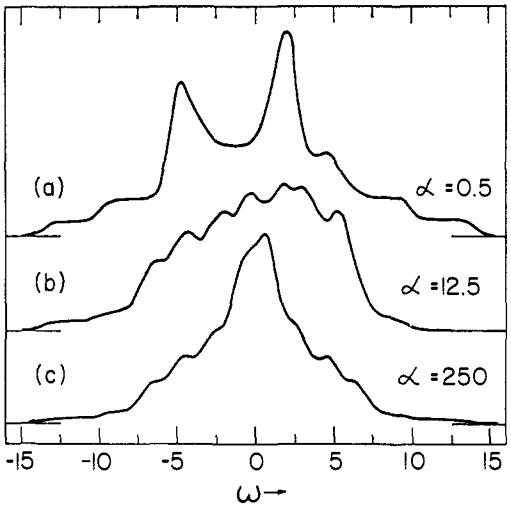

Figure 1. Calculated, Gaussian-broadened, polycrystalline line shapes for a spin-$^1/_2$ nucleus in an axially symmetric two-spin ($^1/_2$, $^7/_2$) system; α is a measure of the relative Zeeman and quadrupolar energies of the spin-$^7/_2$ nucleus; the abscissa units are $\gamma_I\gamma_S\hbar/2r^3 = 1$; the zeros of the spectra occur at $\omega_0 = \gamma_I H_0$.

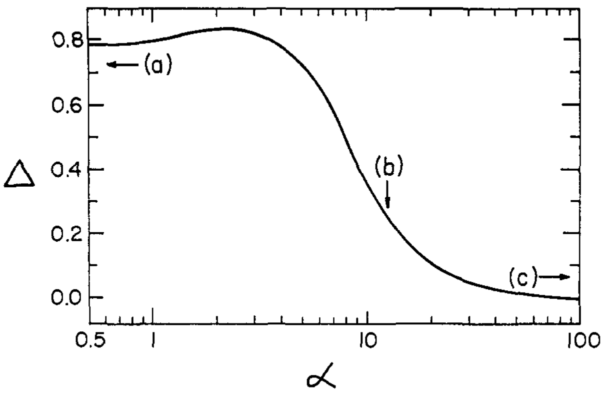

Figure 2. Variation in the second moment of the spin-$^1/_2$ nucleus in the two-spin ($^1/_2$, $^7/_2$) system as a function of α; $\Delta = (M_2 - M^0_2)/M^0_2$ where M_2 is the second moment and M^0_2 is the second moment in the absence of quadrupolar effects.

eq 1. Therefore, the Hamiltonian, $\mathcal{H}_S$, for nucleus S in the laboratory frame is[6]

$$\mathcal{H}_S = -\gamma_S\hbar H_0S_z + \frac{e^2qQ}{4S(2S-1)}\{{}^1/_2(3S_z{}^2 - S^2) \times (3\cos^2\theta - 1) + {}^3/_2[S_z(S^+ + S^-) + (S^+ + S^-)S_z]\sin\theta\cos\theta + {}^3/_4[(S^+)^2 + (S^-)^2]\sin^2\theta\} \quad (7)$$

The Zeeman quantized spin functions of S were used as a basis set; the matrix elements of $\mathcal{H}_S$ were calculated, the matrix was diagonalized, and the transformation matrix was obtained. The latter was used to calculate $\langle S_{x,z}\rangle_i$ and thereby $\Delta\omega_i$.

Line shapes for a polycrystalline sample were obtained from numerical values for $\Delta\omega_i$ in 400 divisions of the interval $0 \leq \theta \leq \pi$, such that each line consisted of 3200 points, each point being weighted by its probability, $\sin\theta$. The lines were then folded with a rather narrow Gaussian function. In this way line shapes were calculated for the entire range of the parameter

$$\alpha = |\gamma_S\hbar H_0[e^2qQ/4S(2S-1)]^{-1}| \quad (8)$$

with $S = {}^7/_2$. Figure 1 shows lines calculated for three values of α. The parameter α gives the relative magnitudes of the Zeeman and quadrupole interactions for the S nucleus. It is seen that as the quadrupole interaction becomes larger, or the Zeeman smaller, the extremities of the spectrum do not broaden; however, the intensity is redistributed toward the wings. Also, the line shapes for intermediate α are very asymmetric. This reflects the fact that the Zeeman and quadrupole terms in $\mathcal{H}_S$ depend differently on S_z so that the $+m_z$ and $-m_z$ states are affected differently. However, in spite of the asymmetry, the zero of the first moment remains at ω_0 for the entire range of α. The asymmetry in Figure 1 corresponds to Zeeman and quadrupole interactions of the same sign in eq 8. The asymmetry is reversed if they are of opposite sign, so it can, in principle, be used to establish the sign of the quadrupole coupling constant.

The second moment can be a sensitive function of α as shown by the results in Figure 2 for the unbroadened line. The sharpest changes occur in the region $30 > \alpha > 3$, so line-shape and M_2 observations as a function of H_0 in this region might enable one to establish the magnitude of the quadrupole coupling constant in addition to its sign. Beyond the range of α given in Figure 2, M_2 does not change noticeably; there are, however, discernible changes in the line shape. The asymptotic value of M_2 for large quadrupole interactions[7] is 1.79 times its value in their absence. Therefore, if such effects were neglected for $\alpha \gtrsim 0.3$, and the observed value of M_2 used to evaluate the internuclear distance r, the true value of r would be 1.10 times the apparent value. Thus, our treatment gives a corrected, upper limit of 1.57 A on the H–Co bond distance of $HCo(CO)_4$ and an upper-limit estimate of 1.42 A for the H–Mn bond in $HMn(CO)_5$. These bond distances should be quite feasible because of the large quadrupole moments of ^{51}Co and ^{55}Mn and the resultant probably small values of α.

At present, we are trying to fit the $HCo(CO)_4$ proton spectrum as a function of H_0. Whether or not this is successful will depend on the complications introduced by the scalar coupling and the anisotropy of the proton chemical shift. Similar line-shape and second-moment analyses are planned for the spin-$^3/_2$ and -$^5/_2$ cases.

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(6) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, England, 1961, p 233.

(7) An approximate analysis of this limiting case has been made independently by G. M. Sheldrick, with results similar to ours. We thank him for sending us a preprint of his work.

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The Chemistry of Bisiminium Cations. I. A Synthesis of 1-Deuterio Aldehydes

Sir:

Bisiminium cations (*e.g.*, I and II) are described by Kröhnke[1] as reasonably stable crystalline solids easily

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(1) F. Kröhnke and H. Leister, *Chem. Ber.*, **91**, 1295 (1958).

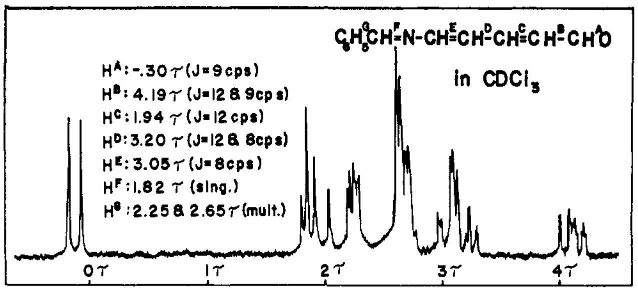
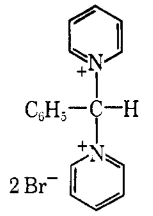
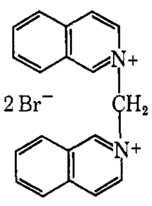


Figure 1.

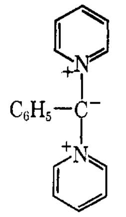
prepared in high yield by warming the corresponding *gem*-dibromides with the requisite heteroaromatic amines. We now report (1) the hydrolysis of these species in isotopically labeled water as part of a simple and inexpensive synthesis of 1-deuterio or 1-tritio aldehydes, and (2) the isolation of an extraordinary intermediate in the hydrolytic process.



I



II

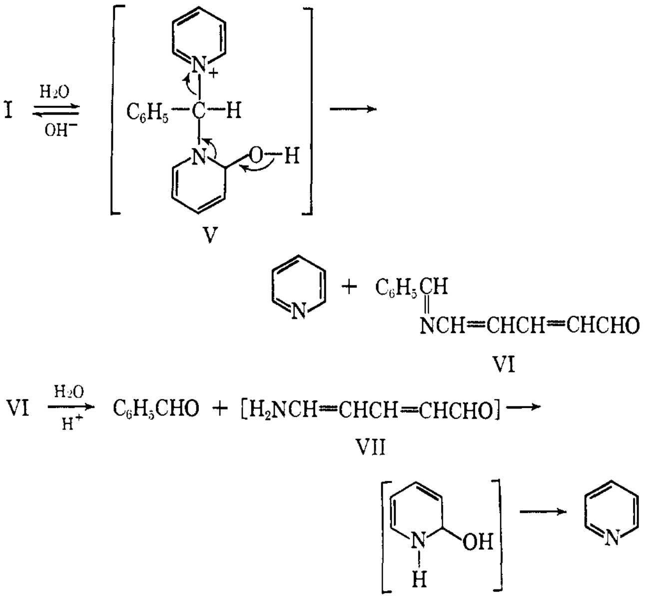


III

Aldehydes labeled with D or T in the 1 position (and compounds easily derived from these precursors) are often required in mechanistic and tracer studies but are not at present readily available. The synthetic procedures either involve tedious multistep low-yield processes or alternatively the use of costly organolithium bases or metal deuteride reducing agents.[2] Kröhnke[1] has shown that I is slowly hydrolyzed in water to benzaldehyde and pyridine. It was our expectation from exchange studies in ylidic systems[3] that sp^3 protons in this and related bisiminium cations should be rapidly exchanged in D_2O *via* the ylide III. Should the exchange proceed faster than the hydrolysis as anticipated, a one-step synthesis of labeled aldehydes from bisiminium cations would have been accomplished. Since *gem*-dihalides are often intermediates in commercial aldehyde syntheses, and D_2O is the one inexpensive source of deuterium, the over-all two-step deuterio aldehyde synthesis looked very attractive.

In accord with the above hypothesis, 1-deuteriobenzaldehyde (IV) of the theoretical equilibrium isotopic purity[4] could be isolated in 91% yield by this pathway. The bisiminium salt I was dissolved in a 0.2 *M* phosphate buffer in D_2O (pD 6.7); the solution was allowed to stand overnight and then refluxed for 3 hr to hydrolyze the exchanged dication. The mixture was acidified and steam distilled to remove IV which was then isolated by ether extraction and distillation. By a similar pathway dideuterioformaldehyde was obtained from II in essentially quantitative yield as its dimedone derivative. The rate of deuterium incorporation of I was followed with the aid of nmr spectroscopy; the reaction is base catalyzed with an exchange half-life of about 5 min in a 50% solution at pD 6.5 at 30°. Concentration problems made a similar study on the dication II impractical, but qualitatively as expected this compound deprotonated somewhat more slowly. Attempts to utilize the intermediate III as an alkylating agent toward electrophilic carbon species (a potential source of acyl substituents) met with failure probably as a result of the steric inaccessibility of the nucleophilic center in this trityl-like anion.

When the bisiminium cation I was refluxed in water to yield benzaldehyde, 2 equiv of pyridine was also produced. This simple stoichiometry, however, superbly masks a remarkable multistep hydrolysis mechanism. If the process is accelerated with OH^-, a reaction intermediate (a pale yellow solid) immediately precipitates in high yield from the aqueous solution and a single equivalent of pyridine is isolated. This material[5] (stable under N_2 in the dark in a refrigerator for a few days) slowly dissolves in water with concomitant formation of benzaldehyde and the second equivalent of pyridine, the latter reaction being catalyzed by mild acid. Analytical and spectral data are only compatible with the enamine Schiff base structure VI for this compound; mp 59–60°; infrared: 6.01, 6.30, 6.46 μ ($CHCl_3$); mass spectroscopy: *m/e* 185 (parent), 156 (P − CHO), 117 (P − C_4H_4O), 108 (P − C_6H_5), 81 (P − C_6H_5CHN); for nmr see Figure 1 (the singlet at τ 1.82 is absent in the deuterated sample).



To our knowledge this is the first isolated Schiff base of an enamine although such compounds are important

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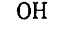
(2) For the best and most recent published procedure for the preparation of 1-deuteriobenzaldehyde and references to ten others routes see: D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, 31, 4303 (1966).

(3) R. A. Olofson, W. R. Thompson, and J. S. Michelman, *J. Am. Chem. Soc.*, 86, 1865 (1964); R. A. Olofson and J. M. Landesberg, *ibid.*, 88, 4263 (1966); R. A. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, *ibid.*, 88, 4265 (1966); also R. A. Olofson and coworkers, unpublished results.

(4) Theory for equilibrium exchange: 95% D; experimental by nmr *vs.* a weighed internal anisole standard: 95 ± 1% D; the per cent D is easily made quantitative by carrying out a second exchange.

(5) This yellow solid was first isolated by Kröhnke[1] but assigned the untenable structure below.



intermediates in the biological action of pyridoxal and some of the chemistry of the nicotinamide nucleotides.[6] Our postulated mechanism for its formation and hydrolysis requires initial addition of OH^- to I to form the pseudo-base V. This hemiacetal derivative can then undergo ring scission with elimination of pyridine to yield the isolated intermediate VI. Hydrolysis of this Schiff base takes place in the usual manner, but the enamine VII which is now generated (or the precursor carbinolamine) can cyclize to the pseudo-base VIII and then undergo dehydration to pyridine. In the total process, then, one pyridine ring is torn asunder and then later reconstituted in a surprisingly clean reaction.

Acknowledgment. This research was supported by a grant from the U. S. Public Health Service (GM 13980).

[6] T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966.

[7] Alfred P. Sloan Foundation Fellow, 1965–1967.

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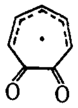
Received July 5, 1967

α-Keto Radicals[1,2]

Sir:

The oxidation of phenols by ceric ion and the detection of the resulting phenoxy radicals in a flow system by esr spectroscopy have been described in the pioneering work of Stone and Waters.[3] We now describe the application of this technique to a variety of enols. Extension of the technique to stable enols, such as the tropolones or hydroxypyridines, is obvious. Thus, reaction of α-tropolone (0.01 *M* in water) with an equal volume of a 0.01 *M* solution of ceric sulfate in 1 *M* sulfuric acid yields radical **1**, a^H = 10.3, 7.1, 7.1, 2.5, and 2.5 gauss, detected ~0.1 sec after mixing.



1

About 3 l. of solution was required to record the spectrum.[4] Ketones that exist with an appreciable enol content, such as cyclohexane-1,3-dione or acetylacetone, are readily converted to a single radical ($RCO\dot{C}HCOR$). Substrates with a low enol content, such as 3-cyano-2-butanone or methyl acetoacetate, give negligible concentrations of radicals under the standard conditions. However, reaction of a solution of these ketones containing 0.1 *M* aqueous potassium hydroxide with the 1 *M* acidic solution of ceric ion yielded appreciable concentrations of the α-keto radicals (Figure 1). In a similar fashion 2-nitropropane in basic solution yields the 1-nitro-1-methylethyl radical upon acidification and oxidation by ceric ion.

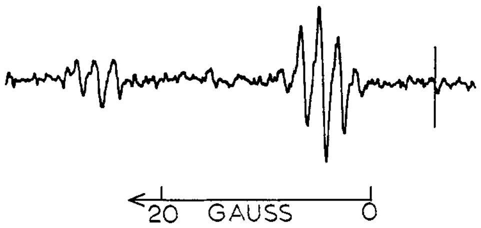
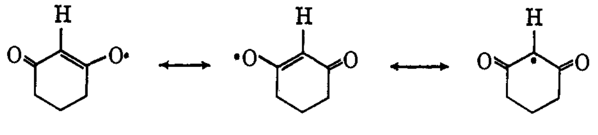


Figure 1. High field of the first-derivative esr spectrum of 1-methyl-2,5-cyclopentanedione radical prepared by reaction of 2-methyl-1,3-cyclopentanedione in basic solution with acidic ceric sulfate. Two of the four 1:4:6:4:1 multiplets are shown; $a_{CH_3}{}^H$ = 20.4, $a_{CH_2}{}^H$ = 1.72 gauss.

The formation of α-keto radicals by the reaction of ketones with hydrogen peroxide and titanous ion[5] suffers from adverse directive effects[6–8] and from the possibility of hydroxyl radical addition to the enol.

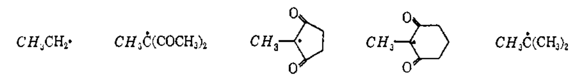
Functionally substituted alkyl radicals are of interest because of the question of spin delocalization.[9] We originally investigated the tropolone radical and β-diketone radicals because of the expectation of unusual stability due to resonance stabilization. However,



resonance stabilization of the type shown appears to be of little importance. Using a value of *Q* of 26 gauss[10] for the α-tropolone radical enables us to predict that more than 75% of the unpaired spin resides on the carbon atoms ((10.3 + 2(7.1) − 2(2.5))/26).[11] Similarly, in the series $CH_3\cdot$, $CH_3COCH_2\cdot$, $CH_3CO\dot{C}HCOCH_3$, the value of a^H decreases only slightly from 23 to 19.3 to 18.6 gauss. Fischer emphasizes that empirical spin densities in the system $(X)(Y)\dot{C}CH_3$ can be estimated by eq 1.[9,12,13] Again, the value of $a_{CH_3}{}^H$ decreases only

$$a_{CH_3}{}^H = 29.3\rho^C \qquad (1)$$

20% as the ethyl radical is substituted by two acetyl groups. This effect is comparable to methyl substitution.[12]



The data of Table I stress the relative unimportance of resonance interactions such as those shown in Scheme I.

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[1] Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. X.

[2] This work was supported by grants from the National Science Foundation (GP-6402X) and the National Institutes of Health (IGM-13000).

[3] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 213 (1964).

[4] Flow rates of ~2–3 ml/sec through Varian Associates cell V-4548.

[5] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

[6] W. T. Dixon, R. O. C. Norman, and A. L. Buley, *ibid.*, 3625 (1964).

[7] J. T. Pearson, P. Smith, and T. C. Smith, *Can. J. Chem.*, **42**, 2002 (1964).

[8] P. Smith, P. B. Wood, and T. C. Smith, *J. Chem. Phys.*, **43**, 1535 (1965).

[9] H. Fischer, *Z. Naturforsch.*, **19a**, 866 (1964); **20a**, 428 (1965).

[10] A value of Q = 26.25 at 96° is measured for the tropenyl radical: G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, and F. R. Hunter, *J. Am. Chem. Soc.*, **87**, 3527 (1965).

[11] Similarly, T. J. Stone and E. A. Waters, *J. Chem. Soc.*, 4302 (1964), concluded that >82% of the spin of *m*-semiquinone radical anion resides on the carbon atoms.

[12] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[13] G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).