

- (2) Subsequently we have found that the product mixture also contains a very small amount of 2,3-dimethyl-1-butene.
- (3) Pyrolysis of tosylhydrazone salts under aprotic conditions generally leads to carbenes. See W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973, p 1, for numerous examples.
- (4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 761 (1969).
- (5) A. M. Foster and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 609 (1973), have found that olefins are formed with a high degree of stereospecificity in the pyrolysis of  $\gamma$ -lactone tosylhydrazone salts. These authors have suggested that a concerted mechanism for olefin formation competes with a diradical pathway, which leads to the other products that are formed.
- (6) These diols have been used previously to establish the stereospecificity of olefin formation in the reactions of the derived thionocarbonates with Ni(0): M. F. Semmelhack and R. D. Stauffer, *Tetrahedron Lett.*, 2667 (1973). We thank Professor Semmelhack for sending us his procedure for preparing the diols.
- (7) B. Le Clef, J. Mommaerts, B. Stelander, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **12**, 404 (1973), have reported that the cyclic ammonium salts formed from secondary glycols undergo  $S_N2$  ring opening by chloride ion to give chlorocarbonates. We minimized this undesired process by limiting the time of the initial reaction to 30 min in refluxing  $CH_2Cl_2$ . Small resonances attributable to chlorocarbonate were observed in the NMR spectra of the crude ammonium salts; however, purification of the moisture sensitive salts was not attempted. Instead, the crude salts were allowed to react with tosylhydrazine in a refluxing mixture of tetrahydrofuran and triethylamine, as described previously<sup>1</sup>, and the resulting CTH's were purified by recrystallization.
- (8) Both CTH's gave satisfactory elemental analyses and exhibited spectral data consistent with the assigned structures.
- (9) The products were separated on a 16 ft  $\times$   $\frac{1}{8}$  in column of 8%  $AgNO_3$  on Chromosorb P. Peak areas were corrected for differences in the response of the thermal conductivity detector to the products. A few percent of toluene was also detected among the volatile products that were trapped.
- (10) This hypothesis nicely rationalizes the observation that the CTH salt derived from bicyclo[3.3.0]octane-1,5-diol gives only bicyclo[3.3.0]oct-1(5)-ene on pyrolysis,<sup>1</sup> since in this rigid ring system C-C bond rotation cannot occur.
- (11) R. J. Cvetanovic, *Adv. Photochem.*, **1**, 115 (1963).
- (12) Not only could the diradicals differ in the conformations and spin states initially populated, but the diradicals formed by oxygen atom addition possess sufficiently large quantities of vibrational energy that fragmentation is competitive with epoxide formation.<sup>11</sup>
- (13) It should also be noted that, while the percentage of olefin formed from pyrolysis of **1** and **7** is about the same, the percentage of oxygen-containing product obtained from the former CTH salt is much lower than that produced from the latter. This reflects the fact that a substantial portion of the diradicals generated by one-bond cleavage in **2** abstracts hydrogen before decarbonylating, leading, after loss of formic acid, to **4**.
- (14) F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Lett.*, 5223 (1970); G. Crank and F. W. Eastwood, *Aust. J. Chem.*, **17**, 1392 (1964); J. S. Josan and F. W. Eastwood, *ibid.*, **21**, 2013 (1968); S. Hanessian, A. Bargiotti, and M. LaRue, *Tetrahedron Lett.*, 737 (1978).
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- (17) Carbene formation by deprotonation of a carbocation intermediate<sup>14</sup> or by norbornadienone ketal pyrolysis<sup>16</sup> is symmetry allowed in the sense that filled orbitals of the reactant correlate directly with those populated in the lowest singlet state of the carbene product. In contrast, linear cheletropic loss of nitrogen from a diazo compound is an orbital symmetry forbidden process. Ab initio calculations on diazomethane suggest that this compound, in fact, decomposes by a nonlinear cheletropic pathway.<sup>18</sup>
- (18) J. Lievin and G. Verhaegen, *Theor. Chim. Acta*, **45**, 269 (1977).

Weston Thatcher Borden,\* Lin Hin Hoo

Department of Chemistry, University of Washington  
Seattle, Washington 98195

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## Wavelength Dependent Photoprocesses in Acenaphthaquinone

Sir:

Typically, the internal conversion  $S_n \rightsquigarrow S_1$  dominates the upper excited state photophysics of polyatomics in fluid media. Exceptions such as azulene<sup>1</sup> and thioketones<sup>2</sup> are rare and noteworthy since they offer an opportunity to elucidate upper state relaxation schemes. We report herein results showing the wavelength dependence of several photoprocesses involving acenaphthaquinone (ANQ).<sup>3</sup> These observations suggest *less*

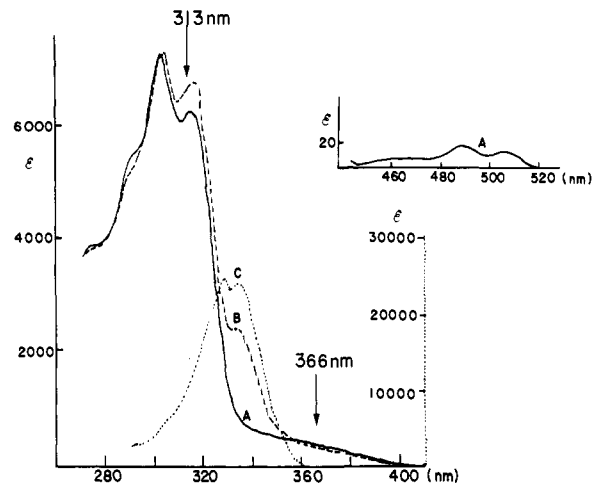


Figure 1. Absorption spectra of acenaphthaquinone in cyclohexane (A) after rigorous purification and (B) before purification, and of (C) 1,8-naphthalic anhydride in benzene (A and B), left-hand scale; C, right-hand scale.

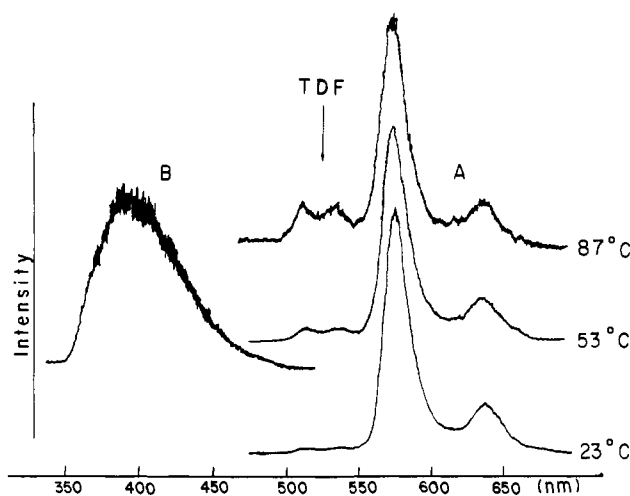


Figure 2. Time-resolved emissions from degassed solutions of  $1.0 \times 10^{-4}$  M acenaphthaquinone in benzene at 25 °C: (A) longer lived emissions recorded with a time delay of 10  $\mu$ s and a sampling gate of 2  $\mu$ s at temperatures indicated; (B) fluorescence from trace 1,8-naphthalic anhydride recorded with a time delay of 0 ns and a sampling gate of 10 ns.

than complete relaxation of an upper excited state in ANQ to the lowest excited states in fluid media.

Absorption spectra data for ANQ are shown in Figure 1. The very weak ( $\epsilon \approx 20$ ) long wavelength absorption near 500 nm is an  $n, \pi^*$  transition,<sup>4</sup> while the more intense absorptions near 300 nm are  $\pi, \pi^*$  transitions. The weaker ( $\epsilon \approx 400$ ) broad shoulder,  $<400$  nm, may be a second  $n, \pi^*$  transition.<sup>4a</sup> The peak previously reported<sup>5</sup> at 338 nm (Figure 1B) is due to 1,8-naphthalic anhydride (NA) (Figure 1C). This troublesome impurity, arising from facile photooxidation of ANQ<sup>6</sup> (discussed below), has a strong ( $\Phi_f = 0.26$ ) (Figure 2B) but short-lived ( $\tau_f < 10$  ns) fluorescence. We estimate that observable impurity fluorescence is detectable at an NA level of  $\geq 0.05\%$  under our experiments.

Nitrogen laser excitation (337 nm, 10 ns pulse) of degassed and sealed samples of purified<sup>3</sup> ANQ in benzene provided the time-resolved<sup>7</sup> emissions in Figure 2. The spectrum of the fast decaying ( $\tau < 10$  ns), short wavelength emission is fluorescence from low levels of NA. The longer lived emissions ( $\tau \approx \mu$ s) are assigned to mixed thermal delayed fluorescence (TDF)<sup>8</sup> and phosphorescence from the  $n, \pi^*$   $S_1$  and  $T_1$  states of ANQ. From the temperature dependence of  $\Phi_{TDF}/\Phi_p$  (Figure 2A),  $\Delta E_{S_1-T_1} = 1780 \pm 120$   $cm^{-1}$ , which is consistent with the  $n, \pi^*$

**Table I.** Relative Efficiencies with 313- and 366-nm Excitation<sup>a</sup>

process	excitation wavelength		rel efficiency ( $\Phi^{366}/\Phi^{313}$ )
	366 nm	313 nm	
phosphorescence, $\Phi_p$	0.0035 <sup>b</sup>	0.0013 <sup>b</sup>	2.7, <sup>b</sup> 2.7 <sup>c</sup> 2.4 <sup>c,d</sup>
photocycloaddition, $\Phi_A$ <sup>e</sup>	0.43	0.12	2.9
	0.48	0.15	
	0.42	0.17	
photooxidation, $\Phi_{Ox}$	0.0054 <sup>f</sup>	0.0025 <sup>f</sup>	2.2
	0.0062 <sup>g</sup>	0.0027 <sup>g</sup>	

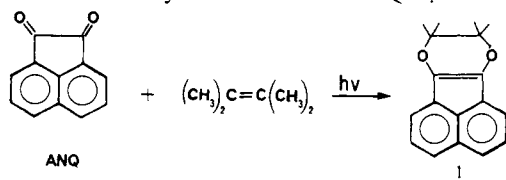
<sup>a</sup> All in degassed benzene solution at 25 °C unless otherwise indicated. Samples irradiated with the monochromated output from a 200-W Xe-Hg source. Source output determined by ferrioxalate actinometry. Runs at 313 and 366 nm in quartz cells showing transmissions of >80% at the excitation wavelengths. <sup>b</sup> Measured relative to the mixed DTF and phosphorescence from optically matched samples of benzil in benzene for which we previously measured  $\Phi = 0.0025 \pm 0.0003$ : T.-S. Fang, unpublished results. [ANQ] =  $1.0 \times 10^{-4}$  M at both wavelengths. <sup>c</sup> Measured independent of absolute quantum yield determinations from the ratio of emission yields, using ferrioxalate actinometry to normalize source output. <sup>d</sup> In acetonitrile. <sup>e</sup> At 0.0010 M ANQ and 0.013 M 2,3-dimethyl-2-butene. Formation of **1** monitored by UV-visible absorption spectroscopy at 450 nm. <sup>f</sup> In nondegassed benzene solution containing  $8.7 \times 10^{-4}$  M ANQ. Formation of NA monitored by UV-visible absorption spectroscopy at 340 nm by correcting for absorption due to unreacted ANQ. <sup>g</sup> Same as in *d* except at  $4.7 \times 10^{-4}$  M ANQ.

assignment. No  $S_1 \rightarrow S_0$  prompt fluorescence has been detected.

The quantum yields of ANQ mixed TDF and phosphorescence (note  $\Phi_{TDF}/\Phi_p = 0.04$  at 25 °C) in benzene were measured under photostationary conditions using 313- and 366-nm excitation (Table I). A wavelength dependence was noted with  $\Phi_p^{366}/\Phi_p^{313} = 2.7$ .

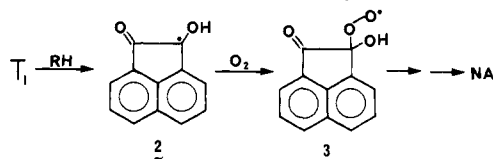
Irradiation of degassed solutions of ANQ in benzene in the presence of 2,3-dimethyl-2-butene results in facile formation of a single photoproduct, mp 174–175 °C.<sup>9</sup> The scarlet (UV-visible maxima in cyclohexane at 450 nm ( $\epsilon$  694), 318 (8800), 306 (8800), 230 (50 000)) adduct is assigned the dioxene structure **1** (Calcd for  $C_{18}H_{18}O_2$ : C, 81.20, H, 6.77. Found: C, 80.81; H, 6.74) based on the NMR data ((in  $CDCl_3$ )  $\delta$  1.37 (s, 12 H), 7.2–7.5 (m, 6 H)) and the absence of a carbonyl stretching frequency in the IR.<sup>10</sup>

The quantum yields for adduct formation in the presence of 0.013 M alkene were determined to be  $\Phi_A^{366} = 0.44 \pm 0.03$  and  $\Phi_A^{313} = 0.15 \pm 0.02$ . Based on further studies of this reaction in our laboratory<sup>11</sup> and, in analogy with photomechanistic studies on phenanthraquinone,<sup>13</sup> we conclude that dioxene **1** is formed by reaction of the ANQ  $T_1$  state.

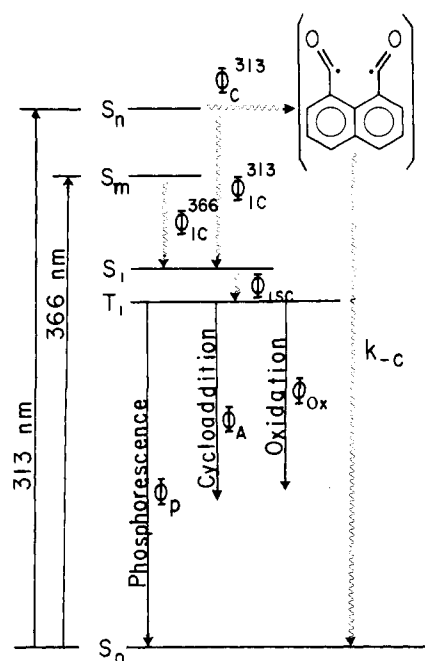


The photooxidation of ANQ in aerobic benzene solutions has been reported previously<sup>6,14</sup> and is thought to be initiated by reaction of the ANQ  $T_1$ . The efficiency of NA formation also is wavelength dependent with  $\Phi_{Ox}^{366}/\Phi_{Ox}^{313} = 2.2$ .

Scheme I is suggested as an explanation for these observations. Excitation at 313 nm populates  $S_n$  which relaxes to  $S_1$  by internal conversion with an efficiency factor of  $\phi_{ic}^{313}$ . Acyl



Scheme I



carbon-acyl carbon bond scission is proposed as a competing pathway<sup>15,16</sup> with an efficiency of  $\phi_c^{313}$  where  $\phi_c^{313} + \phi_{ic}^{313} = 1$ . Excitation at 366 nm populates  $S_m$ , intermediate in energy between  $S_1$  and  $S_n$ , which may be the higher  $n,\pi^*$  state.<sup>4</sup>  $S_m$  relaxes to  $S_1$  with an efficiency of  $\phi_{ic}^{366}$ . The relative efficiency for phosphorescence, cycloaddition, or oxidation is given by  $\Phi^{366}/\Phi^{313} = \phi_{ic}^{366}/\phi_{ic}^{313}$ .<sup>17</sup> If  $\phi^{366} = 1$ , the data in Table I indicate that  $\phi_{ic}^{313} = 0.3$ –0.5.

The observation that  $\Phi_p^{366}/\Phi_p^{313} \approx \Phi_A^{366}/\Phi_A^{313} \approx \Phi_{Ox}^{366}/\Phi_{Ox}^{313}$  suggests that the biradical is too short lived for trapping by  $O_2$  at ordinary atmospheric concentrations ( $\sim 10^{-3}$  M). If this trapping reaction is diffusion limited ( $k \approx 2.5 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>), then  $k_{-c}$  only need be  $\geq 10^7$ – $10^8$  s<sup>-1</sup> to preclude interception under the reaction conditions.

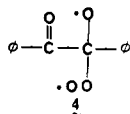
Further work is in progress.

**Acknowledgment.** We thank the U.S. Army Research Office for financial support of this work.

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- (3) ANQ (Aldrich Chemical Co.) was recrystallized several times from alcohol and chromatographed on silica gel, under nitrogen, in a darkened room. The highly fluorescent photooxidation product, 1,8-naphthalic anhydride (see text), was eluted with petroleum ether followed by ANQ upon elution with dichloromethane. ANQ was vacuum pumped dry and stored in the dark prior to use. All sample preparations were done in a darkened room.
- (4) There is general accord that cisoid 1,2-diketones should possess two low energy  $n,\pi^*$  transitions. However, there is disagreement over the detailed assignments of these transitions. For examples, see (a) J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, *J. Am. Chem. Soc.*, **96**, 4385 (1974); (b) P. J. Wagner, R. G. Zepp, K.-C. Liu, M. Thomas, T.-J. Lee, and N. J. Turro, *ibid.*, **98**, 8125 (1976).
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- (7) R. E. Brown, K. D. Legg, M. W. Wolf, L. A. Singer, and J. H. Parks, *Anal. Chem.*, **46**, 1690 (1974).
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- (9) Column chromatography of preparative scale runs provided **1** in isolated yields of 85–90%. The only other product isolated was NA in trace yields.

- (10) In general, cycloaddition of alkenes to 1,2-diketones leads to dioxene and/or oxetane products. See (a) M. B. Rubin, *Fortschr. Chem. Forsch.*, **13**, 251 (1969); (b) A. V. El'tsov, O. P. Studzinskii, and V. M. Grebenkina, *Russ. Chem. Rev. Us. Khim.*, **46**, 185 (1977).
- (11) Anthracene ( $E_S = 76.3$ ,  $E_T = 42.0$  kcal/mol<sup>12</sup>), which quenches the ANQ phosphorescence ( $E_T = 49$  kcal/mol) with  $k_Q = 7.2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> in benzene at 25 °C, is an effective quencher of the photocycloaddition reaction in the concentration range of  $10^{-4}$ – $10^{-5}$  M [Q]. Analysis of the Stern–Volmer data indicates that the state reactive in the cycloaddition must have a lifetime  $> 1$   $\mu$ s which is consistent only with the T<sub>1</sub> state.
- (12) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973.
- (13) (a) J. J. Bohning and K. Weiss, *J. Am. Chem. Soc.*, **88**, 2893 (1966); (b) S. Farid and K.-H. Scholy, *Chem. Commun.*, 412 (1968); (c) Y. L. Chow, T. C. Joseph, H. H. Quon, and J. N. S. Tam, *Can. J. Chem.*, **48**, 3045 (1970).
- (14) (a) Intermediates such as **4** were proposed recently in the 1,2-diketone



sensitized photooxidation of pyrimidines: H.-S. Ryang and S. Y. Wang, *J. Am. Chem. Soc.*, **100**, 1302 (1978). (b) Also see N. Shimizu and P. D. Bartlett, *ibid.*, **98**, 4193 (1976), for the photooxidation of alkenes sensitized by 1,2-diketones.

- (15) Acyl carbon–acyl carbon photocleavage in 1,2-diketones is well documented in both the vapor and condensed phases. See ref 10a.
- (16) The same wavelength dependence of  $\Phi_p$  is observed in acetonitrile (Table I, footnote *d*). Therefore, the wavelength dependencies in Table I do not appear to be due to a competing deactivation of S<sub>n</sub> via a mechanism that specifically involves benzene.
- (17) Relaxation also could occur by the path S<sub>m</sub>  $\xrightarrow{h\nu}$  T<sub>m</sub>  $\xrightarrow{h\nu}$  T<sub>1</sub>.

Tai-Shan Fang, Lawrence A. Singer\*

Department of Chemistry  
University of Southern California  
Los Angeles, California 90007

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## Photorearrangements of Bicyclo[3.2.1]oct-2-en-7-ones. A Substituent Effect Study. Mechanistic Studies in Photochemistry. 19<sup>1</sup>

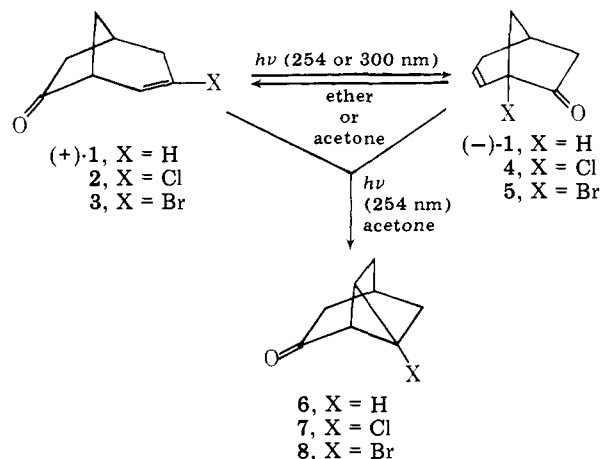
Sir:

In a recent communication, Berson and coworkers<sup>2</sup> reported a thermal [1,3] acyl shift for bicyclo[3.2.1]oct-2-en-7-one (**1**). We report a parallel study on the photochemically activated process and compare the effect of halogen substitution on the photorearrangement. Furthermore, the study of the triplet-sensitized reactions of this series of ketones has revealed that the photosensitized [1,3] acyl shift occurs from a non-quenchable state, whereas the more common oxadi- $\pi$ -methane (ODPM) rearrangement arises from a quenchable triplet state in accord with an earlier analysis by Dalton.<sup>3</sup>

The photorearrangement of bicyclo[3.2.1]octenone (**1**) and four halogen-substituted derivatives (**2–5**) were selected in order (1) to test the effect of a heavy atom on the intersystem crossing efficiency for  $\beta,\gamma$ -unsaturated ketones,<sup>4</sup> (2) to explore the effect of substituents on the excited-state reactivity in the [1,3] acyl and the oxadi- $\pi$ -methane rearrangements, and (3) to compare the relative efficiencies for these rearrangements with different substituent positions ( $\alpha$  and  $\gamma$ ).

The ketones chosen for study were synthesized and characterized by standard methods.<sup>5</sup> For the direct irradiation of ketone (–)-**1**, a [1,3] acyl migration rearrangement gave the enantiomeric ketone (+)-**1**. In order to observe this process, the resolved ketone was synthesized by oxidation of resolved 7-hydroxy-3-bromobicyclo[3.2.1]oct-2-ene (from the brucine salt of the phthalate half-ester).<sup>5b</sup> Direct irradiation racemized the starting ketone as did sensitized irradiation (although more slowly than the oxadi- $\pi$ -methane rearrangement to tricyclic ketone **6**). Likewise, halogen-substituted ketones **2–5** were

Scheme I. Photochemistry of 1- and 3-Substituted Bicyclo[3.2.1]oct-2-en-7-ones **1–5**



examined under direct and acetone-sensitized irradiation conditions (Scheme I).

It is clear from these exploratory irradiations that the chlorine and bromine substituents do not alter the nature of the product on direct irradiation.<sup>6</sup> Apparently, intersystem crossing (S<sup>1</sup>  $\rightarrow$  T) is not competitive with the [1,3] acyl shift (or other processes from the excited singlet state). Additional evidence for the absence of intersystem crossing was the absence of detectable phosphorescence from **3** EPA in glasses (77 K).

Sensitized irradiations of **1–5** employing acetone gave the expected oxadi- $\pi$ -methane rearrangement products,<sup>7</sup> the 1-substituted tricyclo[3.2.1.0<sup>2,7</sup>]octan-3-ones (**6–8**) and the same [1,3] acyl shift products observed on direct irradiation.<sup>7,8</sup> Thus, the [1,3] acyl shift appears to be ubiquitous, occurring by thermal, excited singlet, and triplet-sensitized activation.

A more quantitative assessment of the photochemistry of this ketone series is given in Table I. In order to determine the [1,3] efficiency for the degenerate rearrangement of **1**,<sup>10,11</sup> the time-dependent decrease in the optical rotation was followed. The quantum efficiency was obtained from the following relationship

$$\Phi_{\text{rac}} = (K_0/A_1)[1/2 \ln(\alpha_0/\alpha)]$$

where  $K_0$  is the moles of ketone present,  $A_1$  is total number of einsteins absorbed by the ketone,  $\alpha_0$  and  $\alpha$  are the initial and final polarimetric rotations, and  $\Phi_{\text{rac}}$  is the photoracemization quantum efficiency. The photoracemization quantum efficiency was assumed to be the efficiency for a concerted [1,3] migration<sup>10</sup> (corresponding to both the disappearance ( $\Phi_{\text{dis}}$ ) and appearance ( $\Phi_{\text{app}}$ ) efficiencies for the other ketones studied).

As seen from Table I, the effect of substitution on the reversible [1,3] migration is substantial. The sum of the forward and reverse efficiencies is lower by a factor of 3–5 when H is replaced by halogen. Since neither intersystem crossing nor new reaction processes are observed, the results indicate that decay processes are enhanced with substitution. Radiationless decay is likely since the fluorescence efficiencies of the first three ketones decrease in the order  $\Phi_f$  for **1**  $\gg$  **2**  $>$  **3**.

The sensitized rearrangement is seen to be much more sensitive to the presence of a heavy atom. Both when the halogen is attached to the  $\gamma$  position or when it is located on the  $\alpha$  bridgehead carbon, a ten- to twentyfold decrease in product formation efficiency is observed. To ensure that these lower efficiencies were not an artifact of the energy transfer step from the sensitizer, a selected series of these ketones was employed as quenchers of acetone phosphorescence.<sup>12</sup> Ketones **1**, **2**, and **3** quenched the phosphorescence emission of acetone