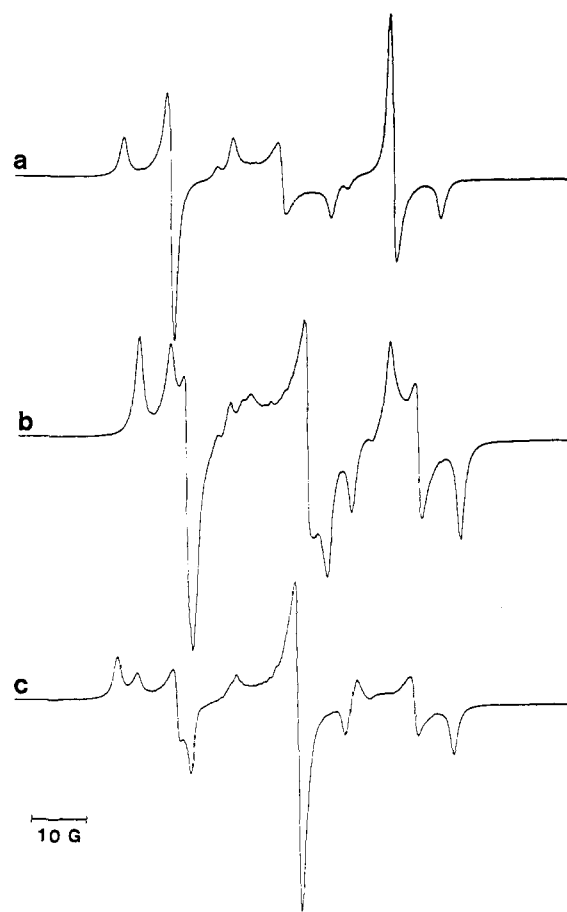


Figure 3. (a) Simulated spectrum of phenacyl using model hyperfine coupling tensors (see text) and assuming $g_x = g_y = g_z = 2.0023$. (b) Same as a except $g_x = 2.0053$. (c) Same as a except $g_x = 2.0083$.

Table I. The Assessed g Tensor and the Hyperfine Coupling Tensors to the α Protons of Phenacyl Radicals^a

	x	y	z
g	2.0076	2.0038	2.0023
$A(H_\alpha)$, G	-10.0	-30.0	-19.5

^a The accuracies: ± 0.0002 for g and ± 0.3 G for A . The assumed orientations of the tensors are shown in Figure 2.

of parameters but considering only the normal transitions ($\Delta M_s = \pm 1$ and $\Delta M_I = 0$). It is evident that many finer aspects of the observed spectrum are attributes of the forbidden transitions.

Pyrolysis. Unlike the photolysis discussed above, when the pyrolyzate of phenacyl iodide at 500° was trapped in an argon matrix, the resulting matrix showed a symmetric but extremely complex esr spectrum. The spectrum could not be attributed to the phenacyl radical I.

It has been shown that, when the molecules being trapped possess a proper amount of thermal energy relative to the "hardness" of the matrix surface being formed, a matrix can be produced in which the trapped molecules exhibit a strong preference toward certain orientation.¹¹ For molecules possessing a well-defined molecular plane, the preferred orientation is that in

(11) P. H. Kasai, W. Weltner, Jr., and E. B. Whipple, *J. Chem. Phys.*, **42**, 1120 (1965); **44**, 2581 (1966).

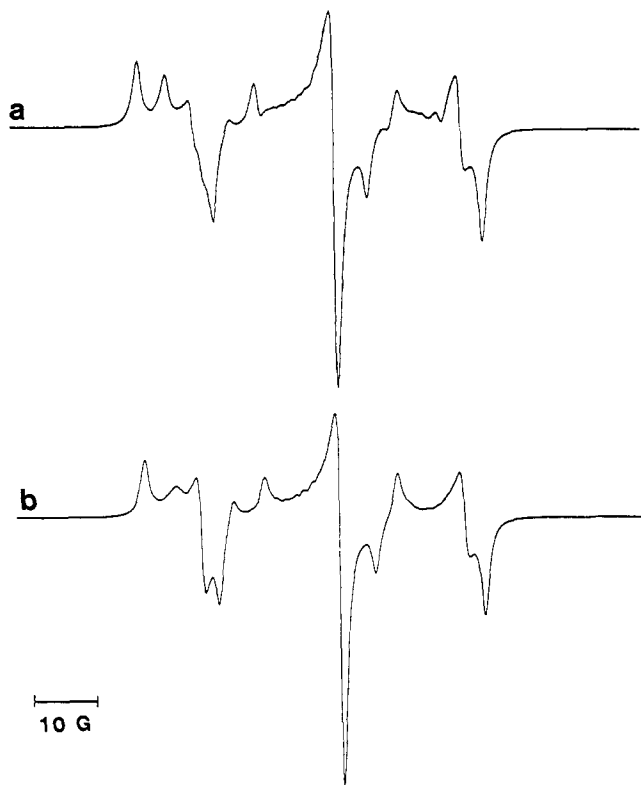


Figure 4. (a) Simulated spectrum of phenacyl radical using the parameters given in Table I. (b) Simulated spectrum using the same set of parameters but allowing only the normal transitions.

which the molecular plane lies parallel to the surface of the sapphire rod. Needless to say, the preferred orientation, if achieved, would greatly facilitate the assignment of the spectrum. The argon matrix containing the pyrolyzate of phenacyl iodide showed little indication of such orientation.

Figures 5a and 5b are the esr spectra of a neon matrix containing the pyrolyzate at 500° of phenacyl iodide observed with the magnetic field parallel to and perpendicular to the plane of the sapphire rod, respectively. The effect of the preferred orientation is quite conspicuous. Particularly noticeable is the single-crystal-like pattern obtained when the magnetic field is applied perpendicular to the plane of the sapphire rod. As indicated in the figure, it can be readily recognized as a (1:2:1) triplet of (1:3:3:1) quartets of (1:2:1) triplets. Their spacings are measured to be 16.5, 6.0, and 1.0 G, respectively. It was noted that these spacings are extremely close to the known isotropic coupling constants of the benzyl radicals observed in solution,¹² which are $A(H_\alpha) = 16.40$, $A(H_o) = 5.17$, $A(H_m) = 1.77$, and $A(H_p) = 6.19$ G. The benzyl radical is a planar π radical. If the spectra of Figure 5 are produced by the benzyl radicals strongly oriented in the manner described above, the splittings seen in Figure 5b are expected to be close to the isotropic coupling constants observed in solution (see eq 1c).

A neon matrix containing preferentially oriented benzyl radicals (produced by pyrolysis of benzyl iodide) was therefore prepared and examined. The orientation-dependent spectra identical with Figures 5a and 5b

(12) H. Fisher, *Z. Naturforsch.*, **20**, 488 (1965).

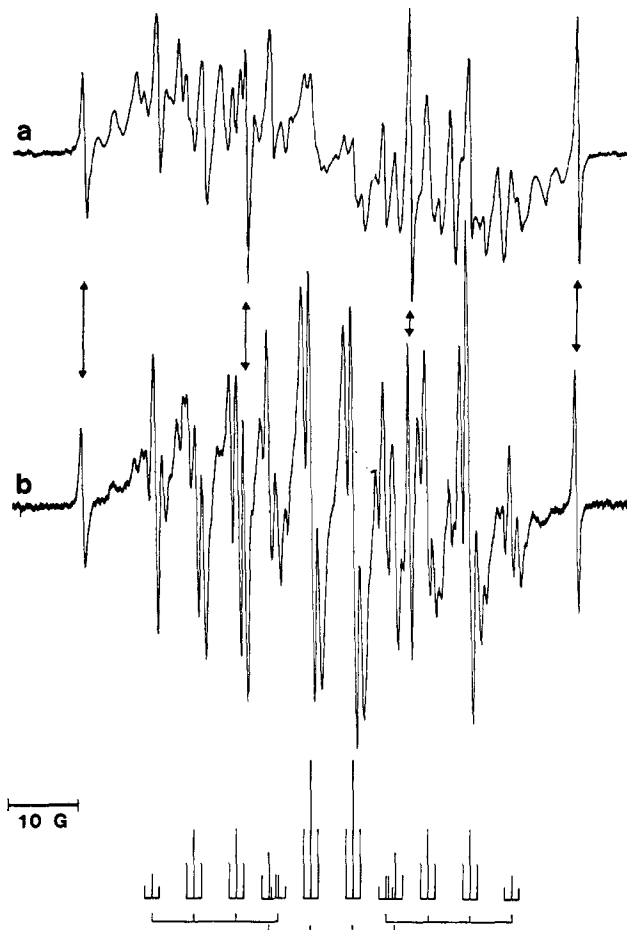
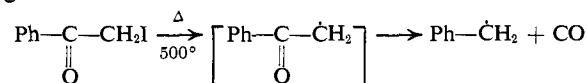


Figure 5. ESR spectra of a neon matrix containing the pyrolyzate of phenacyl iodide observed with the magnetic field (a) parallel to and (b) perpendicular to the plane of the sapphire rod. The quartets indicated by the arrows are due to methyl radicals.

were observed. We are thus led to conclude the following



and that, in a neon matrix, the coupling tensors to the ortho and para protons of the benzyl radical become accidentally degenerate producing the simple triplet-of-quartet-of-triplet pattern of Figure 5b. Note that, only in the direction perpendicular to the molecular plane, the principal axes of the coupling tensors to all the protons are coincident, and the two α protons and three ortho and para protons become, respectively, magnetically equivalent. The ill-defined spectrum of Figure 5a results from the random azimuth of individual molecular planes atop the plane of the sapphire rod.

Summary and Contents

We have thus shown that, while the photolysis of phenacyl iodide at $\sim 4^\circ\text{K}$ results in the formation of phenacyl radicals (I), the pyrolysis of the same iodide at $\sim 500^\circ$ produces the benzyl radicals due presumably to thermal decomposition of the primary, phenacyl radicals.

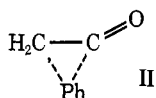
The solution or isotropic spectra of many 2-alkanonyl radicals are known.^{13,14} They all appear to possess

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

(14) D. M. Camaioni, H. F. Walter, and D. W. Pratt, *J. Amer. Chem. Soc.*, **95**, 4057, 7978 (1973).

similar g tensors and coupling constants to the α protons. For example, the g values of 2.0044 and 2.0048 and the A_{1so} to the α protons of 19.8 and 18.1 G have been reported for $\text{CH}_3\text{-CO-CH}_2$ ¹³ and 2-cyclohexanonyl radicals,¹⁴ respectively. The g_{1so} and A_{1so} computed from Table I are 2.0046 and 19.8 G and are very close to the values cited above. The contribution of the resonance structure of the type Ib must be very similar in these radicals. Based upon the ¹³C and ¹⁷O hyperfine coupling constants, it has been reported¹⁴ that the contribution of the type Ib structure in 2-cyclohexanonyl is about 15%.

The decomposition of I to benzyl upon thermal activation is probably a process unique to the phenacyl radical motivated by the much more favorable resonance stabilization of the benzyl radical. It must go through the cyclic transition state shown below, followed by the



decarbonylation. It is not an unexpected transition state since 1-2 migration of an aryl group is one of the most often observed radical rearrangements.

Indeed, if structure II with its spin density at the ortho and para positions is the thermodynamically favored one for phenacyl at 125° and if the decarbonylation occurs only at much higher temperature, all of the anomalous results obtained during the attempts to synthesize dibenzoylethane or any of its 2 and/or 3 methyl substituted homologs could be explained. Kochi, *et al.*,¹⁵ have shown that several aliphatic free radicals rearrange at *ca.* -120° in a manner similar to that which is here implied.

Direct evidence for the structure (II) at 125° or possibly at room temperature should be obtainable from esr studies using ultraviolet photolysis of phenacyl iodide or bisazophenacyl in solution *via* flow technique. These investigations are now in progress at one of our laboratories.

(15) J. K. Kochi, P. J. Krussic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877, 1879 (1969).

Resonance Raman Scattering from Iron(III)- and Copper(II)-Transferrin and an Iron(III) Model Compound. A Spectroscopic Interpretation of the Transferrin Binding Site^{1a}

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Abstract: Laser excitation within the visible absorption band of both the Fe(III) and Cu(II) complexes of human serum transferrin reveals four resonance enhanced Raman bands at 1604, 1505, 1284, and 1173 cm^{-1} . These are assigned to phenolate vibrational modes by comparison with the Fe(III) complex of ethylenediamine di(*o*-hydroxyphenylacetate), EDDHA. The lack of observable frequency shifts upon ¹⁸O substitution in bicarbonate confirms that bicarbonate does not contribute significantly to the resonance Raman spectrum. This observation does not preclude direct binding of bicarbonate to iron, but the primary role of bicarbonate in the formation of Fe(III)-transferrin is apparently to induce a protein conformation change which brings the binding groups into proximity. The visible absorption band is assigned to phenolate \rightarrow Fe(III), $p\pi-d\pi^*$ charge transfer (probably $p\pi-d\sigma^*$ for Cu(II)), and the close similarity of this band for Fe(EDDHA)⁻ and Fe(III)-transferrin implies participation of *two* tyrosines in the binding site of the protein. The Raman excitation profiles of Fe(EDDHA)⁻ and Fe(III)-transferrin show unprecedentedly complex behavior, within which a progression of peaks with a uniform 1000 cm^{-1} spacing can be observed. This is interpreted as reflecting enhanced Raman scattering from successive excited state vibrational levels involving the phenolate C-O stretching mode.

The two binding sites of the serum iron-transport protein transferrin display an extraordinary avidity for iron. With an apparent binding constant, $K = 10^{24}$,² transferrin effectively protects its charge of bound iron from hydrolysis and chelation by serum components. Yet upon encounter with a reticulocyte, the

binding affinity changes dramatically, and iron is released to a membrane-bound iron receptor site for eventual incorporation into hemoglobin.³

Although the detailed physical structure of the iron binding site of transferrin remains largely unresolved, several facts regarding the nature of the site are known. Chemical modifications^{4,5} have suggested that tyrosine and histidine participate in metal binding. Spectro-

(1) (a) This work was supported by a grant from Research Corp. and a faculty research fellowship from the University of Michigan (to B.P.G.) and NIH Grant GM13498 and NSF Grant GP41008X (to T.G.S.); (b) the University of Michigan; (c) Princeton University.

(2) R. Asa, A. G. Malstrom, P. Saltman, and T. Vanngard, *Biochim. Biophys. Acta*, **75**, 203 (1963).

(3) J. H. Jandl, J. K. Inman, R. L. Simmons, and D. W. Allen, *J. Clin. Invest.*, **38**, 161 (1959).

(4) W. F. Line, D. Grohlich, and A. Bezkorovainy, *Biochemistry*, **6**, 3393 (1967).

(5) S. K. Komatsu and R. E. Feeney, *Biochemistry*, **6**, 1136 (1967).