through sulfur. The inclusion of higher-order d orbitals of proper symmetry in the sulfur basis for the orbital description no doubt leads to more favorable charge distribution (increased electron density at the electropositive sulfur) due primarily to modification of the nonbonding π-orbitals. The bonding contribution of d orbitals to the actual total energy of such sulfur compound is controversial. The net lowering of the calculated SCF energy with a d-orbital inclusive basis may not be due to a net decrease in the occupied orbital energies but a result of altered Coulomb and exchange terms.[15]

Acknowledgments. We sincerely wish to thank the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for research grants.

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(6) The optimized CSC angles found for **1a, 3a,** and **4a** were 137.3° 126.3°, and 123.3°. Forced rotation in **4**a of the π-acceptor substituted carbon p-orbital out of the CSC plane resulted in a rapid increase in the heat of formation accompanied by an equal (optimized) *conrotation* of the π-donor substituted carbon p-orbital. This would seem to indicate that the stereomode of conversion of **1** ⟶ **2** follows the Woodward-Hoffmann rules even *in a* highly perturbed system.
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Mechanistic Photochemistry of β,γ-Unsaturated Ketones. An Alternative Excited State Assignment for the 1,3-Acyl Shift Reaction of Alkyl β,γ-Enones

Sir:

The photochemistry of β,γ-unsaturated carbonyl compounds is continuing to generate considerable interest.[1,2] Part of the appeal of these bichromophoric molecules is the dichotomy often observed between the results of direct and sensitized irradiations.[1,2] Detailed understanding of the factors that govern the chemical reactivity of β,γ-enone excited states requires definitive knowledge of which excited states are responsible for the various photoprocesses observed.

The 1,3-acyl shift reaction which often occurs on direct irradiation of β,γ-enones has been universally assigned for alkyl β,γ-unsaturated ketones as a ^{1}n,π^* (S_1) reaction.[1,2] The primary basis for this assignment has been the observations that the 1,3-acyl shift of alkyl β,γ-enones is not quenched by triplet quenchers and that sensitized irradiation of these ketones usually yields only processes such as 1,2-acyl shifts and cis-trans isomerization, which are not commonly observed on direct irradiation. There seems to be little doubt that these sensitized reactions occur from the T_1 state which for alkyl β,γ-unsaturated ketones is primarily π,π^* in character.[2a] Houk has attributed the differing reactivity of the S_1 and T_1 states of alkyl β,γ-enones to the n,π^* character of S_1 and the π,π^* character of T_1.[2a,3,4] This explanation is consistent with the fact that β,γ-unsaturated carbonyl compounds with n,π^* T_1 states, e.g., aromatic β,γ-unsaturated ketones and β-diketones, often undergo 1,3-acyl shift reactions originating from the T_1 state.[2] We report results which suggest that at least for some alkyl β,γ-enones, the 1,3-acyl shift observed on direct irradiation is occurring from the ^{3}n,π^* T_2 state rather than the ^{1}n,π^* S_1 state.

We were initially prompted to question the universal assignment of the 1,3-acyl shift reaction of alkyl β,γ-enones to the ^{1}n,π^* state by (a) the observation of fluorescence from both β,γ-enones which are reactive and β,γ-enones which are unreactive toward the 1,3-acyl shift;[1e,5] (b) the fact that 1,3-acyl shifts are often unable to compete with intramolecular γ-hydrogen abstraction from the β,γ-enone ^{1}n,π^* state;[1f,j,m,2a,6] and (c) reports that the use of high energy sensitizers, e.g., acetone, sometimes results in sensitized, albeit inefficient, 1,3-acyl shift reactions of alkyl β,γ-unsaturated ketones.[11,m,2a,6d,7] The observations indicate that 1,3-acyl shift reactions can occur from triplet states of alkyl β,γ-enones, and are difficult although not impossible to explain if the 1,3-acyl shift observed on direct irradiation of alkyl β,γ-enones is solely a ^{1}n,π^* state reaction. These problems become significant when it is realized that nothing presently known about the 1,3-acyl shift reaction of alkyl β,γ-enones rules out the possibility that it is occurring from T_2, an upper triplet state predominantly n,π^* in character,[2a,3] located a few kilocalories per mole above the π,π^* T_1 state,[2a,11] and too short-lived to allow triplet quenching. Reaction from T_2 (^{3}n,π^*) would readily explain both the apparent lack of competition of the 1,3-acyl shift with S_1 processes (fluorescence and intramolecular γ-hydrogen abstraction) and the occasional observation of sensitized 1,3-acyl shift reactions when high energy sensitizers, which may be capable of transferring energy to T_2, are used. In addition, 1,3-acyl shift reaction from the β,γ-enone ^{3}n,π^* state is consistent with (a) Houk's calculations[2a,3] on reactivity as a function of excited state configuration; (b) the much greater reactivity of alkanone ^{3}n,π^* states than ^{1}n,π^* states toward α-cleavage processes;[8,9] and (c) the observation of triplet 1,3-acyl shift reactions from β,γ-unsaturated ketones with lowest n,π^* triplet states.[2a]

If the 1,3-acyl shift is occurring from T_2, then β,γ-enones, which on direct irradiation yield a 1,3-acyl shift but no T_1 photoproducts, must undergo reaction from T_2 at a rate much faster than the rate of internal conversion from T_2 (^{3}n,π^*) to T_1 ($^3\pi,\pi^*$).[10] Processes other than internal conversion are observed only rarely from upper triplet states.[11] 1,3-Acyl shifts from T_2 seem conceivable for some alkyl β,γ-unsaturated ketones, however, given that (a) β,γ-enone ^{3}n,π^* states, particularly for α-alkyl substituted β,γ-enones, should be very reactive toward α-cleavage processes,[12] and (b) internal conversion in alkyl β,γ-enones from a ^{3}n,π^* T_2 state to a $^3\pi,\pi^*$ T_1 state may be slower than normal T_2 to T_1 internal conversion to the extent that the two states are localized on different nonconjugated chromophores.[13,14]

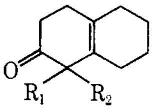
In order to gain further insight into whether the 1,3-acyl shift observed on direct irradiation of alkyl β,γ-enones is a ^{1}n,π^* S_1 reaction or a ^{3}n,π^* T_2 reaction, we have embarked upon a detailed study of the efficiency (Φ_f) and lifetime (τ_f) of the fluorescence of β,γ-unsaturated ketones, including both enones which are "reactive" and enones which are "unreactive"

Table I. Φ_f^{rel} and τ_f Values

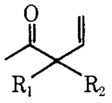
β,γ-Enone[a]	1	2	3	4	5	6
τ_f, ns[b]	1.8	2.6	4.0	1.9	2.2	2.6
Φ_f^{rel} [c]	1.0	1.3	1.7	1.0	1.3	1.8

[a] Approximately 0.1 M solutions in spectral grade hexane or heptane. [b] Fluorescence lifetimes measured by the single photon counting technique. Absolute error ±15%. [c] Quantum yields of fluorescence measured relative to **1** for **1–3** and relative to **4** for **4–6**. λ_{ex} 310 nm. Error ±10%.

toward the 1,3-acyl shift.[15] In our preliminary studies we have looked at the effect of α-methyl substitution by determining Φ_f^{rel} and τ_f values of β,γ-enones **1–6**.



1, $R_1 = R_2 = H$
2, $R_1 = CH_3; R_2 = H$
3, $R_1 = R_2 = CH_3$



4, $R_1 = R_2 = H$
5, $R_1 = CH_3; R_2 = H$
6, $R_1 = R_2 = CH_3$

Engel[1a,m] and Nakanishi[16] have recently reported dramatic effects of α-methyl substitution on β,γ-enone photoreactivity. For example, direct irradiation of **1** yields only the T_1 1,2-acyl shift reaction product, while photolysis of the α,α-dimethyl derivative **3** gives 1,3-acyl shift, but no T_1 $^3\pi,\pi^*$ products.[1a] Engel, assuming that the 1,3-acyl shift is a $^1n,\pi^*$ reaction, argues that k_r^s/k_{st}, the ratio of the S_1 rate constants for the 1,3-acyl shift reaction and intersystem crossing, must be 150 times greater for **3** than **1**,[17] an effect which he attributes primarily to large increases in k_r^s with α-methyl substitution rather than to large decreases in k_{st}.[1a] This seems to be a very reasonable assumption for alkyl β,γ-enones given that α-methyl substitution is known to considerably enhance the reactivity of ketone n,π^* states toward α-cleavage processes,[9b,18] while leading to small decreases in the rate constant for S_1 to T_1 intersystem crossing for alkanones [9a,b] and, apparently, alkyl β,γ-enones.[1e] Thus, if the 1,3-acyl shift really is an S_1 reaction, then we would expect from eq 1 and 2 that "reactive" alkyl β,γ-enones such as **3** which undergo 1,3-acyl shifts on direct irradiation will have $k_r^s \gg k_{st}$ and hence much lower Φ_f values and much shorter fluorescence lifetimes, τ_f, than "unreactive" enones such as **1** ($k_r^s \ll k_{st}$) which yield only T_1 photoproducts on direct irradiation.[19] On the other hand, if the 1,3-acyl shift is a T_2 reaction, then intersystem crossing and the 1,3-acyl shift will not be competitive and Φ_f^{rel} and τ_f values may show small increases in going from **1** to **3** and from **4** to **6**, in light of the apparent effect of α-alkylation on k_{st}.[1e,9a,b]

$$\Phi_f = k_f/(k_f + k_{st} + k_r^s) \qquad (1)$$

$$\tau_f = 1/(k_f + k_{st} + k_r^s) \qquad (2)$$

Relative quantum yields of fluorescence, Φ_f^{rel}, and absolute fluorescence lifetimes, τ_f, for β,γ-enones **1–6** are given in Table I. We find that α-methyl substitution leads to modest *increases* in both Φ_f^{rel} and τ_f for both cyclic and acylic β,γ-enones.[20] Given the assumptions discussed above, these results are inconsistent with the universal assignment of the 1,3-acyl shift to the $^1n,\pi^*$ state and provide evidence that for these β,γ-unsaturated ketones this reaction is occurring from the $^3n,\pi^*$ T_2 state.[21] This, in turn, implies that k_r^t/k_{ic}, the ratio of the T_2 rate constant for the 1,3-acyl shift process to the rate constant for T_2 to T_1 internal conversion, must increase dramatically for these alkyl β,γ-enones with α-methyl substitution. Although the generality of our conclusions remains to be determined, it is clear that one can no longer automatically assume that 1,3-acyl shift reactions observed on direct irradiation of alkyl β,γ-unsaturated ketones are occurring from the $^1n,\pi^*$ state.[22,23]

Acknowledgment is made to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also wish to thank Professor David I. Schuster for stimulating discussions and communicating his results to us prior to publication.

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(10) This is similar to the requirement imposed by the assumption that the 1,3-acyl shift is an $^1n,\pi^*$ reaction. In that case the rate of reaction from S_1 must be much greater than the rate of intersystem crossing for β,γ-enones which yield 1,3-acyl shift but no T_1 photoproducts on direct irradiation.

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(12) Introduction of the β,γ-double bond should enhance the already high reactivity of the carbonyl $^3n,\pi^*$ state toward α-cleavage processes.[9a,b]

(13) The extent to which the $^3n,\pi^*$ and $^3\pi,\pi^*$ states are localized on the carbonyl and olefin chromophores, respectively, should be a sensitive function of the relative orientation of the two groups.[2a] This suggests that the internal conversion rate will be very conformation dependent.

(14) For a recent report of an S_2 reaction from a cycloheptadienone see J. Eriksen, K. Krogh-Jespersen, M. A. Ratner, and D. I. Schuster, *J. Am. Chem. Soc.*, **97**, 5596 (1975).

(15) The usefulness of fluorescence lifetime measurements in determining the reactivity of S_1 states of β,γ-unsaturated ketones has also been demonstrated by Schuster and co-workers in the accompanying paper, D. I. Schuster, J. Eriksen, P. S. Engel and M. A. Schexnayder, *J. Am. Chem. Soc.*, following paper in this issue.

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(17) This argument tacitly assumes that if intermediates, e.g., radicals, are formed, the efficiency with which they yield the 1,3-acyl shift photoproduct is unaffected by α-methyl substitution. Although this assumption is probably not rigorously correct, the overall effect of α-methyl substitution on the yield of 1,3-acyl shift and T_1 products leaves no doubt that if the 1,3-acyl shift is a $^1n,\pi^*$ reaction then k_r^s/k_{st} must increase dramatically with α-methyl substitution.

(18) See, for example, J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*,

21, 499 (1970), and references therein.

(19) Variations in k_f with structure for β,γ-enones **1–6** may lead to changes in Φ_f but will have little effect on τ_f because $k_f \ll 1/\tau_f$ for these enones. The k_f values can be approximated from the electronic absorption spectrum. See, for example, N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1965, p 48.

(20) Similar τ_f values are observed by Schuster and co-workers for β,γ-enones **1–3.**[15]

(21) The only way the τ_f values for **1–3** can be consistent with 1,3-acyl shift from the $^1n,\pi^*$ state is if k_{st} decreases dramatically, e.g., by a factor of 50, in going from **1** to **3**. This seems highly unlikely in view of the small effects of α-methyl substitution on alkanone and β,γ-enone k_{st} values.[1e,9]

(22) A referee has noted that alkyl β,γ-enones which undergo the 1,3-acyl shift on direct irradiation do not always yield this reaction with acetone sensitization. He suggests that this creates a problem for the proposal that 1,3-acyl shifts can occur from the enone $^3n,\pi^*$ T_2 state. It seems likely to us, however, that the efficiency of energy transfer from the acetone $^3n,\pi^*$ state to the alkyl β,γ-enone $^3n,\pi^* T_2$ state will be very sensitive to the energy of the β,γ-enone T_2 state and hence may vary considerably from enone to enone.

(23) Note Added in Proof. For a related discussion, see K. Schaffner, *Tetrahedron*, **32,** 641 (1976).

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Received February 17, 1976

Photochemistry of Ketones in Solution. 50.[1] Fluorescence Lifetimes of β,γ-Unsaturated Ketones. Structural Dependence of Rate Constants for Reaction and Decay of Singlet Excited States

Sir:

The intense interest shown in recent years in the photochemistry of β,γ-unsaturated ketones (β,γ-UK) is a reflection of the many competing reaction pathways characteristic of these systems, a virtual microcosm of ketone and olefin photochemistry.[2] The subtle dependence of photochemical reactivity on structural features of these ketones has been particularly intriguing: alkyl substitution, ring enlargement, and conformational modifications often completely alter the reaction course.[2] The configuration and multiplicity of the several reactive excited states are also primary controlling factors.[2,3]

Attempts to account for the variation in reaction pathways between one system and another have been complicated and indeed thwarted by the lack of quantitative reactivity data.[2] As is well appreciated, the only valid way to judge reactivity for excited states is measurement of specific rate constants.[4] The singlet excited state lifetime τ_S is governed by the rate constants for fluorescence (k_f), radiationless decay to the ground state (k_{ds}), intersystem crossing to the triplet manifold (k_{ST}), and reaction (k_r^S) according to eq 1. The rate constant k_i for any given process with quantum efficiency Φ_i is given by eq 2.

$$\tau_S^{-1} = k_f + k_{ds} + k_{ST} + k_r^S \tag{1}$$

$$k_i = \Phi_i \tau_S^{-1} \tag{2}$$

In an attempt to lend order to the bewildering array of factors which appear to govern the photoreactivity of β,γ-UK, we have measured the singlet lifetimes of a number of these ketones (shown below) by monitoring their fluorescence decays in fluid solution at room temperature.[5,6,7] All compounds were carefully and repeatedly purified using appropriate techniques (distillation, gas-liquid chromatography, liquid chromatography) to ensure that the observed fluorescence in each case was not derived from impurities. All ketones show broad structureless fluorescence in cyclohexane solution with maxima between 400 and 420 nm and excitation spectra (λ_{max} 300-315 nm) corresponding to the carbonyl $n \rightarrow \pi^*$ transition. Quantum yields for fluorescence (Φ_f) were determined (λ_{ex} 313 nm) by comparison of corrected emission intensities with that of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (Φ_f = 0.18 in cyclohexane).[8] The fluorescencce lifetimes in Table I were deterined by single photon counting with data treatment by computer convolution.[9,10]

Rate constants for various singlet-derived processes are given in Table I where quantum yield data are available from this and earlier work.[11] Values of k_{ST}, which are of particular interest, are calculated from values of Φ_{ST}, derived from eq 3 and 4,

$$\Phi_P^{dir} = \Phi_{ST} \Phi_R^T \tag{3}$$

$$\Phi_P^{sens} = \Phi_{ST}^{sens} \Phi_{ET} \Phi_R^T \tag{4}$$

where Φ_P^{dir} is the quantum efficiency for formation of triplet-derived products on direct photolysis of the ketone, and Φ_R^T is the fraction of ketone triplets which afford the product; Φ_P^{sens} represents the efficiency of forming the same product on triplet sensitization and equals Φ_R^T under conditions where the triplet yields of the sensitizer (Φ_{ST}^{sens}) and triplet energy transfer (Φ_{ET}) are each unity. In cases where the [1,2]-acyl shift product is not observed on direct photolysis, its yield is estimated to be less than 5% of the yield of the major observed product in order to provide an upper limit to k_{ST}.

It should be noted first of all that the values of k_f vary only slightly for this series of compounds, within a factor of 7, a point which was not established by previous studies.[2] Calculation of k_f directly from room temperature uv spectra of β,γ-UK gives values in good agreement with experiment.

The balance of this initial report will focus on the relation-

Table I. Fluorescence Lifetimes and Reactivity Data of β,γ-Unsaturated Ketones

Compd	τ_S, ns	Φ_f	k_f, s^{-1}	$k_{1,3}^{S}$,[a] s^{-1} ($\Phi_{1,3}$)	k_{ST}(A),[b] s^{-1} (Φ_{ST}^{A})
1a	1.56 ± 0.05	2.1×10^{-3}	1.3×10^6	1.8×10^8 (0.28)[11a]	$<1.0 \times 10^8$ (<0.16)[11a]
1b	0.41 ± 0.05	9.6×10^{-4}	2.3×10^6	9.8×10^7 (0.04)[11a]	$<1.6 \times 10^8$ (<0.067)[11a]
3	0.66 ± 0.05	5.4×10^{-4}	8.2×10^5	1.5×10^7 (0.01)[11a]	2.5×10^8 (0.17)[11a]
1c	~0.1	4.6×10^{-4}	$\sim 4.6 \times 10^6$	*c*	*d*
1d	0.61 ± 0.05	9.2×10^{-4}	1.5×10^6	*c*	*d*
1e	0.47 ± 0.05	6.9×10^{-4}	1.5×10^6	*c*	*d*
2a	1.7 ± 0.1			$<5.9 \times 10^6$ (<0.01)[11b]	5.9×10^8 (1.0)[11b]
2b	2.4 ± 0.1			6.3×10^7 (0.15)[11b]	*e*
2c	3.4 ± 0.1			7.1×10^7 (0.24)[11b]	$<1.2 \times 10^8$ (<0.4)[11b]
4	2.25 ± 0.05	2.0×10^{-3}	8.9×10^5	5.8×10^7 (0.13)[11e]	*d*
5	5.0 ± 0.1	3.5×10^{-3}	7.0×10^5	6.0×10^6 (0.03)[11c]	*d*
6	4.91 ± 0.05	7.2×10^{-3}	1.5×10^6	*d*	*d*

[a] Rate constant for singlet-derived [1,3]-acyl shift required by mechanism A, assuming no partitioning of a biradical intermediate (see footnote 12). [b] Rate constant for intersystem crossing required by mechanism A (see text). [c] [1,3]-Acyl shift not observed. [d] Relevant quantum yield not reported. [e] Data indicate $\Phi_R^T < \Phi_P^{dir}$, inconsistent with eq 3.