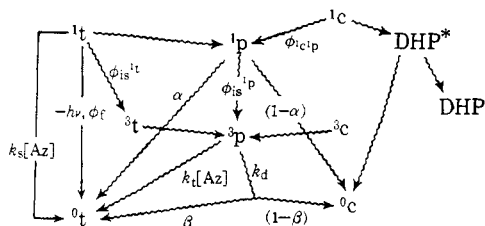


**Scheme I.** Combination of Singlet and Triplet Paths for Stilbene Photoisomerization



triplets, respectively, and other symbols have their usual meaning.<sup>17</sup> The mechanism predicts that photo-stationary [t]/[c] ratios for direct excitation should depend on azulene concentration according to eq 1,

$$\left(\frac{[t]}{[c]}\right)_s = \frac{\epsilon_c}{\epsilon_t} \phi_{1c1p} (1 + K_s[Az]) \times \left\{ \frac{\alpha(1 - \phi_{is}^{1p})(1 + K_t[Az]) + \phi_{is}^{1p}(\beta + K_t[Az])}{(1 - \phi_f)(1 - \beta) + (1 - \phi_{is}^{1t} - \phi_f)(1 - \phi_{is}^{1p})} \times \frac{\alpha}{\{\beta - \alpha + (1 - \alpha)K_t[Az]\}} \right\} \quad (1)$$

where  $K_s = k\tau_{1t}$  and  $K_t = k_t/k_d = \beta r_s$ . In the absence of intersystem crossing,  $\phi_{is}^{1p} \sim \phi_{is}^{1t} = 0$ , eq 1 reduces to eq 2 so that  $r_d = K_s$ . The value of  $K_s$  has been shown

$$\left(\frac{[t]}{[c]}\right)_s = \frac{\epsilon_c}{\epsilon_t} \frac{\phi_{1c1p}}{1 - \phi_f} \frac{\alpha}{1 - \alpha} (1 + K_s[Az]) \quad (2)$$

to be  $\sim 15 M^{-1}$  in the case of *trans*-stilbene,<sup>15</sup> and would be expected to be similar or smaller for the bromostilbenes.<sup>19</sup> If on the other hand intersystem crossing were the only pathway leading to isomerization, eq 1 would reduce to eq 3 and the dependence on azulene

$$\left(\frac{[t]}{[c]}\right)_s = \frac{\epsilon_c}{\epsilon_t} \frac{\phi_{1c1p}}{1 - \phi_f} (1 + K_s[Az]) \frac{(\beta + K_t[Az])}{(1 - \beta)} \quad (3)$$

would deviate somewhat from linearity, with  $r_d > r_s$ .<sup>15</sup> Examination of the data in Table II shows that bromine enhances intersystem crossing when bonded at a para position but is totally ineffective in this respect when bonded at a meta position. This striking positional dependence of radiationless heavy-atom induced spin-orbital coupling is to our knowledge unprecedented.<sup>20</sup> The data for *p*-bromostilbene can be fitted to eq 1 by assuming that the unactivated process competing with fluorescence is  $\phi_{is}^{1t} \simeq 0.33$  at 30°,<sup>2-4</sup> and using  $\phi_{is}^{1p} = 0.28$ . The smaller value of  $r_s$  for *p*-bromostilbene suggests that the same positional dependence applies to the  $^1T \rightarrow ^0S$  radiationless process, since  $r_s$  should be approximately related to the inverse of  $k_d$ .

The positional dependence is probably related to the difference between meta and para coefficients of the highest occupied and lowest unoccupied MO's of stilbene,  $c_m = 0.0791$  and  $c_p = 0.3138$  in the Hückel approximation. Spin-orbit coupling occurs *via* interaction with upper  $\sigma\pi^*$  and  $\pi\sigma^*$  singlet and triplet

(17) Details of interactions of stilbene triplets with quenchers are discussed in a recent paper.<sup>18</sup>

(18) J. Saltiel and B. Thomas, *J. Amer. Chem. Soc.*, **96**, 5560 (1974).

(19) A smaller  $K_s$  value would result if  $\tau^{1t}$  is decreased owing to competing intersystem crossing.

(20) The positional dependence observed in dibromonaphthorbornenes is not analogous since substitution was not directly on a carbon of the  $\pi$ -system.<sup>21</sup>

(21) N. J. Turro, G. Kavarnos, V. Fung, A. L. Lyons, Jr., and T. Cole, Jr., *J. Amer. Chem. Soc.*, **94**, 1392 (1972).

states.<sup>22,23</sup> Qualitatively, spin-orbit coupling matrix elements can be approximated by one-center terms and can be reduced to a center by center sum of the  $\pi$ -electron coefficients times the appropriate  $\sigma$  orbital coefficients.<sup>23</sup> If, as in the case of bromine substitution the center bearing bromine dominates then the expression describing the probability of spin-orbit coupling will be dominated by the appropriate  $\pi$  and  $\sigma$  MO coefficients at that center.<sup>22</sup> It is sensible, therefore that since the  $\pi$ -coefficient of stilbene is nearly zero at the meta position, substitution at that position should cause no enhancement in the rate constants for intersystem crossing.

**Acknowledgment.** This research was supported by National Science Foundation Grants GP-7941 and GP-24265.

(22) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 269.

(23) B. R. Henry, personal communication.

(24) (a) Fellow of the Alfred P. Sloan Foundation, 1971-1973; (b) National Institutes of Health Predoctoral Research Fellow, 1965-1969.

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### A Low Temperature Infrared Spectral Study of Iron(II) Dioxygen Complexes Derived from a "Picket Fence Porphyrin"

Sir:

The nature of the dioxygen-iron bond in  $HbO_2$  and  $MbO_2$ <sup>1</sup> is becoming clarified through studies of crystalline model compounds. Recently we reported the synthesis,<sup>2</sup> magnetic properties, Mössbauer spectra, and X-ray crystallographic structure<sup>3</sup> for a reversibly formed iron(II) dioxygen complex, **1**, derived from a "picket fence porphyrin" and an axial imidazole (Figure 1). This complex has an end-on angular  $FeO_2$  bond with  $Fe-O-O$  136 (4)°,  $Fe-O$  1.75 (0.02) Å,  $O-O$  1.25 (0.08) Å, and  $Fe-N$  (*N*-Me-Im) 2.07 (0.02) Å, in accord with Pauling's<sup>4</sup> suggested structure. There are two types of dioxygen coordination—one coplanar and the other normal to the axial base.<sup>3</sup>

Earlier we were unable to assign an ir or Raman band to  $\nu(O_2)$  at 300°K even with the aid of <sup>18</sup>O substitution.<sup>2</sup> We now report the low temperature (−175°) solid-state (KBr) ir spectrum of **1** which exhibits a remarkably sharp (half width 1  $cm^{-1}$ ), intense peak at 1385  $cm^{-1}$ . Typical data are displayed in Figure 2. The 1385- $cm^{-1}$  peak is not an artifact arising from the supporting medium, as it may also be observed at −175° in a fluorocarbon lube mull. Control experiments suggest that the 1385  $cm^{-1}$  feature represents  $\nu(O_2)$ . The peak is not observed, for example, upon replacement of dioxygen by other axial bases such as in

(1) Abbreviations used in this paper are: Hb, hemoglobin; Mb, myoglobin; *N*-MeIm, *N*-methylimidazole; *N*-*n*-BuIm, *N*-*n*-butylimidazole; THF, tetrahydrofuran.

(2) J. P. Collman, R. R. Gagne, T. R. Halbert, J. C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973).

(3) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Nat. Acad. Sci. U. S. A.*, **71**, 1326 (1974).

(4) (a) L. Pauling, *Stanford Med. Bull.*, **6**, 215 (1948); (b) *Nature*, (London), **203**, 182 (1964).

the analytically characterized **2** and **3**. Removal of O<sub>2</sub> from diamagnetic **1** under vacuum affords the high spin ( $\mu(25^\circ) = 4.9$  BM) five-coordinate **4**, which does not show the 1385-cm<sup>-1</sup> band, but readmitting O<sub>2</sub> totally restores the ir spectroscopic pattern of **1**. The same low temperature 1385-cm<sup>-1</sup> peak is found in **5**, which has *N-n*-BuIm as an axial base.<sup>5</sup> Isotopic substitution of **1** by treating with <sup>18</sup>O<sub>2</sub> (>90% enrichment) gave somewhat inconclusive results. The <sup>18</sup>O<sub>2</sub> complex **7** shows only a very weak low temperature 1385-cm<sup>-1</sup> band, which may be attributed to the small amount of <sup>16</sup>O<sub>2</sub> complex **1**. Apparently, the expected new peak is obscured by an intense porphyrin absorption at 1305 cm<sup>-1</sup> (simple harmonic oscillator calculation predicts  $\nu(^{18}\text{O}-^{16}\text{O})$  at 1306 cm<sup>-1</sup>). Similarly, a complex prepared from <sup>18</sup>O<sub>2</sub> (50% statistical enrichment) shows no new bands expected for <sup>18</sup>O-<sup>16</sup>O complexes. These are probably obscured by another intense porphyrin peak at 1345 cm<sup>-1</sup>.

Retrospective examination of the 1385-cm<sup>-1</sup> region in the room temperature ir spectrum of **1** reveals a weak, broad absorption which may have the same integrated intensity as the very sharp low temperature peak. The dramatic sharpening of this peak at lower temperatures may be accounted for by a rapid thermal equilibrium between several rotameric states which differ slightly in their O<sub>2</sub> stretching frequencies. Lowering the temperature apparently brings about an increase in the population of the most stable conformer. The effect may be related to structural features such as the two O<sub>2</sub> orientations, bumping interactions with the *tert*-butyl methyl groups, and a large thermal motion of the terminal oxygen—all evident from the X-ray diffraction data.

Comparison of the 1385-cm<sup>-1</sup>  $\nu(\text{O}_2)$  frequency with those of other O<sub>2</sub>-containing compounds<sup>6-9</sup> (Table I)

**Table I.** Comparison of Oxygen-Stretching Frequencies for Compounds with the O-O Moiety

	$\nu(\text{O}_2)$ , cm <sup>-1</sup>	Ref
O <sub>2</sub> (R)	1556	6
O <sub>2</sub> ( <sup>1</sup> $\Delta$ )	1483.5	7
<b>1</b>	1385	Present work
<b>5</b>	1385	Present work
KO <sub>2</sub>	1145	6
Co(acacen)(B)O <sub>2</sub>	1123-1140	9
(NH <sub>4</sub> )HO <sub>2</sub>	836	6
Na <sub>2</sub> O <sub>2</sub>	738	8

suggests that the dioxygen unit in **1** has substantial double bond character. Notably the frequency is  $\sim 250$  cm<sup>-1</sup> above  $\nu(\text{O}_2)$  in KO<sub>2</sub><sup>6</sup> as well as in several dioxygen-cobalt complexes thought to contain coordinated O<sub>2</sub><sup>9,10</sup>. In fact, our 1385-cm<sup>-1</sup> band lies only  $\sim 100$  cm<sup>-1</sup> below  $\nu(\text{O}_2)(^1\Delta)$ —a reasonable lowering if there is moderate

(5) We find a similar peak at  $-175^\circ$  in the dioxygen complex **6** which is paramagnetic at  $25^\circ$  and has an axial THF ligand: J. P. Collman, R. R. Gagne, and C. A. Reed, *J. Amer. Chem. Soc.*, **96**, 2629 (1974). The low temperature magnetic properties of **6** have not been fully clarified but we are surprised by the insensitivity of the  $\nu(\text{O}_2)$  frequency to changes in the axial ligand.

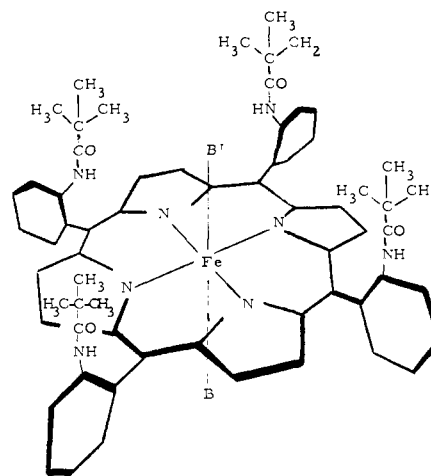
(6) H. Siebert, "Schwingungs spektroskopie in der Anorganischen Chemie," Springer Verlag, Berlin, 1966, pp 40, 51.

(7) L. Herzberg and G. Herzberg, *Astrophys. J.*, **105**, 353 (1947).

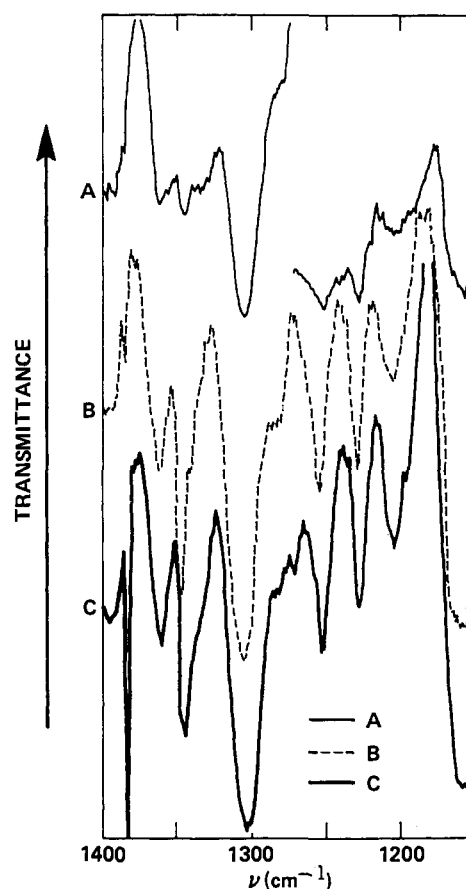
(8) J. C. Evans, *Chem. Commun.*, 682 (1969).

(9) A. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970).

(10) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 61 (1970).



**Figure 1.** Fe complexes of *meso*-tetra( $\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamide-phenyl)porphyrin: **1**, B = *N*-MeIm, B' = O<sub>2</sub>; **2**, B = *N*-MeIm, B' = *N*-MeIm; **3**, B = *N-n*-BuIm, B' = *N-n*-BuIm; **4**, B = *N*-MeIm, B' = Vacant; **5**, B = *N-n*-BuIm, B' = O<sub>2</sub>; **6**, B = THF, B' = O<sub>2</sub>; **7**, B = *N*-MeIm, B' = <sup>18</sup>O<sub>2</sub>(90% <sup>18</sup>O).



**Figure 2.** Infrared spectra of (A) **4** at  $-175^\circ$ , (B) **7** at  $-175^\circ$ , and (C) **1** at  $-175^\circ$ .

$d\pi-p\pi$  back-bonding. Both ir and X-ray<sup>3</sup> data, therefore, are entirely consistent with the formulation of the diamagnetic model MbO<sub>2</sub> complexes, **1** and **5**, as involving low-spin Fe(II) and coordinated singlet oxygen. That our 1385-cm<sup>-1</sup> band is 280 cm<sup>-1</sup> higher than the value of  $\nu(\text{O}_2)$  recently reported by Caughey<sup>11</sup> for HbO<sub>2</sub>

(11) C. H. Barlow, J. C. Maxwell, W. J. Wallace, and W. S. Caughey *Biochem. Biophys. Res. Commun.*, **55**, 91 (1973).

is disturbing. Hydrogen bonding of the terminal oxygen with the distal imidazole in HbO<sub>2</sub> might afford some lowering of  $\nu(\text{O}_2)$ , but surely not by 280 cm<sup>-1</sup>. In view of this large difference and the low resolution indicated in Caughy's published spectra,<sup>11</sup> we intend to reinvestigate the ir spectra of Hb<sup>16</sup>O<sub>2</sub> and Hb<sup>18</sup>O<sub>2</sub> at low temperatures.

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### $\gamma$ -Halotiglates. I. A Simple, Efficient Position-Specific Annulation of Unsymmetrically Substituted Cyclohexanones

Sir:

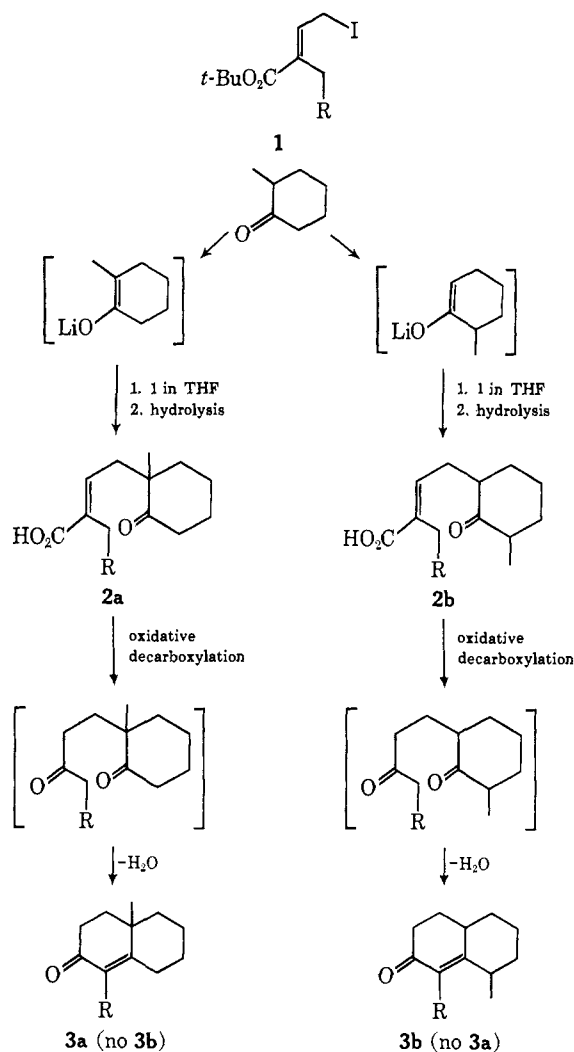
For some time,<sup>1</sup> we have been seeking a superior method of introducing a 3'-ketoalkyl substituent specifically at either the  $\alpha$  or  $\alpha'$  position of an unsymmetrically substituted ketone. The desired product, a structurally specific  $\delta$ -diketone is the requisite intermediate for a *position-specific* "Robinson annelation"<sup>2</sup> of the starting ketone. We now wish to report a new and viable solution to the problem of position-specific annelation. We have found that  $\gamma$ -iodotiglate esters,

(1) (a) Preliminary reports of our continuing work with  $\gamma$ -halotiglates were made in the following oral communications: 159th National Meeting of the American Chemical Society, Houston, Texas (Feb 1970), Abstract ORGN 117; 161st National Meeting of the American Chemical Society, Los Angeles, Calif. (March 1971), Abstract ORGN 030, ORGN 138; Second International Symposium on Synthesis in Organic Chemistry, Cambridge, England (July 1971). (b)  $\gamma$ -Iodotiglates, **1**, were prepared from chloroacetaldehyde and  $\alpha$ -carbalkoxyalkylidene-triphenylphosphoranes, followed by iodide exchange (in acetone); details will be described in P. L. Stotter and K. A. Hill, " $\gamma$ -Halotiglates. II. A High Yield Stereoselective Preparation," manuscript submitted for publication.

(2) Annelations proceeding *via* introduction of a 3'-ketoalkyl substituent  $\alpha$  to an existing ketone and subsequent cyclodehydration of the resulting  $\delta$ -diketone intermediate may be classed in two categories depending on the method of introducing the 3'-ketoalkyl substituent. For examples of introduction of 3'-ketoalkyl substituents by Michael or Michael-type addition to electrophilic olefins see (a) E. C. DuFeu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937); (b) G. Stork, A. Brizzolara, H. Landesman, J. Szmuzkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963); (c) J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964), and references cited therein. (d) S. Danishefsky and R. Cavanaugh, *J. Amer. Chem. Soc.*, **90**, 520 (1968), and references cited therein. (e) S. Danishefsky and B. H. Migdalof, *ibid.*, **91**, 2806 (1969). (f) C. H. Heathcock, J. E. Ellis, J. E. McMurry, and A. Coppolino, *Tetrahedron Lett.*, 4995 (1971). (g) G. Stork and B. Ganem, *J. Amer. Chem. Soc.*, **95**, 6152 (1973). For examples of introduction of 3'-ketoalkyl substituents by alkylations using "masked ketoalkyl" alkylating agents see (h) O. Wichterle, J. Prochazka, and J. Hoffmann, *Collect. Czech. Chem. Commun.*, **13**, 300 (1948); (i) G. Stork, S. Danishefsky, and M. Ohashi, *J. Amer. Chem. Soc.*, **89**, 5459 (1967); G. Stork and J. E. McMurry, *ibid.*, **89**, 5461, 5463, 5464 (1967); (j) D. Caine and F. N. Tuller, *J. Org. Chem.*, **34**, 222 (1969). For general review articles, see (k) J. H. Brewster and E. L. Eliel, *Org. React.*, **7**, 99 (1953); E. D. Bergmann, D. Ginsberg, and R. Pappo, *ibid.*, **10**, 179 (1959); I. V. Torgov, *Pure Appl. Chem.*, **6**, 525 (1963); G. Stork, *ibid.*, **9**, 131 (1964); L. Velluz, J. Valls, and G. Nominé, *Angew. Chem., Int. Ed. Engl.*, **4**, 181 (1965); G. Stork, *Horm. Steroids, Proc. Int. Congr. 3rd*, 101 (1970) (*Excerpta Med. Found. Int. Congr. Ser.*, No. 219).

**1**,<sup>1b</sup> function well as "masked ketoalkyl" alkylating agents for lithium enolates (specifically generated<sup>3,4</sup> under aprotic conditions) and for enamines;<sup>2b</sup> the alkylated products are easily isolated as carboxylic acids (e.g., **2** in Scheme I) in good to excellent yields. Oxida-

Scheme I



tive decarboxylation readily degrades the side-chain  $\alpha,\beta$ -unsaturated acid to the requisite 3'-ketoalkyl functionality, which can directly cyclize under basic catalysis to a single structural isomer of the desired annelated product (e.g., enone **3**). To illustrate the overall procedure, as outlined in Scheme I, we have position-specifically annelated 2-methylcyclohexanone producing either **3a** or **3b** in greater than 70% overall yield, uncontaminated by the alternative structural isomer.

We chose to investigate  $\gamma$ -halotiglates, **1**, as alkylating agents in this scheme for the following reasons. (a) As allylic halides, they offered the promise of *high reactivity* in the alkylation of structurally specific enolates and enamines (thus reducing the probability

(3) (a) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963); (b) H. O. House and B. M. Trost, *ibid.*, **30**, 2502 (1965), and references cited therein.

(4) (a) G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, **90**, 4462, 4464 (1968); (b) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969); H. O. House, M. Gall, and H. D. Olmstead, *ibid.*, **36**, 2361 (1971).