

under conditions of strict air exclusion. Qualitative rates for the conversion of Ia to II and III (approximate  $t_{1/2}$  in parentheses) decrease in the order: oxidized  $(\text{Ph}_3\text{P})_3\text{RhCl}$  (2 days) > oxidized  $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$  (5 days) >  $(\text{PPh}_3)_3\text{RhCl}$  (14 days) >  $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$  (30 days).<sup>12b</sup>

One possible explanation of this oxygen effect is that  $[(\text{PPh}_3)_2\text{RhCl}]_2$  is formed by oxidation of one of the  $\text{Ph}_3\text{P}$  ligands of  $(\text{PPh}_3)_3\text{RhCl}$  to triphenylphosphine oxide<sup>13b</sup> with the dimeric complex being catalytically active. This has been ruled out by synthesis of  $[(\text{PPh}_3)_2\text{RhCl}]_2$ <sup>14</sup> and demonstrating that it is unreactive toward Ia (in  $\text{CHCl}_3$  solution) over a period of 72 hr. Upon bubbling  $\text{O}_2$  through the solution, ring opening to give II and III was initiated, with  $t_{1/2} < 48$  hr.

It would thus appear that the  $\text{O}_2$ -containing complex is the actual catalyst precursor. The report that  $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$  also forms an  $\text{O}_2$  complex<sup>15</sup> suggests that the mode of activation may be similar to that of the triphosphine complex. We wish to emphasize that the actual catalytic species in these systems is very much in doubt and we make no claims that the  $\text{O}_2$  complexes are in themselves catalytically active—only that they more accurately describe the catalyst precursors. Our results demonstrate that great caution should be exercised in interpreting results based on these and related catalyst systems unless the “ $\text{O}_2$ -history” of the catalyst is well-defined.<sup>16</sup>

The nature and stereochemistry of the substituents at  $\text{C}_6$  exert considerable influence on the rate of the ring opening process. Using the oxidized  $(\text{PPh}_3)_3\text{RhCl}$  catalyst, Ib opens very slowly ( $t_{1/2} \cong 9$  days)<sup>12b</sup> to give III in 95% yield, while Ic is converted rapidly ( $t_{1/2} \cong 12$  hr)<sup>12b</sup> to 5-methyl-5-carbomethoxy-1,3-cyclohexadiene.<sup>19, 20</sup> Under identical conditions Id is recovered unchanged after 10–12 days. The reasons for these rate differences are not obvious, apparently reflecting a delicate balance of steric and electronic influences on the tendency of the  $\text{C}_1\text{—C}_5$   $\sigma$  bond to open in the presence of the catalyst.

In view of the uncertainty of the catalytically active species, mechanistic speculation at this time would seem premature. However, a rhodium–olefin interaction appears to be an important part of the ring-opening process since the dihydro derivatives of Ia and Ic are completely unreactive even at 55–60° over periods of several weeks.

Further studies designed to elucidate the nature of the active catalysts and influences of ring size and nature and stereochemistry of substituents on these reactions are in progress.

**Acknowledgments.** The authors express their thanks to Professor R. E. K. Winter for several valuable dis-

(14) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Amer. Chem. Soc.*, **96**, 2762 (1974).

(15) C. T. Mortimer and S. J. Ashcroft, *Inorg. Chem.*, **10**, 1326 (1971).

(16) Other workers have shown that hydrogenation and double-bond isomerization rates are similarly affected by the presence of oxygen.<sup>17, 18</sup>

(17) H. van Bekkum, F. van Rantwijk, and T. van de Putte, *Tetrahedron Lett.*, **1** (1969).

(18) R. L. Augustine and J. F. Van Peppen, *Chem. Commun.*, 497, 571 (1970).

(19) The diene product was identified by nmr spectroscopy and by comparison of uv and ir data with those previously reported: J. Wolinsky, R. Novak, and R. Vasileff, *J. Org. Chem.*, **29**, 3596 (1964).

(20) The oxygen effect is also dramatic for this system. Argon-purged solutions of Ic and  $(\text{PPh}_3)_3\text{RhCl}$  exhibit  $t_{1/2} \cong 5$  days.

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## An External Heavy Atom Effect on Excited State Quenching and Exciplex Decay

Sir:

Photoisomerization of olefins related to stilbene has been the subject of extensive investigation.<sup>1</sup> In various compounds both singlets and triplets can isomerize,<sup>1–4</sup> and in several cases induced olefin photoisomerization has proved to be a useful mechanistic probe in determining excited state decay channels.<sup>5–8</sup> An area of interest to both photochemists and spectroscopists has been the induction of singlet–triplet intersystem crossing by external and internal heavy atoms.<sup>9–11</sup> It has recently been shown that the stilbene system can be strongly perturbed by internal halogen atoms.<sup>1, 3, 12, 13</sup> In the present paper we report an investigation of the external heavy atom effect in some stilbene-like olefins using cis–trans isomerization as a probe.

The stilbene-like olefins used in the present study are the dimethylfluoroborates of *trans*-1,2-bis(3-pyridyl)ethylene (**1**) and *trans*-1,2-bis(4-pyridyl)ethylene (**2**). The possibility for investigating induced intersystem crossing pathways was suggested by the finding of contrasting photochemistry for these compounds in the presence and absence of oxygen. Irradiation of degassed acetonitrile solutions of **2** led to no isomerization, and only a small amount ( $\phi \ll 0.01$ ) of as yet unidentified product (possibly an adduct) could be detected. In contrast an air equilibrated solution showed very rapid ( $\phi \sim 0.4$ ) isomerization of **2** to the cis isomer with subsequent cyclization to the phenanthrene derivative at a slightly slower rate. Similar results were obtained with **1** although a small amount of trans  $\rightarrow$  cis isomerization ( $\phi = 0.13$ ) occurred even in degassed solutions.

(1) For a recent review see, J. Saltiel, J. D'Agostino, E. D. Megarity, M. Wrighton, and O. C. Zafriou, *Org. Photochem.*, **3**, 1 (1973).

(2) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 446, 451 (1974).

(3) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 3907 (1968), and earlier references therein.

(4) G. Fischer, K. A. Muszkat, and E. Fischer, *Isr. J. Chem.*, **6**, 965 (1968).

(5) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(6) I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).

(7) R. A. Caldwell and R. P. Gajewski, *J. Amer. Chem. Soc.*, **93**, 532 (1971).

(8) I. E. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, **94**, 3859 (1972).

(9) N. Christodouleas and S. P. McGlynn, *J. Chem. Phys.*, **40**, 166 (1964); S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodouleas, *J. Phys. Chem.*, **66**, 2499 (1962).

(10) D. O. Cowan and R. L. E. Drisko, *J. Amer. Chem. Soc.*, **92**, 6281 (1970).

(11) R. F. Fleming, F. H. Quina, and G. S. Hammond, *J. Amer. Chem. Soc.*, submitted.

(12) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962); K. Krüger and E. Lippert, *Z. Phys. Chem. (Frankfurt am Main)*, **66**, 393 (1969).

(13) J. Saltiel, D. W. L. Chang, and E. D. Megarity, unpublished manuscript. We thank Professor Saltiel for a preprint of this paper.

The most consistent explanation appeared to be that oxygen was inducing intersystem crossing to the triplet<sup>14</sup> and that the observed isomerization<sup>17</sup> then occurred from triplet states of **1** and **2**. Since the difference between singlet and triplet state isomerization was so striking for **1** and **2**, it appeared attractive to use these olefins as probes to investigate the external heavy atom effect with a variety of organic halogen compounds.

Direct irradiation of **1** in degassed acetonitrile solutions containing varying amounts of different organic bromine compounds resulted in fluorescence quenching with concurrent trans  $\rightarrow$  cis isomerization. Similar Stern–Volmer kinetics were observed both for fluorescence quenching and trans  $\rightarrow$  cis isomerization, after accounting for the inherent isomerization of **1**. In contrast aliphatic chlorine compounds such as chloroform, carbon tetrachloride, and ethylene chloride neither quenched fluorescence of **1** nor induced its isomerization. Table I compares results obtained with **1** using

**Table I.** Fluorescence Quenching and Induced Isomerization of *trans*-1,2-Bis(*N*-methyl-3-pyridyl)ethylene Fluoroborate

Quencher	$(k_q\tau)_{fluor}^a$	$(k_q\tau)_{rxn}^b$	Slope	Intercept	$\phi_{t\rightarrow c}^{max\ c}$
Benzene <sup>d</sup>	19 $\pm$ 1	0			
Chlorobenzene	23 $\pm$ 1	29	0.082	2.3 <sup>c</sup>	<i>e</i>
Bromobenzene	39 $\pm$ 1	38	0.078	3.0	0.33 $\pm$ 0.07
Iodobenzene	70 $\pm$ 5	104	0.030	3.1	0.32 $\pm$ 0.08
2-Bromoethanol	7.8 $\pm$ 0.1	6.1	0.57	3.5	0.29 $\pm$ 0.03
Bromoethane	33 $\pm$ 2	36	0.093	3.3	0.30 $\pm$ 0.03
1,2-Dibromoethane	2.6 $\pm$ 0.2	3.1	0.68	2.1	0.48 $\pm$ 0.08
Ethanol	14 $\pm$ 0	0			

<sup>a</sup>  $(k_q\tau)_{fluor}$  = slope of  $\phi_f/\phi_i$  vs. molar concentration of quencher. The lifetime,  $\tau$ , of **1** is 3.8  $\pm$  0.1 nsec (by single photon counting). <sup>b</sup>  $(k_q\tau)_{rxn}$  = intercept/slope of  $1/\phi_{t\rightarrow c}$  vs.  $1/concn.$  <sup>c</sup> Calculated as  $1/intercept$ , i.e., the reaction quantum yield at infinite quencher concentration. <sup>d</sup> Benzene showed no enhanced isomerization and only a small amount of an unknown reaction. <sup>e</sup> Although some isomerization is observed another unidentified product is also detected.

several halogen-containing compounds. The bromoalkanes, bromoethane and 1,2-dibromoethane, produce limiting isomerization yields of 0.30 and 0.48 respectively; in each case trans  $\rightarrow$  cis isomerization is the only detectable photoreaction. Comparison of the value of 0.6 for the fraction of cis isomer in the high-energy sensitized photostationary state with these limiting values enables an estimate that quenching by the bromides results in formation of the reactive triplet with minimum efficiencies of 0.5–0.8. Since good Stern–Volmer plots were obtained for the isomerization efficiencies up to the highest concentrations used in these studies, the lower-than-unity limiting triplet yields cannot be accounted for by a second enhanced intersystem crossing (eq 1) unless triplet quenching occurs



without affecting the cis/trans decay ratio. Two possibilities for the lower values are (a) inefficiency in the

(14) Other workers<sup>15,16</sup> have recently observed related, but generally less dramatic, effects of oxygen with other diarylethylenes.

(15) P. Bortulos and G. Galiazzo, in press, cited in ref 16.

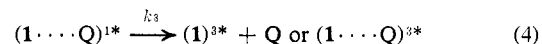
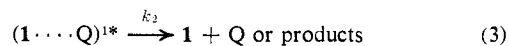
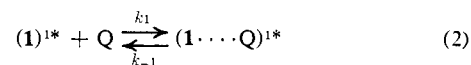
(16) G. Fischer and E. Fischer, *Mol. Photochem.*, in press.

(17) Investigations with sensitizers such as Michler's ketone or benzophenone result in cis–trans isomerization as the only permanent photosensitized reaction. For **1**,  $\phi_{t\rightarrow c}^{sens} = 0.4$  while **2** gives a much lower value.

isomerization process and (b) a quenching process that produces triplets of **1** with lower-than-unit efficiency. It is difficult to determine if the former occurs since photosensitizers promote isomerization of **1** and **2** with varying efficiencies,<sup>17</sup> probably due to competing electron transfer reactions. The second possibility appears somewhat less attractive since all quenchers used to date give more or less similar limiting values.

An external heavy atom effect was also observed with **2**. The behavior here, however, was noticeably different from that of **1**. Although fluorescence quenching by bromoethane and 1,2-dibromoethane followed ordinary Stern–Volmer kinetics, the isomerization quantum yield varied sharply from that expected. At very low concentrations of quencher ( $\approx 10^{-3}$  M) where no significant fluorescence quenching was observed, quantum yields of induced isomerization were in the range of 0.2–0.4. Furthermore, no variation of  $\phi_{t\rightarrow c}$  was observed upon increasing the concentration of heavy atom quencher from 0.012 to 2.3 M. These results can be explained by the formation of a long-lived exciplex between **2** and acetonitrile.<sup>18</sup> This exciplex would then interact with low concentrations of heavy atom quencher and isomerize, thus apparently separating the isomerization kinetically from fluorescence quenching. A mechanism involving exciplex formation between **2**\* and solvent acetonitrile is reinforced by the observation that **1** fluoresces at least ten times more strongly ( $\phi_f \sim 0.8$ ) than **2** ( $\phi_f \sim 0.05$ ) in acetonitrile.

The effect of several aromatic halogen compounds and 2-bromoethanol on fluorescence and isomerization of **1** was also investigated. Since it has been previously shown that the non-halogen containing analogs of these compounds efficiently quench fluorescence of **1** by paths that do not result in triplet formation,<sup>20,21</sup> it appeared of interest to determine whether the introduction of a heavy atom into such quenchers could influence decay channels or quenching rates. As data in Table I indicate, iodobenzene, bromobenzene, and 2-bromoethanol all quench the fluorescence of **1** while concurrently inducing trans  $\rightarrow$  cis isomerization. The results are consistent with the mechanism outlined in eq 2–4.<sup>22</sup>



(18) Such complexes have been observed between small polar molecules and aromatics in other cases.<sup>19</sup>

(19) E. A. Chandross, *Proceedings of the International Exciplex Conference*, 1974, in press.

(20) J. W. Happ, M. T. McCall, and D. G. Whitten, *J. Amer. Chem. Soc.*, **93**, 5496 (1971).

(21) D. G. Whitten, J. W. Happ, G. L. B. Carlson, and M. T. McCall, *J. Amer. Chem. Soc.*, **92**, 3499 (1970).

(22) Steady-state kinetics lead to the limiting values of  $k_q^{obsd}$  given by eq 5–7. Since  $k_q^{obsd}$  for bromobenzene is larger than that for

$$k_q^{obsd} = \frac{k_1(k_2 + k_3)}{k_{-1} + (k_2 + k_3)} \quad (5)$$

$$\text{where } (k_2 + k_3) \gg k_{-1}, k_q = k_1 \quad (6)$$

$$\text{where } (k_2 + k_3) \ll k_{-1}, k_q = K_1(k_2 + k_3) \quad (7)$$

benzene only by a factor of ca. 2 and  $k_q^{obsd}$  for 2-bromoethanol is substantially smaller than that for ethanol, it appears either that eq 6 applies or that, if eq 7 applies, increases in the second term are balanced by decreases in  $K_1$ . However, since values of  $k_q^{obsd}$  are all within an order of magnitude of the diffusion-controlled limit for the aromatic quenchers, eq 6 must apply in these cases.

The limiting yield of induced intersystem crossing is  $\phi_{isc}^{lim} = k_3/(k_2 + k_3)$ . For iodobenzene, bromobenzene, and 2-bromoethanol the limiting isomerization yields are nearly the same as those for bromoalkanes, indicating that the exciplex formed in eq 2 is almost entirely diverted away from the normal path (eq 3) to triplet formation (eq 4). It appears significant that a prominent external heavy atom effect is observed for such a wide variety of quenchers. These results also emphasize the distinction between exciplex formation and decay processes and indicate the role substituents can play in introducing alternate channels for radiationless decay.<sup>2,3</sup>

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### Electron Paramagnetic Resonance Study of Conformation in $\beta$ -Haloalkyl Radicals

Sir:

We wish to report the preparation and observation by epr of the  $\beta$ -chloro- and  $\beta$ -bromo-*tert*-butyl radicals,  $\text{ClCH}_2\dot{\text{C}}(\text{CH}_3)_2$  (I) and  $\text{BrCH}_2\dot{\text{C}}(\text{CH}_3)_2$  (II), by x-irradiation of isobutyl chloride and isobutyl bromide, respectively, in a matrix of adamantane-*d*<sub>16</sub> at 77°K. Alkyl radicals with  $\beta$ -chlorine substituents are known to prefer an eclipsed conformation (1) in solution,<sup>1,2</sup> and it has been suggested<sup>2</sup> that bromine would have the same effect on radical structure, but no well-characterized  $\beta$ -bromo radicals have previously been reported. In fact, we find that whereas radical I does prefer the eclipsed conformation 1 in an adamantane matrix as well as in solution,<sup>1</sup> radical II prefers the staggered conformation 2, and furthermore the ultimate fates of the two radicals are quite different upon warming the sample.

The second-derivative epr spectrum of radical I is shown in Figure 1, together with a computer simulation based on the parameters of Table I. The chlorine hfs is smaller and the *g* value is larger in adamantane than in solution.<sup>1</sup> The positive temperature dependence of

Table I. Epr Parameters of  $\beta$ -Halogenated *tert*-Butyl Radicals

Radical	$\text{ClCH}_2\dot{\text{C}}(\text{CH}_3)_2$	$\text{BrCH}_2\dot{\text{C}}(\text{CH}_3)_2$
Temp	-58°	-71°
$a_{\text{X}}$ , G	19.5 ( <sup>35</sup> Cl)	6.7 ( <sup>81</sup> Br)
	16.2 ( <sup>37</sup> Cl)	6.3 ( <sup>79</sup> Br)
$a_{\text{H}}(\text{CH}_2)$ , G	6.3	21.4, 42.7 (av 32.0)
$a_{\text{H}}(\text{CH}_3)$ , G	21.1	21.4
<i>g</i>	2.0044	2.0010

(1) K. S. Chen, I. H. Elson, and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 5341 (1973).

(2) (a) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6485 (1972). The tentative identification of the 2-bromoallyl radical ( $a_{\text{Br}} = 1.35$  G,  $g = 2.00181$ ) in this paper is supported by the similar values found for the  $\beta$ -bromo-*tert*-butyl radical. (b) It has been stated that for radicals of the type  $\text{R}_n\text{MCH}_2\dot{\text{C}}\text{H}_2$  where M is from the first row of the periodic table the preferred geometry will be staggered and where M is from rows 2, 3, or 4 the preferred geometry will be eclipsed. D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973).

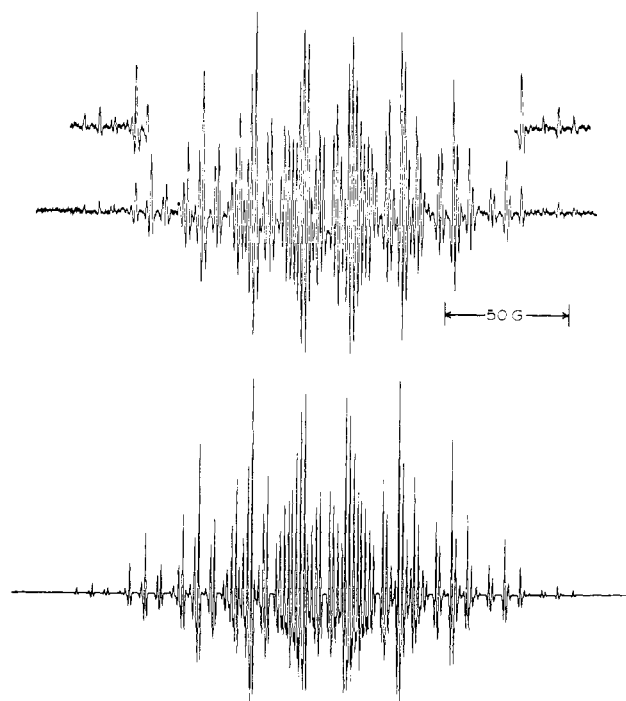
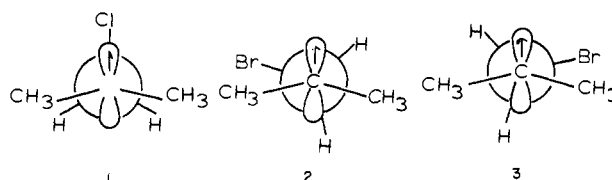


Figure 1. Second-derivative epr spectrum of the  $\text{ClCH}_2\dot{\text{C}}(\text{CH}_3)_2$  radical in  $\text{C}_{10}\text{D}_{16}$  at  $-58^\circ$  (top) compared with its computer simulation (bottom): line width = 0.60 G, relative abundances of <sup>35</sup>Cl: <sup>37</sup>Cl = 3:1.

the methyl proton hfs, like that of *tert*-butyl radical,<sup>3</sup> indicates a nonplanar equilibrium radical site geometry while the negative temperature dependence of the chlorine hfs demonstrates a less favorable overlap of the chlorine with the unpaired electron orbital as the conformation is changed from the equilibrium position. The absence of line width alternation and the small size and equivalence of the methyl proton hfs indicates that the chlorine prefers to be eclipsed with the unpaired electron orbital.

The spectrum of radical II can best be fitted by computer simulation with the assumption of six equivalent methyl protons, one methylene proton with hfs accidentally equal to the methyl proton hfs, one methylene proton with hfs twice this value, and resolved <sup>79</sup>Br and <sup>81</sup>Br hfs in the ratio of their natural abundances. The broadened lines to be expected for the two methylene protons in the region of intermediate rate of exchange are present in the spectrum; however, the radical reacts irreversibly with the matrix before the high temperature limit (which would make the methylene protons equivalent with hfs equal to 32 G) is reached. The parameters are given in Table I and the spectrum together with the computer simulation is shown in Figure 2. The assignment of the methylene proton hfs was checked by preparation of the deuterated species  $\text{BrCD}_2\dot{\text{C}}(\text{CH}_3)_2$ .



(3) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972); D. E. Wood and R. F. Sprecher, *Mol. Phys.*, **26**, 1311 (1973).