first triplet state. The best hypothesis appears to be that, at 2537 Å., 1,3-butadiene is excited to the upper singlet state. It follows that the 0-0 level must lie at even longer wave lengths. The simplest conjugated diene from which fluorescence has been observed is ergosterol.<sup>10</sup> In this case, the fluorescent spectrum exactly reproduces the absorption spectrum but is shifted by nearly 1000 Å. to the red. A similar situation obtains in lumisterol, another cyclic 1,3-diene.<sup>10</sup> In both molecules, there is no detectable absorption which corresponds to the 0-0 band from the ground singlet to the upper singlet. It seems possible that in 1.3-butadiene the 0-0 band may lie at a wave length as low in energy as 90 kcal./mole ( $\sim$ 3200 Å.). Since the lowest triplet lies at 60 kcal./mole,<sup>9</sup> the gap that separates these two levels is in no sense "large." [The upper singlet-lowest triplet separation in benzene is 25.5 kcal./mole.<sup>11</sup>]

(10) E. Havinga, R. J. De Kock, and M. P. Rappoldt, Tetrahedron, 11, 276 (1960).

(11) H. Ishikawa and W. A. Noyes, Jr., J. Chem. Phys., 37, 583 (1962).

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## On the Equations Used to Analyze Isotropic Nuclear Magnetic Resonance Shift Data for Systems Involving a Rapid Equilibrium

Sir:

The equation

$$\frac{\Delta H_i}{H} = \frac{\Delta f_i}{f} = -\frac{A_i}{2S} \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{kT} [3 + \exp(\Delta G/RT)]^{-1}$$
(1)

has been used many times<sup>1-11</sup> to analyze the results of isotropic n.m.r. shifts of nickel chelates in solution where there is a square-planar (singlet)  $\rightleftharpoons$  tetrahedral (triplet) equilibrium in solution. In this equation  $\Delta H_i$ and  $\Delta f_i$  are the isotropic shifts from the diamagnetic position of the resonance magnetic field and frequency, respectively, of a given nucleus.  $A_i$  is the isotropic hyperfine coupling constant for the *i*th proton,  $\gamma_e$ and  $\gamma_{\rm H}$  are the magnetogyric ratios of the electron and proton, respectively, g is the spectroscopic splitting factor for the paramagnetic species, and  $\Delta G$  is the free energy change for the above-mentioned equilibrium. The other symbols have their usual significance.

(1) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, J. Chem. Phys., 37, 347 (1962).

(2) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, Mol.

Phys., 5, 497 (1962).
(3) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, Discussions Faraday Soc., 34, 77 (1962).

(4) W. D. Phillips and R. E. Benson, J. Chem. Phys., 33, 607 (1960). (5) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L.
 Cairns, J. Am. Chem. Soc., 84, 4100 (1962).
 (6) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, 85, 397

(1963).

(7) D. R. Eaton, A. D. Josey, and W. A. Sheppard, ibid., 85, 2689 (1963).

(8) R. H. Holm, A. Chakravorty, and G. O. Dudek, ibid., 86, 379 (1964).

(9) A. Chakravorty and R. H. Holm, ibid., 86, 3999 (1964).

(10) A. Chakravorty and R. H. Holm, Inorg. Chem., 3, 1010 (1964).

(11) G. W. Everett, Jr., and R. H. Holm, J. Am. Chem. Soc., 87, 2117 (1965).

As noted in footnote 31a of ref. 8, the 2S in the denominator of eq. 1 is involved with the relationship between the unpaired electron spin density and the  $A_i$ values. This point will not concern us further here. Equation 1 reduces (when  $\Delta G \rightarrow -\infty$ ) correctly to eq. 2<sup>12</sup> which is applicable to fully paramagnetic systems in which the isotropic shifts obey the Curie law

$$\frac{\Delta H_i}{H} = -\frac{A_i}{2S} \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{3kT}$$
(2)

The observed isotropic shifts for a system in rapid equilibrium will be the isotropic shifts for the diamagnetic species (zero by definition) and paramagnetic species, weighted by their mole fractions in solution. If we call the mole fraction of triplet molecules  $N_{\rm T}$ , then the isotropic shifts are given by

$$\frac{\Delta H_i}{H} = -\frac{A_i}{2S} \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{3kT} N_T$$
(3)

It is easily shown that the equilibrium constant Kfor the singlet-triplet equilibrium is  $K = [(1/N_T)]$ -1]<sup>-1</sup>, and also since  $\Delta G = -RT \ln K$  we have:  $\Delta G = RT \ln [(1/N_T) - 1]$ .<sup>13</sup> We get immediately that  $N_{\rm T} = [\exp(\Delta G/RT) + 1]^{-1}$ , so that the correct equation for isotropic shifts, when an equilibrium is involved, is

$$\frac{\Delta H_i}{H} = -\frac{A_i}{2S} \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{3kT} [\exp(\Delta G/RT) + 1]^{-1} \quad (4)$$

Furthermore, the equation given<sup>6,8</sup> for the molar magnetic susceptibility of these systems

$$\chi_{\rm M} = \frac{2g^2 N \beta^2}{3kT} [1 + 1/3 \exp{(\Delta G/RT)}]^{-1}$$
 (5)

and the corollary equation<sup>6,8,10,11</sup> for the free energy change in terms of the measured effective magnetic moment values,  $\mu_{\text{eff}}$ 

$$\Delta G = RT \ln 3 \left[ \frac{\mu_{\infty}^2}{\mu_{\text{eff}}^2} - 1 \right]$$
 (6)

are incorrect and should in fact be, respectively

$$\chi_{\rm M} = \frac{2g^2 N \beta^2}{3kT} [\exp(\Delta G/RT) + 1]^{-1}$$
 (7)

and

$$\Delta G = RT \ln \left[ \frac{\mu_{\infty}^2}{\mu_{\text{eff}}^2} - 1 \right]$$
(8)

The error no doubt arose from a misapplication of the formula<sup>14</sup> for the magnetic susceptibility of a substance which has a singlet ground state and a thermally accessible triplet state separated from the ground state by an energy J. The molar susceptibility of such a system is correctly given by

$$\chi_{\rm M} = \frac{2g^2 N \beta^2}{3kT} [1 + 1/3 \exp(J/kT)]^{-1}$$
 (9)

However, it is not permissible to replace the energy quantity J by a free energy  $\Delta G$ , while retaining the degeneracy factor 1/3. The degeneracy factor is embodied

(12) H. M. McConnell and R. E. Robertson, J. Chem. Phys., 29, 1361 (1958).

- (13) The analogous eq. 5 of ref. 6 is in error.
   (14) B. N. Figgis and R. L. Martin, J. Chem. Soc., 3837 (1956).

in the entropy change  $\Delta S$ , which is a component of  $\Delta G$ since  $\Delta G = \Delta H - T \Delta S$ . Indeed, the electronic entropy factor, due to the degeneracy of the triplet state, is R ln 3 as pointed out by Holm, et al.,<sup>8</sup> but this factor will be included in the  $\Delta S$  values calculated from the data if the proper equation is used.  $\Delta G$ values in the literature, calculated from the incorrect equation, are too high by RT ln 3, and the  $\Delta S$  values are too low by  $R \ln 3 = 2.2$  e.u. Fortunately the calculated  $A_i$  values are unaffected by this error.<sup>14a</sup>

(14a) NOTE ADDED IN PROOF. Holm, et al., have pointed out the discrepancy, by a factor of three, between the equilibrium constants calculated from eq. 6 and those based on the actual mole fractions of the singlet and triplet molecules in solution determined from the measured susceptibilities (R. H. Holm, A. Chakravorty, and G. W. Everett, Jr., Progr. Inorg. Chem., 7, in press).

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## Nucleophilic Acylation Utilizing an Ylid Intermediate. A Simple Synthesis of Benzaldehyde- $d_{1^1}$

Sir:

We wish to report that  $\alpha$ -keto acids can be decarboxylated to aldehydes under mild conditions in the presence of carboxylic acid anhydrides and pyridine,<sup>2</sup> and to point out some useful applications and some important general mechanistic implications of this type of reaction.

In the case of phenylglyoxylic acid (I), we have used acetic, phenylacetic, and benzoic anhydrides. The latter gives the best yield of benzaldehyde because of the avoidance of Perkin-type condensation reactions which occur with the other anhydrides.<sup>3</sup> In one run, a solution of 13 mmoles of phenylglyoxylic acid (I), 27 mmoles of benzoic anhydride, and 140 mmoles of pyridine in 50 ml. of benzene was heated at reflux for 13 hr. The yields of benzaldehyde and carbon dioxide were 75 and 88%, respectively. Glyoxylic and pyruvic acids were similarly decarboxylated.<sup>4</sup>

This reaction is the basis of a very simple synthesis of benzaldehyde- $d_1$ . Phenylglyoxylic acid- $d_1$  is readily prepared by dissolving the commercially available<sup>5</sup> protium compound in heavy water and evaporating to dryness.<sup>6</sup> The benzaldehyde, prepared from I which had been twice subjected to exchange in this way, was shown by n.m.r. integration to contain about 92% deuterium in the aldehyde group.<sup>7</sup>

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) Neither of the two catalysts is effective alone.

(3) T. Cohen, I. H. Song, and J. H. Fager, Tetrahedron Letters, 237 (1965).

(4) However, these reactions were complicated by serious side reactions, since the aldehydes were produced in much lower yield (11-15%) than carbon dioxide (43-50%).

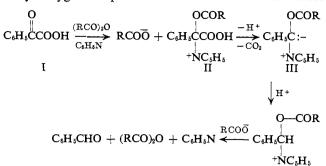
(5) K & K Laboratories, Inc., Jamaica 33, N.Y.

(6) Another procedure for exchanging the carboxyl hydrogen involves adding heavy water to a benzene solution of the protium acid and then removing the water by azeotropic distillation.

(7) Benzaldehyde-di has been prepared previously by considerably more laborious routes involving catalytic deuteration of benzoyl chloride over a poisoned palladium catalyst at 140°8 or lead tetraacetate cleavage of a deuterated dihydrobenzoin, which was in turn prepared by reduction of benzil with lithium aluminum deuteride.

(8) A. F. Thompson and N. H. Cromwell, J. Am. Chem. Soc., 61, 1374 (1939).

A reasonable path for this reaction involves nucleophilic attack of pyridine at the keto carbonyl group and subsequent or simultaneous acylation<sup>10,11</sup> of the carbonyl oxygen to produce the intermediate II. Loss



of a proton and carbon dioxide would produce the ylid III which, upon protonation and deacylpyridination (essentially the reverse of the first step), would yield the benzaldehyde.<sup>12-15</sup> Pyridine ylids of this type<sup>17</sup> are intermediates in many carbanionoid reactions.<sup>18</sup>

If this mechanism is valid, one might expect the decarboxylation of  $\alpha$ -halo acids to be brought about by pyridine under mild conditions. That this is indeed the case is demonstrated by the reaction of pyridine with  $\alpha$ -bromophenylacetic acid in refluxing benzene. Carbon dioxide, which is vigorously evolved, and Nbenzylpyridinium bromide are quantitatively produced. Decarboxylation of the pyridinium salt V to the ylid VI is presumably a key step in this reaction.<sup>19</sup>

$$C_{6}H_{5} \xrightarrow{V} C_{6}H_{5}$$

$$C_{6}H_{5} \xrightarrow{-CH} COOH \xrightarrow{-H^{+}} C_{6}H_{5} \xrightarrow{-\overrightarrow{C}H} NC_{6}H_{5}$$

$$VI$$

The intermediate III is mechanistically equivalent to the conjugate base of benzaldehyde and as such suggests a variety of conceivable synthetic and degradative uses. For example, intermediates such as III should

(9) K. B. Wiberg, ibid., 76, 5371 (1954).

(10) This step could be executed by an external acylating agent, such as the N-acylpyridinium ion, or internally by a mixed anhydride of the phenylglyoxylic acid. (11) We should like to term this reaction "acylpyridination."

(12) Very recently, a related ylid-type mechanism has been proposed as one possibility for the decarboxylation of oxamic acid in aniline solution at 150°: J. Watson and P. Haake, J. Org. Chem., 30, 1122 (1965).

(13) An alternative mechanism, which is analogous to the thiamineinduced decarboxylation of pyruvic acid, 14 is also available. It involves removal of the  $\alpha$ -proton of an N-acylpyridinium ion, condensation of the keto acid with the resulting zwitterion, decarboxylation, and cleavage. However, this mechanism requires dilution of the deuterium ion content of the solution by the  $\alpha$ -hydrogen of the pyridine, and this is ruled out by the high deuterium content of the benzaldehyde produced from the deuterated acid.

(14) R. Breslow, J. Am. Chem. Soc., 80, 3719 (1958); R. Breslow and E. McNelis, *ibid.*, 81, 3080 (1959).

(15) An entirely different type of mechanism is apparently utilized in the decarboxylation of I by amino acids and amino lactams, although that induced by simple primary amines under vigorous conditions<sup>16</sup> might proceed by a mechanism similar to that proposed here: A. S. Endler and E. I. Becker, *J. Phys. Chem.*, **61**, 747 (1957). (16) W. Langenbeck, "Die Organischen Katalysatoren," 2nd Ed., Springer-Verlag, Berlin, 1949.

(17) Decarboxylations of picolinic acid and related compounds proceed through another type of ylid intermediate in which the negative charge resides on the  $\alpha$ -carbon atom of the pyridinium ring: B. R. Brown, Quart. Rev. (London), 5, 131 (1951); P. Haake and J. Mantecon,

J. Am. Chem. Soc., 86, 5230 (1964).
(18) F. Kröhnke, Angew. Chem., 65, 605 (1953); F. Kröhnke, Angew.
Chem. Intern. Ed. Engl., 2, 225 (1963); J. A. Berson and T. Cohen, J.
Am. Chem. Soc., 78, 416 (1956).

(19) Under very much more vigorous conditions (190°), pyridine betaine hydrochloride is reported to yield methyl chloride, pyridine, and carbon dioxide: E. von Gerichten, Ber., 15, 1251 (1882).