

synthetic intermediate, **4**, which is the subject of considerable discussion and the object of extensive biochemical experimentation, remains uncharacterized from natural or synthetic sources.

**Acknowledgments.** This research was supported first by Public Health Service Grant CA-12107-13 and then by A. I. 13939-01. Auxiliary support from the Merck and CIBA-GEIGY Companies are gratefully acknowledged. The 250-MHz NMR spectra were measured on facilities supported by RR-00297-08. The possibility of utilizing  $\beta$ -sulfinyl- $\alpha,\beta$ -unsaturated ketones was also investigated by Professor Theodore Cohen and co-workers at the University of Pittsburgh. These studies, with other dienes, preceded our work described above. We thank Professor Cohen for several valuable discussions on this subject.

## References and Notes

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- (7) The formation of an unsaturated ketone by the elimination of "PhSOH" from a  $\beta$ -phenylsulfinyl ketone under conditions of chloroform reflux was described by B. M. Trost and R. A. Kunz, *J. Org. Chem.*, **39**, 2648 (1974). In the case at hand, it appears that substantial elimination is occurring under the conditions of the cycloaddition (cf. **13**  $\rightarrow$  **13a**). Unfortunately, compounds of the type **13a** are not readily separated in pure form from excess diene, **9**, and its decomposition products. Hence we are unable to define with precision whether any of the PhSOH elimination is occurring under the conditions of unmasking intermediate **11**. We note that in all the reactions described herein, no structure corresponding to **11** was, in fact, detected. Hence, it may be the case that all of the elimination is taking place at the stage corresponding to **13**  $\rightarrow$  **13a**.
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- (10) The sulfoxides were prepared from the corresponding sulfides by oxidation with sodium metaperiodate. The sulfides were prepared from the  $\beta$ -dicarbonyl compounds using the methodology of Ireland and Marshall. The stereochemistry of the sulfoxides is not known with certainty.
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- (15) The structure of this compound was established by (a) infrared, NMR, and mass spectra; (b) its combustion analyses within 0.4% of theory.
- (16) The diethyl ester, diethyl acetal was described by Plieninger<sup>5</sup> as an oil.
- (17) Plieninger<sup>5</sup> had recognized the formation of the "ketone cleavage" product **34** from the sodium borohydride reduction. However, since no NMR spectra were measured, the formation of the tetrahydro allylic alcohols **32** and **33** was missed. In our work these substances were not separated from one another.
- (18) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **42**, 1197 (1977).
- (19) The structures of the synthetic dienols **30** and **31** were rigorously established by their conversion to their tetrahydro acetates. These are in turn readily differentiated through 250-MHz NMR spectroscopy. The details will be published in the full paper.
- (20) The  $R_f$  values were determined on commercial (E. M. Merck) precoated silica gel (60F-254 TLC) plates.
- (21) Chemical shifts are reported in parts per million relative to internal 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt hydrate (Aldrich).
- (22) The allylic couplings of the C-3 vinylic proton with the C-1 methine proton are clearly seen in the signals of the former. In the methine signal itself, this appears as line broadening and is not directly measured owing to additional broadening due to the hydroxyl group.
- (23) Eschenmoser and co-workers have effected decarboxylation-dehydration of 4-carboxycyclohex-2-en-1-ols through the use of amide acetals. This elegant reaction, leading to 1,3-cyclohexadienes, is much slower than the direct process described here leading to an aromatic ring. The effect of stereochemistry on the Eschenmoser process has also not been determined; see A. Ruttiman, A. Wick= AND A. Eschenmoser, *Helv. Chim. Acta*, **58**, 1450 (1975).

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Received April 28, 1977

## Differences in the Intrinsic Barriers between Ground- and Excited-State Electron-Transfer Reactions from Spectroscopic Franck-Condon Parameters<sup>1</sup>

Sir:

There has been a great deal of recent interest in the electron-transfer reactions of transition metal excited states.<sup>2-4</sup> Much of this interest derives from the possibilities of utilizing the large energy differences between ground- and excited-state species in photovoltaic cells<sup>5</sup> or to decompose water.<sup>6,7</sup> These excited-state reactions are also becoming important in the study of highly exergonic electron-transfer reactions in which renewed interest has been stimulated by quantum corrections to the earlier approaches.<sup>8-11</sup> Both the practical and the theoretical interest in such systems depends on the magnitudes of the intrinsic or reorganizational barriers to electron transfer. An important point which seems to have escaped the notice of investigators in this area is that difference between the intrinsic barriers for ground-state and excited-state electron transfer processes is closely related to simple spectroscopic parameters.

The best example of these differences in excited-state and ground-state properties is provided by the Cr(bpy)<sub>3</sub><sup>3+,2+</sup> couple. Ground-state electron-transfer reactions of Cr(bpy)<sub>3</sub><sup>2+</sup> tend to be very rapid; e.g., the Cr(bpy)<sub>3</sub><sup>2+</sup> reduction of Fe<sup>3+</sup> and Ru(bpy)<sub>3</sub><sup>3+</sup> have rate constants of  $7.3 \times 10^8$  and  $2.6 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, respectively, for reactions which have free energy changes of  $\Delta G^\circ = -24$  and  $-35$  kcal mol<sup>-1</sup>.<sup>4</sup> These observations have been used to estimate a "self-exchange" rate constant of  $k_{11} \approx 4 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup><sup>2</sup> for the Cr(bpy)<sub>3</sub><sup>3+,2+</sup> couple using the Marcus relation<sup>8</sup>

$$k_{12} = (K_{11}k_{22}K_{12}f_{12})^{1/2} \quad (1)$$

$$\log f_{12} = (\log K_{12})^2 / [4 \log (k_{11}k_{22}/Z^2)]$$

$$Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$$

In contrast the electron transfer quenching reactions of the <sup>2</sup>E excited state of Cr(bpy)<sub>3</sub><sup>3+</sup> have been found to be approximately an order of magnitude slower with comparable reagents. Thus, for <sup>2</sup>E oxidations of Fe<sup>2+</sup>, Ru(bpy)<sub>3</sub><sup>2+</sup>, and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, the rate constants are  $2.8 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> (in 0.05 M H<sub>2</sub>SO<sub>4</sub>; a value of  $4.1 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> has been found when  $\mu = 1^4$ ),  $4 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> ( $\mu = 0.2$ ),<sup>4</sup> and  $5.9 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> (in 0.05 M H<sub>2</sub>SO<sub>4</sub>), respectively; the respective free energy changes are  $-16$ ,  $-4$ , and  $-32$  kcal mol<sup>-1</sup>. The value of  $k_{11} \approx 4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for the Ru(bpy)<sub>3</sub><sup>3+,2+</sup> couple (estimated by Sutin and co-workers),<sup>2b,c</sup> and eq 1 implies a "self-exchange" rate constant of about  $3 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup> for the (<sup>2</sup>E)Cr(bpy)<sub>3</sub><sup>3+</sup>/Cr(bpy)<sub>3</sub><sup>2+</sup> couple; the value of  $k_{11} \approx 1.6 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> reported recently by Meyer and co-workers<sup>3d</sup> results in a slightly larger value for this rate constant.<sup>12</sup>

That electron-transfer reactions are slower for excited-state than ground-state species implies that a change in bond lengths, angles, etc., occurs in the excited-state reactions (or that these reactions differ in "adiabaticity").<sup>12</sup> These differences in the ground-state and excited-state internuclear coordinates (Franck-Condon parameters) are also manifested in a Stokes shift of the <sup>2</sup>E  $\rightarrow$  <sup>4</sup>A phosphorescence compared to the <sup>4</sup>A  $\rightarrow$  <sup>2</sup>E absorption. The <sup>4</sup>A  $\rightarrow$  <sup>2</sup>E absorption of Cr(bpy)<sub>3</sub><sup>3+</sup> is obscured by a relatively intense <sup>4</sup>A  $\rightarrow$  <sup>4</sup>T band. However, assignment of this transition to a shoulder at  $\sim 600$  nm would correspond to a Stokes shift of  $\sim 0.15 \mu\text{m}^{-1}$ , a reasonably typical value for chromium(III) complexes.<sup>13</sup> This suggests an average difference of  $\sim 0.08 \mu\text{m}^{-1}$  ( $\sim 2.3$  kcal mol<sup>-1</sup>) between the (<sup>2</sup>E)Cr(bpy)<sub>3</sub><sup>3+</sup> excited state and the (<sup>4</sup>A)Cr(bpy)<sub>3</sub><sup>3+</sup> ground-state Franck-Condon parameters. Since the effective reorganizational barriers for the self-ex-

change reaction correspond to the achievement of nuclear configurations intermediate between those of chromium(III) and chromium(II), between half and all of the differences in  ${}^2E$  and  ${}^4A$  Franck-Condon parameters would contribute to the difference in reorganizational barriers of excited-state and ground-state electron-transfer reactions.<sup>14,15</sup> Thus the excited-state and ground-state self-exchange reactions are expected to differ by a factor of between 10 and  $10^2$ . A factor of  $\sim 10^3$  was inferred above from experimental observations.

Since there is always a Stokes shift between ground-state absorption and excited-state emission, there should always be a difference in the reorganizational barriers for the respective electron-transfer reactions. Thus the frequent assumption<sup>3d</sup> that the self-exchange rates of excited-state and ground-state polypyridyl-ruthenium(III)-ruthenium(II) reactions are the same cannot be correct unless these reactions are limited only by diffusion. In fact, the  $\text{Ru}(\text{bpy})_3^{2+}$  system exhibits a very large Stokes shift ( $\sim 0.6 \mu\text{m}^{-1}$ ),<sup>2b</sup> a part of which may be due to the configurational differences of the initially populated excited state and the emitting state.<sup>16</sup> The excited-state to ground-state decay in this system has some of the features of a unimolecular electron-transfer reaction with a 9 kcal mol<sup>-1</sup> "activation barrier" ( $k = 2 \times 10^6 \text{ s}^{-1}$ ).<sup>14</sup> This corresponds to a difference of  $\sim 0.3 \mu\text{m}^{-1}$  in excited-state and ground-state Franck-Condon parameters and about a  $10^3$  difference in excited-state and ground-state self-exchange rates. The observations of Sutin and co-workers<sup>2</sup> are consistent with slower excited-state than ground-state self-exchange rates.

In systems for which there is a greater barrier to excited-state than to ground-state electron transfer, as we find for  $\text{Cr}(\text{bpy})_3^{3+}$  and as probably is the case for  $\text{Ru}(\text{bpy})_3^{2+}$ , this effect is another limitation on the utilization of these systems in such applications as the construction of photovoltaic cells since the degradative recombination reactions will tend to have smaller barriers than the excited-state redox reactions which produce the effect. On the other hand, there is no apparent reason that there should not be systems in which the reactivity order of ground and excited states is reversed from that found here.

Excited-state electron-transfer reactions of ( ${}^2E$ )  $\text{Cr}(\text{bpy})_3^{3+}$  have been followed using standard flash photolysis techniques<sup>17</sup> and monitoring the  ${}^2E$  excited state absorbance at 445 nm.<sup>4e</sup>

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- A frequently used approximation calculates transition state properties as an average of the ground-state properties oxidant and reductant weighed by the respective force constants. Thus,  $\bar{r}^\ddagger = (k_{II}r_I + k_{III}r_{III})/(k_{II} + k_{III})$ , where the  $r_i$  and  $k_i$  are respectively the appropriate bond lengths and force constants for the metal in the II and III oxidation state and  $\bar{r}^\ddagger$  is the bond length in the transition state. In general  $k_{II} \leq k_{III}$  and this implies  $\lambda_{II} \leq \lambda_{III}$ .
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Received April 4, 1977

## On Hydrogen Abstraction by the $\pi, \pi^*$ Singlet State<sup>1,2</sup>

Sir:

The efficient reduction of the carbonyl group in its  ${}^3(n, \pi^*)$  state by hydrocarbon hydrogen donors is well documented;<sup>3</sup> that in the  ${}^1(n, \pi^*)$  is less so, but recent work suggests<sup>4</sup> that the expected intermolecular similarity<sup>5,6</sup> with the triplet obtains, as is probably the case intramolecularly also.<sup>7</sup> With the singlet ( $n, \pi^*$ ) reaction the product formation is in competition with return to ground state via a common hypersurface. The corresponding  ${}^3(\pi, \pi^*)$  state is, on the other hand, poorly reduced by hydrocarbon donors,<sup>7,8</sup> and such capacity as it has may be acquired by mixing with the  $n, \pi^*$  state.<sup>7,9</sup>

Recently we have reported that the second excited state of adamantanethione (**1**) is reduced by cyclohexane to give the sulfide **2** and the thiol **3** accompanied by the inevitable 1,3-dithietane dimer.<sup>10</sup> We now wish to report that the hydrogen abstraction is, at least in part, a radical process and that the  $S_2$  thione is among the most indiscriminate hydrogen abstractors known.

The thione **1** (0.04 M) was irradiated at 254 nm to about 5% conversion in a number of hydrocarbons (Table I) in admixture with cyclohexane. The relative reactivities for both sulfide and thiol formation are expressed (per C-H bond) with respect to the formation of **2**. The relative total insertion per C-H bond with respect to cyclohexane as standard is also given. The process is much more indiscriminate than that of benzophenone triplet or *tert*-butoxy radical and surpasses the promiscuity of chlorine. Only fluorine and methylene are comparable.<sup>11</sup> The lack of discrimination in the abstraction is related in re-

