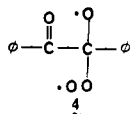


- (10) In general, cycloaddition of alkenes to 1,2-diketones leads to dioxene and/or oxetane products. See (a) M. B. Rubin, *Fortschr. Chem. Forsch.*, **13**, 251 (1969); (b) A. V. El'tsov, O. P. Studzinskii, and V. M. Grebenkina, *Russ. Chem. Rev. Us. Khim.*, **46**, 185 (1977).
- (11) Anthracene ($E_S = 76.3$, $E_T = 42.0$ kcal/mol¹²), which quenches the ANQ phosphorescence ($E_T = 49$ kcal/mol) with $k_Q = 7.2 \times 10^9$ M⁻¹ s⁻¹ 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 μ s which is consistent only with the T₁ 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 Φ_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_n via a mechanism that specifically involves benzene.
- (17) Relaxation also could occur by the path S_m $\xrightarrow{h\nu}$ T_m $\xrightarrow{h\nu}$ T₁.

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Photorearrangements of Bicyclo[3.2.1]oct-2-en-7-ones. A Substituent Effect Study. Mechanistic Studies in Photochemistry. 19¹

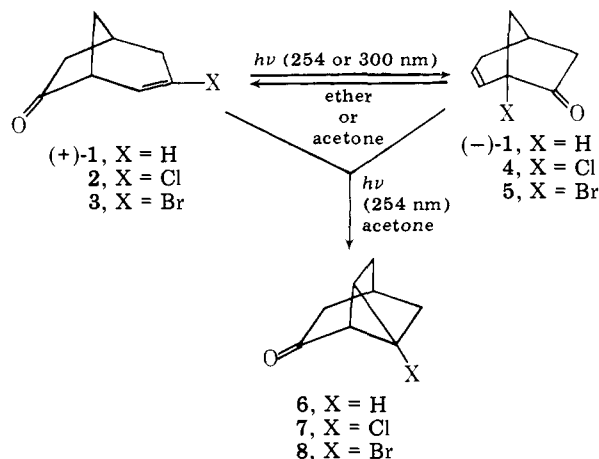
Sir:

In a recent communication, Berson and coworkers² 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- π -methane (ODPM) rearrangement arises from a quenchable triplet state in accord with an earlier analysis by Dalton.³

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 β,γ -unsaturated ketones,⁴ (2) to explore the effect of substituents on the excited-state reactivity in the [1,3] acyl and the oxadi- π -methane rearrangements, and (3) to compare the relative efficiencies for these rearrangements with different substituent positions (α and γ).

The ketones chosen for study were synthesized and characterized by standard methods.⁵ 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).^{5b} Direct irradiation racemized the starting ketone as did sensitized irradiation (although more slowly than the oxadi- π -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.⁶ Apparently, intersystem crossing (S¹ \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- π -methane rearrangement products,⁷ the 1-substituted tricyclo[3.2.1.0^{2,7}]octan-3-ones (**6–8**) and the same [1,3] acyl shift products observed on direct irradiation.^{7,8} 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**,^{10,11} 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, α_0 and α are the initial and final polarimetric rotations, and Φ_{rac} is the photoracemization quantum efficiency. The photoracemization quantum efficiency was assumed to be the efficiency for a concerted [1,3] migration¹⁰ (corresponding to both the disappearance (Φ_{dis}) and appearance (Φ_{app}) efficiencies for the other ketones studied).

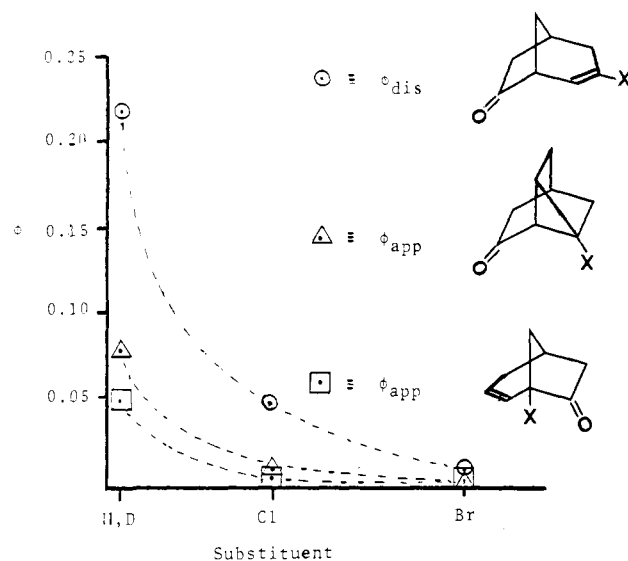
As seen from Table I, the effect of substitution on the reversible [1,3] migration is substantial. The sum of the forward and reverse efficiencies is lower by a factor of 3–5 when H is replaced by halogen. Since neither intersystem crossing nor new reaction processes are observed, the results indicate that decay processes are enhanced with substitution. Radiationless decay is likely since the fluorescence efficiencies of the first three ketones decrease in the order Φ_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 γ position or when it is located on the α 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.¹² Ketones **1**, **2**, and **3** quenched the phosphorescence emission of acetone

Table I. Quantum Efficiencies^a for [1,3] Acyl Migration and Oxadi- π -methane (ODPM) Rearrangements

| Direct (in ether) | | | |
|-------------------------|---------------------|------------------------------|---|
| ketone | Φ_{dis} | $\Phi_{1,3}$ | $\Sigma\Phi_{1,3}$ (forward and reverse) ^b |
| 1 (-) ^c | 0.42 \pm 0.04 | 0.42 ^d \pm 0.04 | 0.84 (1 (-) + 1 (+)) |
| 2 | 0.211 \pm 0.02 | 0.14 \pm 0.02 | 0.25 (2 + 4) |
| 3 | 0.16 \pm 0.02 | 0.088 \pm 0.009 | 0.15 (3 + 5) |
| 4 | 0.16 \pm 0.02 | 0.11 \pm 0.01 | |
| 5 | 0.095 \pm 0.01 | 0.062 \pm 0.007 | |
| Sensitized (in acetone) | | | |
| ketone | Φ_{dis} | Φ_{ODPM} | $\Phi_{1,3}$ |
| 1 | 0.22 \pm 0.02 | 0.080 \pm 0.008 | 0.048 \pm 0.008 |
| 2 | 0.030 \pm 0.004 | 0.0062 \pm 0.001 | 0.0041 \pm 0.0005 |
| 3 | 0.015 \pm 0.004 | 0.0033 \pm 0.0003 | 0.0036 \pm 0.0005 |
| 4 | 0.046 \pm 0.005 | 0.03 \pm 0.003 | 0.009 \pm 0.001 |
| 5 | 0.021 \pm 0.002 | 0.007 \pm 0.0009 | 0.0029 \pm 0.0004 |

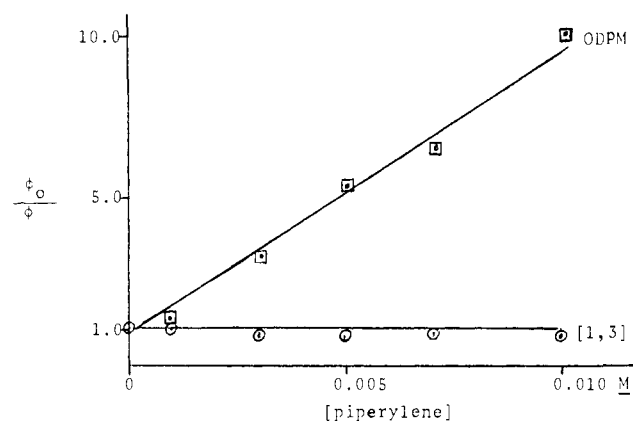
^a Ketones were irradiated at 300 (direct) and 254 nm (sensitized). Solutions of $\sim 10^{-2}$ M were degassed with purified N_2 and irradiated in a merry-go-round apparatus (Southern New England, RPR-100) and were run in duplicate. Analysis was by GLC employing an internal standard. Actinometry was by potassium ferrioxylate.⁹ A 10% error in light output was used to calculate the standard deviation. Values reported were those extrapolated to zero conversion. ^b The sum of the forward and reverse appearance quantum efficiencies for the reversible [1,3] migration. ^c Racemization of the active ketone **1** was followed polarimetrically at 578, 546, 436, and 365 nm. The mechanism for the racemization was assumed to be a concerted [1,3] acyl migration.¹⁰ ^d The racemization quantum efficiency was assumed equal to Φ_{dis} and Φ_{app} for **1a** (see text). GLC analysis showed no new products in low conversion runs (~ 2 half-lives).

**Figure 1.** Quantum efficiency vs. halogen substituent for the sensitized reactions of ketones **1**, **2**, and **3**.

with relative efficiencies of 1.00, 0.64, and 1.48. The corrected reactivity value for each of these ketones is graphically presented in Figure 1, further emphasizing the effect of a heavy atom¹³ on the sensitized reactions.

Further studies on the sensitized rearrangements showed that the two reactions originated from separate excited states. Employing sensitizers of successively lower n, π^* triplet energies, e.g., acetone ($E_T = 80$ kcal/mol) and acetophenone (74), the bromo ketones **3** and **5** showed a rapid decline in the ratio of [1,3] to ODPM product. Benzophenone ($E_T = 68$ kcal/mol) gave very little of these products and considerable side products. A more direct indication was the differential piperylene quenching of the [1,3] and ODPM rearrangements of **3**. The acetophenone-sensitized ODPM reaction was quenched, whereas the [1,3] migration was not affected (Figure 2). Thus, a nonquenchable excited state, possibly a higher, n, π^* state, is responsible for the [1,3] acyl shift while a lower lying π, π^* triplet is the ODPM precursor.^{3a}

Alternatively, the [1,3] migration of these bicyclic ketones may be occurring on the ground-state surface in accord with Berson's report on the thermal rearrangement of **1**.² Our at-

**Figure 2.** *cis*-Piperylene quenching of the acetophenone-sensitized rearrangements of **3**.

tempts to intercept intermediates (either an excited triplet, a singlet, or a ground-state diradical) with piperylene (up to 2 M in direct irradiation) were unsuccessful. If the excited-state surfaces funneled the reactant molecules onto the ground-state rearrangement surface, then the inability to quench the [1,3] migration and to effect intersystem crossing from the singlet excited state to the triplet would not be exceptional.¹³

Finally, it has recently been suggested that the ODPM rearrangement may arise from an excited singlet state for a substituted bicyclo[2.2.2]octenone.¹⁴ Our results would suggest that such is not the case for the bicyclic ketones examined in this study and for related analogues. Thus, the ODPM rearrangement remains a triplet-state process, while the [1,3] migration has been shown to occur with direct or sensitized irradiations.

Acknowledgments. This work was supported by the Kansas University Research Fund and by the National Institutes of Health (GM 16611). Acknowledgment for the ¹⁹F NMR study is made to Professor John Swenton, The Ohio State University, and for helpful discussions with Professor Richard Schowen of this department.

References and Notes

- (1) For part 18, see R. S. Givens and B. Matuszewski, *Tetrahedron Lett.*, 865 (1978).

- (2) J. M. Janusz, L. J. Gardiner, and J. A. Berson, *J. Am. Chem. Soc.*, **99**, 8509 (1977).
- (3) (a) J. C. Dalton, M. Shen, and J. J. Snyder, *J. Am. Chem. Soc.*, **98**, 5023 (1976); (b) see also D. I. Schuster, J. Eriksen, P. S. Engel, and M. A. Schexnayder, *ibid.*, **98**, 5025 (1976).
- (4) While numerous studies have shown inter- and intramolecular heavy-atom enhancement of intersystem crossing for π, π^* states of aromatic hydrocarbons, little or no enhancement has been observed for ketones, particularly when the n, π^* states are the lowest excited states (see, for example, P. J. Wagner, *J. Chem. Phys.*, **45**, 2335 (1966), and D. Kearns and W. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966)). For β, γ -unsaturated ketones, the lowest singlet excited state is n, π^* , but the triplet excited state is not known. Houk's calculation^{7a} suggests that it has appreciable π, π^* character.
- (5) (a) Details of the synthesis and characterization of all compounds will be given in our full paper to be published later. The 3-halo ketones **2** and **3** were synthesized by oxidation of the corresponding bicyclic alcohol (R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970)). The 1-halo ketones **4** and **5** were obtained by direct irradiation of the corresponding 3-halo ketones. The unsubstituted **1** was obtained by hydrolysis of the Grignard reagent from the ketal of **3**. (b) The rotations of the resolved ketone were $[\phi]_D^{25} -54.13$ (578 nm), -63.73 (546), -133.70 (436), -309.76 (365) (c 1.03, ether). The optical purity was determined to be 20% from the relative areas of the CF_3 NMR absorptions for the α -methoxy- α -trifluoromethylphenylacetic esters of the resolved alcohol precursor to **3**. This optical purity is somewhat higher than predicted from Berson's study² though comparison of the two is difficult. The absolute configurations are according to Berson.
- (6) Analysis of the crude reaction mixture from irradiation of bromo ketone **3** revealed no buildup of HBr during either the direct or sensitized rearrangements. Furthermore, analysis of the product mixture from **3** showed no formation of **1**, the photoreduction product expected from **3**.
- (7) Several reviews detail much of the current information on these rearrangements: (a) K. N. Houk, *Chem. Rev.*, **76**, 1 (1976); (b) W. G. Dauben, G. Lodder, and J. Ipaktschi, *Fortschr. Chem. Forsch.*, **54**, 73 (1975); (c) S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973); (d) K. Schaffner, *Tetrahedron*, **32**, 641 (1976).
- (8) M. A. Schexnayder and P. S. Engel, *Tetrahedron Lett.*, 1153 (1975); *J. Am. Chem. Soc.*, **94**, 9252 (1972).
- (9) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. (London)*, Ser. A, **235**, 518 (1956).
- (10) The conclusions are not altered if a mechanism invoking an acyl-allyl diradical is employed in this analysis. The quantum yield for diradical formation would be twice that given in Table I (i.e., $\Phi = 0.82$) which is unusually large (see ref 7a and 11). Stereochemical investigations also indicate a stereospecific reaction consistent with a concerted [1,3] acyl migration (R. L. Coffin, R. S. Givens, and R. G. Carlson, *J. Am. Chem. Soc.*, **96**, 7554 (1974)). Complete details of this interesting result will be given in the full paper.
- (11) Several papers on the intermediacy of diradicals on [2 + 2] cycloadditions are pertinent. See, for example, G. Kaupp, *Justus Liebigs Ann. Chem.*, 844 (1973); *Angew. Chem., Int. Ed. Engl.*, **11**, 313 (1972), and **10**, 340 (1971). Discussions of the diradical intermediates for the [1,3] migration can be found in ref 2, 7, and 13.
- (12) Emission of the 440-nm band of acetone (77 K in 1:2 EA) was quenched by adding known concentrations of each of the ketones. The slopes of the linear Stern-Volmer quenching plots were used to obtain the relative quenching efficiencies.
- (13) J. Michl, *Mol. Photochem.*, **4**, 243, 256, 287 (1972).
- (14) (a) S. D. Parker and N. A. J. Rogers, *Tetrahedron Lett.*, 4389 (1976); (b) T. Eckerolay, S. D. Parker, and N. A. J. Rogers, *ibid.*, 4393 (1976).

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Anion Radicals of Pheophytin and Chlorophyll a: Their Role in the Primary Charge Separations of Plant Photosynthesis

Sir:

Photosynthesis in algae and green plants functions via two chlorophyll-mediated systems which cooperatively oxidize water (photosystem II, PS II) and reduce carbon dioxide (PS I). PS I utilizes far-red photons ($\lambda \leq 700$ nm) to yield an oxidized chlorophyll pair, P700⁺ (midpoint potential, $E_m \sim +0.4$ to 0.5 V vs. NHE) and a strong reductant, a bound ferredoxin with $E_m \sim -0.54$ to -0.59 V, which is capable of reducing the nicotinamide adenine dinucleotide required to fix CO₂. PS II operates in red light ($\lambda \leq 680$ nm) to generate a second chlorophyll cation (P680⁺) sufficiently electropositive to oxidize water to oxygen ($E_m \geq 0.8$ V) and a weak reductant ($E_m = 0$ to -0.2 V) believed to be a plastoquinone anion radical (see ref 1-8 for reviews).

Table I. Variation of ESR Line Width with Microwave Power

| $T, ^\circ\text{C}$ | microwave power, mW | Chl a ⁻ | $\Delta H, \text{G}^a$ deut Chl ⁻ | Pheo ⁻ |
|---------------------|---------------------|--------------------|---|-------------------|
| 25 | 0.01 | 10.5 | | 10.3 |
| | 0.1 | 10.8 | | 10.5 |
| | 1.0 | 11.5 | | 11.6 |
| | 10.0 | 15.0 | | 15.0 |
| -60 ^b | 0.01 | 11.3 | | 11.3 |
| | 0.1 | 11.6 | | 11.2 |
| | 1.0 | 13.2 | | 13.0 |
| | 10.0 | 17.6 | | 17.2 |
| -140 | 0.01 | 12.1 | 4.8 | 12.2 |
| | 0.1 | 12.8 | 5.2 | 12.5 |
| | 1.0 | 13.5 | 5.0 | 13.1 |
| | 10.0 | 13.0 | 5.3 | 12.6 |

^a ΔH = peak to peak line width of the first derivative ESR signal.

^b Near-freezing point.

However, recent redox, optical, and magnetic results⁹⁻¹⁷ indicate that additional electron acceptors mediate the transfer of charge from P680 to plastoquinone and from P700 to the iron-sulfur protein. Examination of the emf, ESR, and optical parameters attributed to these short-lived acceptors of PS I and II leads us to suggest that chlorophyll and its free base, pheophytin, act as the primary electron acceptors of PS I and II, respectively. We provide here redox, optical, and paramagnetic characteristics of the anion radicals of chlorophyll (Chl) and pheophytin (Pheo) in vitro to test this hypothesis.

Evidence for anions of Chl and Pheo comes from electrolytic, photolytic, and radiolytic experiments.¹⁸⁻²⁵ Nonetheless, unambiguous spectral characterization of the radicals has been complicated or prevented by the tendency of the anions to add^{26,27} or lose¹⁸ protons in the presence of trace acids or bases. We find that solutions of Pheo⁻ and Chl⁻ in dimethylformamide (DMF) which are stable for more than 2 months can be obtained by controlled potential electrolysis if oxygen is rigorously excluded and the solvent has been pretreated on activated molecular sieves followed by contact of the electrolyte and solvent with activated neutral alumina according to the methods described by Bard,²² Borg,²¹ Fajer,²⁸ Parker,²⁹ and co-workers. Electrolysis requires addition of 1 (± 0.1) electron per chlorin molecule to yield the optical spectra of Pheo⁻ and Chl⁻ shown in Figure 1. The reactions are reversible: one-electron oxidations of the radicals regenerate better than 90% of the original chlorins. The spectra displayed in Figure 1 do not exhibit any of the optical features associated with protonation of the radical, as in the Krasnovskii product,^{24,26,27} or with the deprotonation at the C-10 position known as the phase test.¹⁸

Electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) spectra of Pheo⁻ and Chl⁻ were obtained by generating the radicals electrolytically in ampoules equipped with both ESR sampling tubes and optical cells in order to monitor the electronic spectra immediately before and after the magnetic measurements. Within experimental error, no differences in ESR and ENDOR parameters are detected in samples prepared in deuterated DMF (99.5% d_7) even after prolonged standing, again indicating that no significant reactions occur with solvent protons at sites of high spin densities.

The featureless ESR signals obtained from Chl⁻ and Pheo⁻ readily saturate with increasing microwave power (Table I) and yield the ENDOR spectra shown in Figure 2. Peaks a_1 and a_2 display ENDOR features typical of methyl groups in frozen matrices.^{30,31} Self-consistent field molecular orbital calculations³² for free base and metallochlorin anions indicate (Figure 3) that the 1- and 5-methyl groups should exhibit substantial hyperfine splitting constants in a ratio of