mL (6 mmol) of TFSA at room temperature. After 18 h, acetic acid was evaporated off under reduced pressure at 30 °C. The residue was diluted with water followed by neutralization with aqueous sodium hydrogen carbonate. The solution was extracted with methylene chloride. The extract was dried and concentrated. The resulting residue was chromatographed on silica gel with 5:1 methylene chloride–ethyl acetate to give **6** (39 mg; 16%), **7** (60 mg, 23%), and 4-acetoxyphenol (17 mg, 11%).

Acid-Catalyzed Reaction of 3 with 2,2,2-Trifluoroethanol. The procedure was the same as that for the reaction of **3** with acetic acid: 263 mg of **3**, 10 mL of trifluoroethanol, and 0.44 mL of TFSA. After workup, the product was separated by silica gel chromatography using 1:1 methylene chloride–*n*-hexane as the eluent to give **6** (19 mg, 8%), **7** (43 mg, 16%), 2-((trifluoro)ethoxy)phenol (6 mg, 3%) [mass spectrum, *m/e* 192 (M^+); ^1H NMR ($CDCl_3$) 4.36 (2 H, q, $J = 8$ Hz), 5.96 (1 H, s), 6.88 (4 H, s)], and 4-((trifluoro)ethoxy)phenol (61 mg, 32%) [mass spectrum, *m/e* 192 (M^+); ^1H NMR ($CDCl_3$) 4.39 (2 H, q, $J = 8$ Hz), 5.86 (1 H, s), 6.85 (4 H, s)]. The structure of ((trifluoro)ethoxy)phenol was deduced by acetylation to 4-((trifluoro)ethoxy)phenyl acetate: NMR ($CDCl_3$) 2.26 (3 H, s), 4.29 (2 H, q, $J = 8$ Hz), 6.85 (2 H, d, $J = 9$ Hz), 7.03 (2 H, d, $J = 9$ Hz). A similar reaction was carried out using BF_3 etherate (5 equiv) in 15 mL of trifluoroethanol. Gas chromatographic yields of 2- and 4-((trifluoro)ethoxy)phenol were 4.0% and 33.6%, respectively.

Acid-Catalyzed Reaction of 3 with Methanol. A solution of 263 mg of **3** in 4 mL of methanol was bubbled through with anhydrous BF_3 gas for 1 h at 0 °C. The solution was then poured into saturated aqueous sodium hdyrogen carbonate and extracted with methylene chloride. After evaporation of the solvent, the product was chromatographed to give **7** (55 mg, 21%), 2-methoxyphenol (4 mg, 3.2%), and 4-methoxyphenol (19 mg, 15%). Gas chromatographic yields of 2- and 4-methoxyphenol were 3.0% and 16.1%, respectively.

Acid-Catalyzed Reaction of 3 with Acetonitrile. The procedure was the same as that for the reaction of **3** with acetic acid: 263 mg of **3**, 5.25 mL of acetonitrile, and 0.2 mL of TFSA. After workup, the product was separated by silica gel chromatography using 3:2 methylene–EtOAc as the eluent to give 4-acetamidophenol (23 mg, 15%). In addition, an unidentified compound was obtained: 168 mg (55%); colorless plates; mp 176–177 °C; ^1H NMR ($CDCl_3/Me_2SO\text{-}d_6$) 2.40 (3 H, s), 2.46 (3 H, s), 6.5–7.8 (8 H, m), 8.95 (1 H, s), 9.70 (1 H, s). Anal. ($C_{15}H_{16}N_2O_3S$): C, H, N.

Acid-Catalyzed Reaction of 3 with Ethanethiol. A solution of 263 mg of **3** in 4 mL of methylene chloride and 7.47 mL of ethanethiol was bubbled through with anhydrous BF_3 gas for 1 h at 0 °C. After workup, the product was separated by silica gel column chromatography to give 2-ethylmercaptophenol (35 mg, 23%) and 4-ethylmercaptophenol (66 mg, 43%).

Acid-Catalyzed Reaction of 3 with Hydrogen Chloride. A solution of 263 mg of **3** in 2 mL of methylene chloride and 7.6 mL of trifluoroacetic acid was bubbled through with anhydrous hydrogen chloride for 2 h at room temperature. After workup, the product was chromatographed to give **7** (55 mg, 21%), 2-chlorophenol (22 mg, 17%), and 4-chlorophenol (13 mg, 10%). Gas chromatogrpahic yields of 2- and 4-chlorophenol were 18.0% and 13.5%, respectively.

Registry No. 1, 410711-17-4; **2**, 4846-21-3; **3**, 65109-75-3; **4**, 90-43-7; **5**, 92-69-3; **6**, 65109-80-0; **7**, 65109-81-1; **8**, 83076-97-5; **9**, 65109-77-5; **10**, 83076-98-6; **11**, 4380-77-2; **12**, 5876-92-6; **13**, 65109-76-4; **14**, 39579-09-4; **15**, 65109-83-3; **16**, 83076-99-7; **17**, 4291-29-6; *O*-(4-nitrophenyl)hydroxylamine, 33543-55-4; 4-nitrofluorobenzene, 350-46-9; ethyl acetohydroxamate, 10576-12-2; benzene, 71-43-2; anisole, 100-66-3; phenol, 108-95-2; 2-methoxy-2′-hydroxybiphenyl, 3594-88-5; 4-methoxy-2′-hydroxybiphenyl, 21849-91-2; 2-methoxy-4′-hydroxybiphenyl, 65109-82-2; 4-methoxy-4′-hydroxybiphenyl, 16881-71-3; 2,2′-dihydroxybiphenyl, 1806-29-7; 2,4′-dihydroxybiphenyl, 611-62-1; 4,4′-dihydroxybiphenyl, 92-88-6; ethyl *O*-(4-nitrophenyl)acetohydroxamate, 83077-00-3.

Experimental Evidence for the Intermediacy of Singlet (S_1) and Triplet (T_2) n,π^* States in the [1,3]-Sigmatropic Acyl Shift of Photoexcited 3-Methyl-3-(1-cyclopentenyl)butan-2-one[†1]

David I. Schuster* and Lidia T. Calcaterra

Contribution from the Department of Chemistry, New York University, Washington Square, New York, New York 10003. Received December 10, 1981

Abstract: A series of photochemical investigations of the title compound, a model β,γ-unsaturated ketone, has been carried out to differentiate between reaction pathways resulting in a [1,3]-sigmatropic acyl shift originating in singlet and triplet n,π^* excited states, S_1 and T_2, respectively. These include studies of differential sensitization and quenching of photoreactions, dependence of quantum efficiencies for fluorescence and product formation on temperature, and, finally, the perturbation on these quantities induced by irradiation in the presence of xenon. The results suggest that the [1,3]-sigmatropic acyl shift can occur from both S_1 and T_2 excited states and that the reaction from S_1 requires thermal activation. Intersystem crossing from S_1 to T_2 is enhanced in the presence of xenon, the first example of such heavy-atom enhancement in ketone photochemistry. This particular radiationless transition is not in accord with predictions based on El-Sayed's rules. Furthermore, in this system, reaction from T_2, initiated by α cleavage, appears to occur to the exclusion of decay to T_1, which is the origin of the oxa–di-π-methane rearrangement pathway. The lowest triplet T_1 can only be populated by triplet energy transfer from appropriate sensitizers.

The photochemistry of β,γ-enones is quite rich due to the presence of nearby but unconjugated alkene and carbonyl chromophores.[2] In addition to reactions characteristic of the separate chromophores, there are two reactions of these enones that depend on bichromophoric interactions, namely, the [1,3]- and [1,2]-sigmatropic acyl shifts (1,3- and 1,2-SAS) illustrated in Scheme I. The latter reaction is also known as the oxa–di-π-methane (ODPM) rearrangement.

A large number of investigations[2] allow the conclusion that the ODPM rearrangement arises from the lowest π,π^* triplet state

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[†] Dedicated to George S. Hammond on the occassion of his 61st birthday, in recognition of his many important contributions to the science of organic photochemistry.

(1) Photochemistry of Ketones in Solution. 66. Part 65: Hussain, S.; Schuster, D. I.; El-Bayoumy, K. *Tetrahedron Lett.*, in press.

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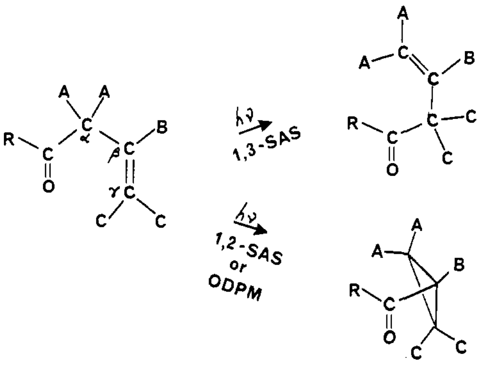
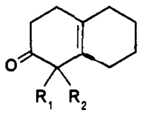
Scheme I



of these enones, which is usually the lowest excited triplet. Thus, the ODPM reaction can be sensitized by typical triplet ketone sensitizers and can be inhibited by typical triplet quenchers such as dienes when the reactive triplet is populated upon direct excitation of the enone. The excitation energy of this state with reference to the ground state is not well established because of the failure thus far to observe bona fide phosphorescence emission from the enone chromophore. Limited studies using sensitizers of varying triplet excitation energy would place this state approximately 74–78 kcal/mol above the ground state.[2b,3]

The mechanistic picture of the 1,3-SAS process is much less well-defined. Early studies indicated that the 1,3-SAS process occurred only on direct excitation of β,γ-enones, in that it could not be quenched by typical triplet quenchers, and that acetone sensitized excitation resulted only in the ODPM rearrangement.[4-9] The simplest logical conclusion was that the 1,3-SAS process originated exclusively from the lowest excited singlet state, which by absorption spectroscopy could be identified as a $^1n,\pi^*$ state. Later reports of triplet-sensitized 1,3-SAS reactions[10-13] suggested that an enone triplet might be a precursor to this process, at least in some systems. We[14,15] and others[16] observed that β,γ-enones invariably show fluorescence emission in solution at ambient temperature. However, attempts to correlate fluorescence intensity with the quantum efficiency (QE) of the 1,3-SAS process for a series of enones **1** gave inconclusive results.[14-16] The data were compatible with reactions occurring from either the S_1 or T_2 n,π^* excited states of these enones. Assuming that the S_1 state was the 1,3-SAS origin, the fluorescence data can be explained if the rate constant for intersystem crossing (ISC) increases with methyl substitution at the α-carbon. However, the T_2 state cannot be excluded as the reaction origin, provided that the ISC rate is relatively insensitive to alkyl substitution at C_α and that the rate of reaction from T_2 is not only competitive with radiationless decay to T_1 but also varies dramatically as a function of the substitution pattern. It was not possible to decide between these mechanistic alternatives on the basis of the available experimental data.[14-16]

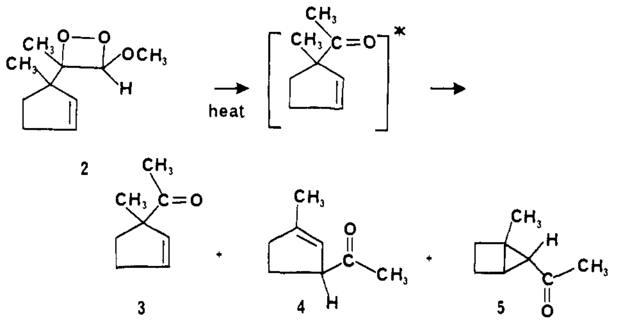


R_1 = H, CH_3

R_2 = H, CH_3

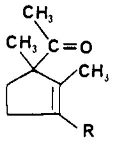
1

Scheme II



Schaffner and his group made two very important contributions in this area.[17,18] In one study (shown in Scheme II) generation of electronic excited states of enone **3** upon thermal decomposition of dioxetane **2**[19] resulted in fluorescence as well as formation of the 1,3-SAS and ODPM rearrangement products **4** and **5**, whose ratio differed from that found on direct and acetone sensitized excitation of **3**.[17] The results were compatible with a mechanism involving formation predominantly of the T_2 n,π^* state of **3** upon thermal decomposition of **2**, which then led to the 1,3-SAS product **4** competitive with radiationless decay from T_2 to T_1 (which is the direct precursor of **5**). The much larger ratio of **4** to **5** found upon direct excitation of **3** suggested that the 1,3-SAS reaction under these conditions arose at least in part from the S_1 excited state.

In a second study,[18] UV excitation of enones **3**, **6**, and **7** resulted in CIDNP effects for the 1,3-SAS products whose polarization was found to be temperature dependent. On the basis of the Kaptein model,[20] the data indicated that a triplet-derived radical pair was the principal reaction intermediate in the 1,3-SAS process in a low-temperature range while a singlet-derived radical pair was the major product precursor in a high-temperature range, the specific temperatures depending upon the substitution pattern on the enone. These results show quite conclusively that both singlet and triplet n,π^* excited states are precursors to the 1,3-SAS products in these systems. The temperature effect was attributed to an activation barrier to the 1,3-SAS reaction from S_1 sufficient to result in competition between reaction and ISC (to T_2) from the S_1 state.



6 R = CH_3

7 R = H

In the present study, we have attempted to distinguish between 1,3-SAS reactions originating from S_1 and T_2 excited states of a β,γ-enone, using for the most part classical photochemical quenching and sensitization techniques pioneered by Hammond and his co-workers twenty years ago.[21] The molecular system

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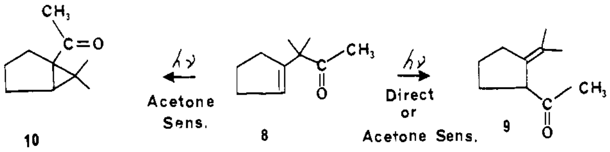
Table I. Quenching of Acetone Fluorescence by Enone 8[a]

enone concn, M × 10³	enone optical density	total optical density	acetone fluorescence, I_{obsd}	acetone fluorescence, I_{cor}[b]
0.0	0.0	0.932	69	69 ± 2
0.5	0.067	0.999	68	71 ± 3
1.14	0.131	1.063	65	71 ± 3
1.78	0.203	1.135	63	73 ± 3
2.37	0.272	1.204	57	69 ± 2

[a] Solutions purged with nitrogen for 5 min prior to measurements on a Hitachi Perkin-Elmer MPF-2A spectrofluorometer. Acetone concentration in hexane corresponded to an optical density of 0.932 at 298 nm. Optical densities were kept below 2.0 to avoid substantial light absorption in the front end of the cell, where fluorescence would not be viewed by the fluorimeter. Excitation was at 298 nm, and fluorescence intensity was measured at 400 nm. The fluorescence intensity at 400 nm of a standard solution of acetone was used to correct for lamp fluctuations. [b] Corrected for inner filter effects (Yang, N. C., et al. *J. Am. Chem. Soc.* 1977, *99*, 3023. Halpern, A. M.; Ware, W. *J. Chem. Phys.* 1971, *54*, 1271).

chosen for this investigation was enone **8**, whose photochemistry was first studied by Engel and Schexnayder.[10] This particular



enone was chosen because it was known to give the 1,3-SAS product **9** on both direct and acetone sensitized excitation, while the ODPM rearrangement product **10** is observed only on sensitization. The ease of synthesis and stability of **8** were also important considerations.

Results

Quenching of Acetone Fluorescence by Enone 8. The question of whether the formation of 1,3-SAS product **9** upon acetone photosensitized excitation of **8** indeed occurs via a triplet excited state of **8** or whether the S_1 state of **8** could be involved under these conditions was addressed by Engel and Schexnayder in their original study of **8**.[10] They concluded that singlet–singlet energy transfer was unlikely because an additional singlet-derived product of **8** (as a result of Norrish type II cyclization) was not formed in the acetone photosensitized reaction while the formation of both **9** and **10** was quenched by biphenyl to the same extent (see below), indicating interception of sensitizer triplets by biphenyl. The yield of **9** was also much greater than could be accounted for by competitive light absorption by **8**. We felt it was desirable to unequivocally establish that singlet states of **8** were not being generated by energy transfer from excited acetone by correlating the quenching by enone **8** of acetone fluorescence with the quantum yield of formation of **9**.

Although the long-wavelength absorption bands around 300 nm in the fluorescence spectra of **8** and acetone overlap almost entirely, the fraction of the incident light at 298 nm absorbed by acetone could be calculated at each concentration of **8** utilized, and the acetone fluorescence data could then be suitably corrected. Also, at the concentration of **8** utilized in these experiments, up to 2.4 × 10⁻³ M, fluorescence due to **8** could not be detected on our instrumentation. The results in Table I demonstrate that any quenching of acetone fluorescence at 400 nm by up to 2.4 × 10⁻³ M **8** is less than the estimated experimental error of 3%. From eq 1 and a lifetime of singlet acetone of 1.8 ns,[22] the maximum

$$I_F^0/I_F^Q = 1 + k_{ET}^{S-S}\tau_S^{acetone}[\mathbf{8}] \qquad (1)$$

rate constant for singlet–singlet energy transfer from acetone to **8** (assuming reduction in fluorescence intensity by at most 3% at the highest concentration of **8** utilized) would be 7 × 10⁹ M^{-1} s^{-1}. The maximum possible yield of singlets of **8** would then be 0.28 (see eq 2) at the concentration of **8** used in the acetone

$$\Phi_S^{sens} = \frac{k_{ET}^{S-S}[\mathbf{8}]}{k_{ET}^{S-S}[\mathbf{8}] + 1/\tau_S^{acetone}} \qquad (2)$$

sensitization experiments (0.031 M). The maximum yield of **9** derivable by a singlet-sensitization mechanism can then be calculated to be ≤0.016 by using eq 3, where Φ_9^{Dir}, the QE for

$$\Phi_9^{sens} = \Phi_S^{sens}\Phi_9^{Dir} \qquad (3)$$

formation of **9** on direct excitation of **8**, was found experimentally to be 0.058 ± 0.006 at 313 nm in cyclohexane, comparable to the reported[10] value of 0.04. This upper limit of 0.016 is much less than the experimental value for Φ_9^{sens} of 0.102 (lit.[10] 0.15). Thus, at least 85% of **9** orginates from a triplet excited state of **8** under the conditions of acetone sensitization at the highest concentrations of **8** utilized in these experiments.

Quenching by Dienes. Engel and Schexnayder[10] reported that the QE from the disappearance of **8** was "hardly affected" by the addition of 0.1 M of 2,2,6,6-tetramethylpiperidinyl-1-oxy, a radical that is a potent quencher of singlet as well as triplet excited states, and that the excited enone did not sensitize dimerization of 1,3-cyclohexadiene. We see no quenching of the fluorescence of **8** by concentrations of up to 6.64 M 2,5-dimethyl-2,4-hexadiene (DMHD), in contrast with the known ability of DMHD and other dienes to quench alkanone fluorescence.[23] If 10% quenching of the fluorescence of **8** is assumed to be within the experimental uncertainty, a most liberal assumption, a maximum value for the rate constant for quenching of excited singlets of **8** by DMHD can be calculated to be (4.2 ± 0.8) × 10⁷ M^{-1} s^{-1}. Similarly, at concentrations of up to 4 M, DMHD had no measurable effect on the yield of **9** on direct excitation of 2.3 M **8** (high concentrations of the enone were required to minimize light absorption by DMHD at the high concentrations required in this experiment), indicating that the precursor to **9** is a very short-lived singlet or triplet excited state.

Under conditions for sensitized excitation, quenching by dienes is kinetically complex since the quencher can intercept both donor and acceptor triplets. However, Cristol and Kaufman[24] have recently shown that linear Stern–Volmer quenching plots (i.e., plots of relative QE for product formation or substrate disappearance vs. concentration of quencher) can be obtained in this type of system (see eq 4) if the ratio of quencher Q to substrate

$$\Phi_P^0/\Phi_P^Q = \left[1 + \frac{k_1[Q]}{k_2[R]}\right](1 + k_q\tau_T[Q]) \qquad (4)$$

R is held constant and if the substrate concentration is always sufficient to quench all sensitizer triplets (rate constant k_2). The rate constants k_1 and k_q represent quenching of sensitizer and substrate triplets, respectively. In our case, the quenching possibilities are even more complex because two triplets of the acceptor (**8**) can be formed (rate constants k_2 and k_3, respectively) by triplet energy transfer from the sensitizer (acetone). For formation of **9**, the quenching relationship of eq 4 has the form of eq 5, where

$$\Phi_P^0/\Phi_P^0 = \left[1 + \frac{k_1[Q]}{(k_2 + k_3)[\mathbf{8}]}\right](1 + k_x\tau_x[Q]) \qquad (5)$$

each triplet of lifetime τ_x is quenched with rate constant k_x, if it is also assumed that the total rate of decay of T_2 (by reaction or decay to T_1) is much faster than either the rate of internal conversion to S_0 or the rate of quenching of T_2 by the quencher, held in our experiments below 0.07 M. Both these assumptions seem quite reasonable. The quencher chosen for the experiment was *cis*-piperylene. Because of the high concentration of enone **8** (up to 0.37 M) required for the Cristol experiment (ratio of

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Table II. Quenching by *cis*-1,3-Pentadiene of the Acetone-Sensitized Formation of Products **9** and **10** from Enone **8**[a]

concn *cis*-1,3-pentadiene, M	ratio of products 9/10	% conversion
none	1.8[b]	54
6.1×10^{-4}	2.1[b]	43
1.2×10^{-3}	5.4	9
2.4×10^{-3}	6	7
1.2×10^{-2}	20[c]	2

[a] Enone concentration, 1.22×10^{-2} M in acetone. Solutions were purged with nitrogen for 5 min prior to irradiation in a "merry-go-round" apparatus using a medium-pressure Hanovia lamp in a Pyrex water-cooled jacket. [b] This ratio is smaller than that usually observed (3.8 ± 0.2) on acetone sensitization of 8 at short conversions and is attributed to the partial conversion of 9 to 10 under conditions of high percentage conversion of starting enone. [c] Photoproduct 10 could not be observed by GLC, so that the detection limit was used to estimate the minimum ratio of products formed under these conditions.

8:quencher = 5.3), the experimental data had to be corrected for (a) direct light absorption (above 270 nm) by **8** in competition with acetone and (b) formation of **9** as a consequence of singlet–singlet energy transfer, estimated by using the limiting rate constant derived above for this process. After the raw quenching data were suitably corrected, it was noted that while 0.123 M piperylene was sufficient to reduce the yield of the ODPM product **10** to below detectable limits, the yield of **9** was reduced only by an amount attributable to quenching of sensitizer triplets by piperylene.

The ratio of **9** and **10** from the acetone sensitized reaction was also measured as a function of increasing quencher concentration (see Table II). Preliminary experiments showed that a concentration of 0.12 M **8** was sufficient to intercept all acetone triplets, i.e., product yields were not increased when the enone concentration was increased above 0.12 M. Contrary to the earlier finding[10] that the ratio of **9** and **10** was not changed in the presence of 0.052 M biphenyl, we observed a definite increase in the ratio of **9** to **10** as the piperylene concentration was increased. This cannot be a consequence of an increase in the percent conversion of **8**, since this would, if anything, favor the formation of **10**.

The data in Table II thus demonstrate that **9** and **10** arise from triplet states of **8** that have different propensities for quenching by piperylene. Also, it is clear that the quencher concentrations used in the Cristol experiment are sufficient to completely inhibit formation of **10**, as postulated. From the dependence of the yield of **10** on the enone concentration, one can derive a value of $(9.4 \pm 0.9) \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ for the rate constant for transfer of triplet excitation from acetone to enone **8** which results in population of the T_1 ($^3\pi,\pi^*$) state of **8**. This value is comparable to values of 1.7×10^7 and $2 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ for quenching of acetone phosphorescence by cyclopentene[25] and enone **3**,[17] respectively.

Differential Sensitization. The above conclusion was confirmed by measurement of the QE of formation of products **9** and **10** on triplet sensitization by acetone (E_T 78), acetophenone (E_T 74), and benzophenone (E_T 69 kal/mol). As shown in Tabel III, lowering the triplet excitation energy by 4 kcal/mol on going from acetone to acetophenone results in no change in the efficiency of formation of **10** but in a 50% decrease in the efficiency of formation of **9**. Attempted photosensitization using benzophenone as a sensitizer resulted in no detectable formation of either **9** or **10**.

The QE for formation of a product P on triplet sensitization is given by eq 6, where the first term is the triplet yield of the

$$\Phi_P{}^{\mathrm{sens}} = \Phi_{ST}{}^{\mathrm{sens}} \Phi_{ET}{}^{T-T} \Phi_P{}^{T} \qquad (6)$$

sensitizer, the second is the efficiency of triplet energy transfer, and the third is the efficiency with which the triplet state of the acceptor affords product P. The efficiency of energy transfer is in turn given by eq 7, where k_{ET} is the rate constant for transfer

$$\Phi_{ET}{}^{T-T} = \frac{k_{ET}{}^{T-T}[R]}{k_{ET}[R] + 1/\tau_T{}^{\mathrm{sens}}} \qquad (7)$$

of triplet excitation from the sensitizer S to the enone E and $\tau_T{}^{\mathrm{sens}}$ is the triplet lifetime of the sensitizer in the absence of E. The rate constant for triplet energy transfer is dependent on the exothermicity of the process and usually occurs at the diffusion-controlled rate when the triplet excitation energy of the donor is at least 3 kcal/mol above that of the acceptor.[26]

The results in Table III show that acetone is a more efficient sensitizer than acetophenone for formation of **9**, while the two sensitizers are equally efficient within experimental error with respect to formation of **10**. The triplet yields of all these photosensitizers are close to unity and the enone concentrations varied only slightly in these reactions. These data therefore require that the two products *must* arise from different triplet excited state percursors and that the precursor to **10** has a triplet excitation energy below that of acetophenone, that is, below 74 kcal/mol. The fact that benzophenone does not sensitize the formation of **10** indicates that the precursor to **10** has an excitation energy above 69 kcal/mol, probably near 72 kcal/mol, while that of the triplet precursor to **9** must be about 74–76 kcal/mol, allowing fairly efficient energy transfer from acetophenone. Earlier calculations[2a,27] indicate that the lowest triplet state of β,γ-enones, and the precursor to the ODPM rearrangement, is the enone π,π^* triplet, except when there are aryl substituents on the enone chromophore.[28] The absorption spectrum of **8** places its S_1 (n,π^*) state at ca. 86 kcal/mol above the ground state, from which the T_2 n,π^* state can be estimated at 78–80 kcal/mol assuming a typically small n,π singlet–triplet energy splitting.[29] This is in reasonable agreement with our estimate of the energy of the triplet state (T_2) precursor to the 1,3-SAS product **9**.

Although these results form a consistent picture, the observed variation with sensitizer of the quantum efficiency in the triplet-sensitized process can also be rationalized if the energy-transfer process involves an exciplex intermediate, since the efficiency would then not necessarily be related in a simple manner to the exothermicity of the overall process. Schexnayder and Engel[11] have previously postulated that exciplexes are formed between aromatic ketone triplets and some β,γ-enones in order to rationalize the low efficiency of sensitized formation of photoproducts in spite of the high rate constant for quenching of the phosphorescence of sensitizer triplets in solution at room temperature by the enone. The importance of such exciplexes in the photochemistry of **8** remains to be determined.

Triplet Sensitization via Dioxetane Thermolysis. The triplet multiplicity of the precursor to the 1,3-SAS product **9** on acetone-sensitized excitation of enone **8** was confirmed by generation of excited states of **8** via thermal decomposition of tetramethyl-1,2-dioxetane **11** (TMD). It is well established that thermal decomposition of **11** results in formation of acetone triplets in high yield and only very small amounts of singlet excited states.[19] When a degassed solution containing 0.3 M TMD and 0.01 M **8** in acetonitrile was heated at 50 °C for 45 min, decomposition of TMD occurred, and compounds **9** and **10** were produced, identified by comparison of their GLC retention times and GC/MS spectra with those of authentic samples prepared previously. Because of the small conversion of **8** achieved in the TMD reaction, the ratio of **9** to **10** as measured by GLC was highly inaccurate and could not be meaningfully compared with the ratio from the acetone sensitized irradiation. The results, however, do unequivocally demonstrate that **9** is produced from **8** upon TMD

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Table III. Quantum Efficiency of the Formation of Products **9** and **10** from Enone **8** with Different Photosensitizers[a]

sensitizer	sensitizer concn, M	E_T, kcal/mol	enone concn, M	irradn wavelength, nm	Φ_9	Φ_{10}	% conversion[b]
acetone	neat	78	3.09×10^{-2}	300	0.102	0.027	6
acetophenone	0.5[c]	74	2.95×10^{-2}	350	0.052	0.023	1
benzophenone	0.1[c]	69	3.10×10^{-2}	350	0.001	0.001[d]	

[a] Quantum yields determined on an optical bench with potassium ferrioxalate as the actionometer by using a split-beam technique. Solutions were purged with nitrogen for 10 min prior to irradiation. The estimated error in the quantum yields is 10%. [b] At conversions higher than ca. 10%, the ratio of **9** to **10** decreases due to the photorearrangement of **9** to **10**. [c] Solvent benzene. Optical density of 0.5 M acetophenone in benzene and of 0.1 M benzophenone in benzene, 9.0 at 350 nm. [d] No products observed by GLC after absorption by sample of 3×10^{-5} einsteins. Value in table is estimate of maximum amount of product that could remain undetected under the given experimental conditions.

Table IV. Temperature Dependence of the Quantum Yield for Formation of **9** upon Direct Excitation of Enone **8**[a]

concn of enone **8**, M	solvent	temp, °C	Φ_9^{Dir}
1.66×10^{-2}	acetonitrile	-14 ± 5[b]	0.044
2.33×10^{-2}	cyclohexane	20 ± 1	0.056
2.33×10^{-2}	cyclohexane	72 ± 1	0.083

[a] Solutions were purged with nitrogen prior to irradiation at 300 nm. Quantum yields are estimated to be precise within ±10%. No transformation of **8** to **9** was observed in the dark at the conditions given in this table. [b] The nitrogen stream used to prevent fogging of the cell during the irradiation caused temperature fluctuations. The average value of the temperature during the course of this experiment is given in the table.

Table V. Temperature Dependence of the Quantum Yield for Formation of **9** upon Acetone-Sensitized Excitation of Enone **8**[a]

temp, °C	Φ_9^{sens}
0 ± 1	0.085
25 ± 1	0.098
43 ± 1	0.087

[a] Enone concentration 1.18×10^{-2} M in acetone solvent. Solutions were purged with nitrogen prior to irradiation at 280 nm. The temperature of the solution was monitored with a thermocouple. The error in the quantum yields is estimated to be ±10%.

Table VI. Temperature Dependence of the Fluorescence Intensity and Singlet Lifetime of Enone **8**[a]

temp, °C	normalized fluorescence intensity	singlet lifetime, ns[b]
−22	2.0 ± 0.2	0.80 ± 0.16
21	1.0 ± 0.1	0.41 ± 0.05
41	0.80 ± 0.08	0.32 ± 0.06
72	0.50 ± 0.05	0.20 ± 0.04

[a] Solutions were purged with nitrogen for 5 min prior to irradiation. Acetonitrile was used as solvent at the two lower temperatures, cyclohexane at the higher temperatures (see text). A standard solution was used to monitor lamp fluctuations. [b] Calculated as described in the text. (See also: Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1974**, *96*, 439.) An overall error of 20% is estimated on the basis of the estimated error in the lifetime of **8** at 20 °C as measured previously in our laboratory (ref 53) and an estimated 10% error in the fluorescence intensity measurements.

decomposition, confirming the role of the $^3n,\pi^*$ state of **8** as precursor to **9**.

Temperature Dependence of Fluorescence and Product Yields. The QE for formation of **9** on direct irradiation of **8** at 300 nm was determined at three different temperatures (see Table IV). Acetonitrile was used as solvent at −14 °C and cyclohexane at 20 and 72 °C. Since solutions of **8** of the same optical density in purified acetonitrile and cyclohexane at room temperature showed identical fluorescence intensity within experimental error, the total rate of decay of excited singlets of **8** must be nearly the same in the two solvents at a given temperature. Therefore, the observation that Φ_9 increases by almost 100% as the temperature is raised from −14 to +72 °C indicates that a true temperature effect on the 1,3-SAS reaction is operative.

However, no increase in Φ_9 under conditions of acetone sensitized excitation was observed when the temperature was raised from 0 to 43 °C (Table V). At the concentration of **8** used in this experiment, $\Phi_{ET}{}^{T-T}$ (eq 7) is less than 1. However, since an increase in temperature should tend if anything to increase both k_{ET} and Φ_{ET} at a fixed concentration of the acceptor (**8**), assuming exciplexes are not involves in the photosensitization, the results indicate that $\Phi_9{}^T$ is temperature independent over this range of temperatures.

The variation of the fluorescence intensity of **8** at 400 nm was also monitored over the temperature range −22 to +72 °C. The results are summarized in Table VI. Acetonitrile was used again as the solvent at the two lower temperatures, cyclohexane at the higher temperatures. The UV absorption spectrum of **8** in acetonitrile is slightly less structured then the spectrum in cyclohexane, but otherwise completely similar, while the fluorescence spectra in the two solvents were identical, with $\lambda_{\max}$ 390 nm. A small increase (approximately 5%) in optical densities of solutions of **8** in cyclohexane between 20 and 72 °C was observed, but at a fixed temperature the fluorescence intensities of solutions of **8** whose optical densities varied by this amount were indistinguishable. The change in fluorescence with temperature was reversible, implying no thermal decomposition of **8** had occurred. The singlet lifetimes given in Table VI were calculated from the relationship in eq 8 on the basis of the measured value[14] of τ_s of

$$\Phi_F{}^a/\Phi_F{}^b = (k_F{}^a\tau_s{}^a)/(k_F{}^b\tau_S{}^b) \qquad (8)$$

0.41 ± 0.05 ns at 20 °C and assuming as usual that k_F (the radiative rate constant) is independent of temperature (a and b, respectively) over this range.

From these data, it is clear that upon direct excitation of **8**, a rise in temperature results in an increase in Φ_9 concomitant with a *decrease* in the fluorescence yield, while Φ_9 on acetone photosensitization is unaffected by a similar change in temperature. These data are consistent with the view that the singlet-derived 1,3-SAS reaction experiences a small energy of activation while no such barrier exists on the pathway leading to **9** from the T_2 $^3n,\pi^*$ state.

Effects of Xenon Perturbation. While the studies described above established that the formation of **9** from **8** under conditions of triplet sensitization proceeds from the triplet n,π^* state of **8** (T_2), they do not define the role of the T_2 state in the photochemistry of **8** upon direct excitation. The participation of the S_1 state in the formation of **9** is strongly suggested by the variation of quantum yields with temperature discussed above, but more definitive evidence was sought. Simple correlation of the quantum efficiency of product formation (Φ_9) with fluorescence quenching would not provide the needed data, since both processes should be identically effected by typical singlet quenchers (which cause decay from S_1 to S_0) regardless of which state is the precursor to **9**. However, if the quenching process were to promote ISC rather than decay from S_1 to S_0, the possibility arises of simultaneously quenching fluorescence and facilitating the formation of **9** via T_2.

Table **VII**. Effect of Xenon on the Fluorescence Intensity of Enone 8 and the Quantum Efficiency of Formation of 9[a]

xenon, atm	rel decrease in fluorescence intensity, %	$\Phi_F{}^\circ/\Phi_F{}^{Xe}$	$\Phi_9{}^{Dir}$
0			0.058
1[b]	8.0	1.08	nd[c]
2.2	21.1	1.25	0.072
2.3	21.0	1.25	nd[c]
2.0	21.7	1.26	nd[c]

[a] Fluorescence intensity and quantum efficiency of reaction measured in cyclohexane solution. Enone concentration 1.7 × 10^{-2} M, corresponding to an optical density of 1.647 at the excitation wavelength of 298 mm. [b] Estimated crudely. [c] Not determined in this run. See text.

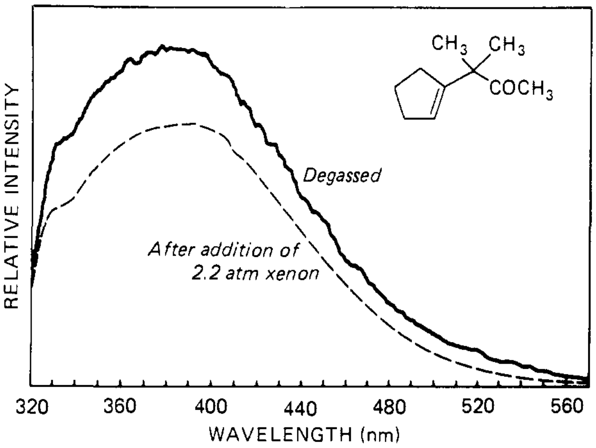

Figure 1. Fluorescence of I in spectrograde cyclohexane in the absence (solid line) and presence (dashed line) of 2.2 atm of xenon.

Heavy-atom perturbation enhances the rates of singlet–triplet radiationless transitions, such as ISC from excited singlets to triplets and from triplets to the singlet ground state.[30,31] Although well-known in the photochemistry of aromatic hydrocarbons and some related systems,[31-34] such effects are virtually unknown in ketone photochemistry.[35,36] Nevertheless, experiments using xenon (Xe) as a potential heavy-atom quencher of the S_1 state of **8** were carried out, and to our surprise and delight, these experiments gave positive and very interesting results.

As is shown in Table VII, irradiation of **8** in the presence of up to 2.3 atm Xe results in a *decrease* in the intensity of fluorescence of **8** and an *increase* in Φ_9. Initial experiments in a standard fluorescence cell in which 1 atm of Xe was dissolved in a cyclohexane solution of **8** indicated that fluorescence quenching may have been taking place, and therefore a special cell was constructed to withstand higher xenon pressures in order to magnify the effect. The fluorescence quenching effect was then found to be well outside the limits of experimental uncertainty (see Figure 1) and was reproducible. No change in the absorption or in the shape of the emission spectra of **8** in the presence of Xe was noted, indicating that there was no detectible complex formation between **8** and Xe that might reduce the fluorescence yield. Optical densities of cyclohexane solutions of **8** before and after addition of Xe were the same within the third decimal place. Similar experiments with acetone showed that there is no decrease in acetone fluorescence in the presence of Xe.

Two solutions of **8** in cyclohexane, differing only in that 2.2 atm of Xe was added to one sample, were irradiated in tandem through a Pyrex filter on an optical bench in an apparatus that alternatively placed each sample in the light beam for fixed and identical periods of time. The yield of **9** was determined by GLC analysis with internal standards (see Experimental Section) and was converted into quantum yields (Table VII) in the usual manner. The increase in Φ_9 in the presence of 2.2 atm of Xe was found to be 38 ± 4%. Two additional runs in which only the starting material was monitored by UV absorbance indicated a 22% increase in the disappearance of **8** in samples containing 2.2–2.3 atm of Xe. The only product detected on GLC analysis was **9**, but quantum efficiencies were not determined in these runs.

Applying the Stern–Volmer quenching equation to the fluorescence data, with a Xe concentration in cyclohexane of 0.45 M calculated from Xe solubility data and Henry's law,[37] the rate constant for fluorescence quenching of **8** by Xe was found to be $(1.38 \pm 0.6) \times 10^9\ M^{-1}\ s^{-1}$. This value is comparable to rates of Xe quenching of excited singlets of polycyclic aromatic hydrocarbons.[33]

None of the ODPM rearrangement product **10** could be detected on GLC analysis of the product mixture from irradiation of **8** in the presence or absence of Xe. In order to ascertain if the Xe quenched the T_1 state of **8**, which is the precursor of **10** (see above), the ratio of **9** to **10** on acetone-sensitized excitation of **8** was determined in the presence of 2.1 atm of Xe in tandem with an identical solution (0.01 M in **8**) without Xe. The ratio was 3.8 ± 0.2 in both instances, implying that the reaction leading from T_1 to **10** (QE 0.027 ± 0.003) is not quenched by the 2 atm of Xe and therefore that **10** should be detectable under conditions that populate T_1. In other systems, Xe also turns out to be an ineffective triplet quencher.[31-33,38] Thus, it can be concluded that the T_1 state of **8** is not populated from S_1 by ISC either in the presence or absence of Xe. Verification of these findings in some other system with a higher QE for the ODPM rrearrangement would be highly desirable.

Dynamic Nuclear Polarization Effects. Encouraged by the dramatic photo-CIDNP effects observed by Schaffner and coworkers[18] in their study of enones **3**, **6**, and **7**, attempts were made to observe such effects with enone **8** in two different laboratories. In experiments carried out at the Institüt für Strahlenchemie in Mülheim,[39] weak polarizations were observed at room temperature in the spectra of **8** and the 1,3-SAS product **9**, consistent with formation of these compounds from a triplet radical pair intermediate. Experiments at Bell Labs,[40] however, gave entirely negative results, not only at room temperature but also at lower and higher temperatures. Apparently, the dynamics of the radical pair processes with **8** are sufficiently different from those of **3**, **6**, and **7** to prevent observation of unequivocal photo-CIDNP effects in this system.

Discussion

The results of these studies are consistent with the kinetic scheme for the photochemical behavior of enone **8** (E) given in Scheme III, where S represents a triplet sensitizer, Q a triplet quencher, and RP a radical pair (singlet or triplet multiplicity). There can be no question now that the ODPM and 1,3-SAS rearrangements arise from different triplet excited states, T_1 $(^3\pi,\pi^*)$ and T_2 $(^3n,\pi^*)$, respectively, on the basis of the differential quenching and sensitization results, as well as sensitization via thermal decomposition of TMD. It is also clear that reaction from T_2 competes effectively with internal conversion to T_1. In fact, the absence of product **10** upon direct excitation of **8** in the presence of Xe, under conditions where T_2 is unquestionably being populated, suggests that radiationless decay from T_2 to T_1 in this system is very inefficient.

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(40) In collaboration with Dr. H. Roth.

Scheme III

$$E_0 \xrightarrow{h\nu} {}^1E^* \qquad (n,\pi^*)$$

$${}^1E^* \rightarrow E_0 + h\nu_F$$

$${}^1E^* \rightarrow [{}^1RP]^? \rightarrow 1,3\text{-SAS} + S_0$$

$${}^1E^* \rightarrow T_2 \qquad (n,\pi^*)$$

$${}^1E^* + Xe \rightarrow T_2 + Xe$$

$$T_2 \rightarrow {}^3RP \rightarrow 1,3\text{-SAS} \qquad (+ S_0?)$$

$$T_2 \xrightarrow{?} T_1 \qquad (\pi,\pi^*)$$

$${}^1E^* \xrightarrow{?} T_1$$

$$T_1 \rightarrow \text{ODPM}$$

$$T_1 \rightarrow E_0$$

$$\text{Sens} \xrightarrow{h\nu} {}^1S^* \rightarrow {}^3S^*$$

$${}^3S^* + E_0 \rightarrow T_1 + T_2$$

$$T_1 \text{ or } T_2 + Q \rightarrow E_0 + {}^3Q^*$$

The inverse temperature dependence of the fluorescence yield of Φ_9 strongly suggests that **9** is being formed, at least in part, from the S_1 state of **8** by a reaction that encounters an energy of activation. If the assumption is made that the formation of **9** occurs exclusively from S_1 over the temperature range from 20 to 72 °C, a value of 4 kcal/mol can be calculated for E_{act}. To the extent that T_2 is a also a precursor to **9** under conditions of direct excitation of **8**, this value would become somewhat higher. The data also indicate that formation of **9** from T_2 experiences no such barrier.

The observed temperature effects could also be explained if ISC from S_1 were thermally activated.[41] This would be the case if ISC occurred preferentially from higher vibrational levels of S_1 and/or to a triplet state slightly higher in energy than S_1, as is known to take place with some anthracene derivatives. Turro has concluded that the rate of ISC for alkanones is expected to be temperature independent,[42] and this would seem likely for enone **8** as well. The sensitization data indicate that both T_2 and T_1 lie energetically well below S_1, so there is no reason to invoke any substantial energy barrier to ISC in this system.[41] Therefore we conclude that the observed temperature effects provide strong evidence for a thermally activated 1,3-SAS process from the S_1 state of **8**. As discussed earlier, Schaffner and co-workers[18] have come to the same conclusion on the basis of temperature-dependent CIDNP effects seen for **3**, **6**, and **7**, but we were unable to obtain consistent CIDNP data for **8**.

The low absolute quantum yields for product formation on both direct and triplet-sensitized excitation of **8** are tentatively attributed to reversible formation of radical pairs (in the 1,3-SAS process) and 1,3-biradicals (in the ODPM rearrangement), which are generally accepted intermediates in these reactions.[2,18,43] Reversible α cleavage is well established experimentally in other systems by photo-CIDNP effects observed in recovered starting materal.[18,28,44,45] The experimental data do not exclude the possibility that at least a portion of the singlet-derived 1,3-SAS process may occur in a concerted manner in competition with a stepwise reaction via a radical pair in this as well as other systems.[60]

The observation that the S_1 state of **8** is sensitive to external heavy-atom perturbation by Xe provides excellent confirmation of the above conclusions. Wagner[35] experimentally demonstrated some time ago that heavy-atom solvents have no effect on the ISC rate of alkanones.[36] Decay rates from triplet n,π^* states to ground states were also predicted[46] to be insensitive to internal heavy atoms in X_2CO where X is a halogen, although that conclusion was disputed.[47] To the best of our knowledge, there has been no documented case prior to the present study of a heavy-atom effect on ISC of ketones. While Morrison and co-workers[48] did observe that an external heavy atom can affect the photochemical behavior of coumarin, an α,β-unsaturated ketone, it was found that the heavy atom does not affect ISC but rather perturbs later stages of the reaction mechanism leading to dimers, specifically rates of spin inversion in intermediate 1,4-biradicals. Thus, the Xe effects on the photochemistry of **8** are entirely unique and unprecedented. Morrison has concluded that intersystem crossing from S_1 π,π^* states of arenes is particularly susceptible to rate enhancement by Xe.[31]

Chae and Givens have recently reported that halogen (Cl and Br) substitution in bicyclo[3.2.1]oct-2-en-7-ones decreases the QE of fluorescence and photoreaction, which they attributed to a heavy-atom enhancement of radiationless decay from S_1 to the ground state.[49] Interestingly, they found no evidence for enhanced intersystem crossing. An even larger effect of the halogens on the efficiency of product formation upon triplet sensitization was observed, attributed to enhanced radiationless decay from T_1 to the ground state. Evidence was also obtained[49] that the triplet sensitized 1,3-SAS and ODPM processes originate from different triplet states T_2 and T_1, respectively. Their data does not exclude the possibility of population and subsequent 1,3-SAS reaction of T_2 on direct excitation of these enones.

While the generality of Xe effects on the photochemical behavior of β,γ-enones obviously remains to be explored, some speculation on these unique observations seems in order. The extensive chromophoric interaction in β,γ-enones results in greatly enhanced n,π^* absorption intensities compared with alkanones and aryl ketones, unless prevented by geometrical constraints, and has been attributed to enhanced π,π^* character in the S_1 state, which increases the allowedness of the transition from the ground state.[2a,50,51] This idea is supported by a number of molecular orbital calculations on model β,γ-enones.[27,52,53] The altered electronic character of the S_1 state of these enones may also make them more susceptible to heavy-atom perturbations, which are established for arene π,π^* singlet states.[31,34]

El-Sayed's rules[54,55] state that ISC in ketones and nitrogen heterocycles and related compounds should preferentially occur between singlet and triplet states of different electronic configuration, on the basis of consideration of the matrix elements governing radiationless transitions within the framework of the Born–Oppenheimer approximation. In the present case, these rules would predict preferential intersystem crossing from S_1 (n,π^*) to T_1 (π,π^*) rather than to T_2 (n,π^*), contrary to the experimental observations. It may be, as suggested by a referee, that El-Sayed's rules are not applicable to bichromophoric systems in which there

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(41) For a discussion, see: ref 29, pp 187–188.

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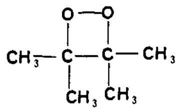
is extensive interaction resulting in highly mixed configurational character of the lowest singlet and triplet excited states, as is the case with many β,γ-enones including **8**.[2a,50,51] However, one could argue that the concepts behind these selection rules for radiationless transitions should be generally applicable,[55] although the degree of selectivity may be reduced in bichromophoric systems compared with "pure" model systems. It is clear that the applicability of these selection rules[54,55] to bichromophoric systems remains to be critically examined. At any rate, our results indicate that in the case of **8** spin orbit coupling appears to be enhanced in the presence of xenon over such coupling in the absence of xenon, although a more precise description of the effect is presently not possible.

This xenon effect may or may not be a general phenomenon in the photochemistry of β,γ-enones, as indicated by the limited number of cases examined so far. The fluorescence of bis(β,γ-enone) **12** is also quenched by Xe, an observation that has been independently reproduced in our laboratory on using freshly prepared samples. However, the fluorescence of enone **13** was not quenched by Xe. There was also no effect of Xe on the fluorescence of acetone.



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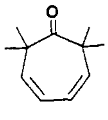

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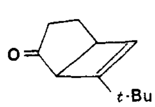

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Finally, it should be noted that this investigation, which was initiated because of the problems that arose in assigning multiplicity to the excited state precursor of the 1,3-SAS process, has important general implications in photochemistry. As in many other reactions in organic photochemistry, the assignment of singlet multiplicity to the precursor of the 1,3-SAS process was based entirely on negative evidence, namely, the fact that the reaction was *not* quenched by typical triplet quenchers and was *not* sensitized by typical sensitizers.[2-10] It is now clear that these observations do not distinguish between reactions occurring from a short-lived singlet excited state and upper triplet excited states.[15-17,28] For systems in which only the T_1 state is lower in energy than S_1, such criteria may be sufficient to justify assignment of singlet multiplicity to the reacting state. However, in unsaturated ketones and probably many other systems where two or more lower energy triplet states are accessible from S_1, it is not possible to make definitive multiplicity assignments from such negative experimental data, and more elaborate experiments such as those described in this paper may be required. Not too long ago, the notion that reactions from an upper triplet state such as T_2 could compete with radiationless decay to T_1 would have been regarded with derision. The results of this and other [17,18] studies in the field of β,γ-enone photochemistry show that T_2 states in some cases may react to the exclusion of internal conversion to T_1, especially when the reaction involves a unimolecular isomerization. The applicability of these findings to other classes of compounds remains to be demonstrated. At the very least, these results indicate that there are more mechanistic alternatives in photochemical reactions that were realized 20 years ago when mechanistic organic photochemistry became a serious intellectual endeavor.

Experimental Section

Instrumentation. ^{1}H magnetic resonance (^{1}H NMR) spectra were recorded on Perkin-elmer Model R-24 or R-20B spectrometers at 60 MHz. Solutions in $CDCl_3$ were utilized containing Me_4Si as the internal standard. Ultraviolet (UV) spectra were recorded on a Perkin-Elmer Coleman 124-D double-beam spectrophotometer, with spectrograde cyclohexane and acetonitrile as solvents. Infrared (IR) spectra were recorded on a Perkin-Elmer 735 grating spectrophotometer using polystyrene calibration. Mass spectra (MS) were taken by W. Davidson (Halcon Research and Development Co.) on a Varian MAT-122 double-focusing mass spectrometer. Fluorescence emission spectra were taken on a Hitachi Perkin-Elmer MPF-2a spectrofluorimeter. A Hewlet-Packard Model 580A chromatograph was used for analytical GLC, with *n*-tridecane as internal standard added to reaction mixtures after irradiation. Response factors of products **9** and **10** were found to be the same within experimental error. A Varian Aerograph Model 920 chromatograph was used for all preparative GLC work, with helium as the carrier gas, sample injection of 20 μL, and collection in U tubes cooled in dry ice–isopropyl alcohol mixtures. A Waters Associates LC200 chromatograph with an M6K injection port and M600 pump was used for HPLC analyses.

Synthesis of 3-Methyl-3-(1-cyclopentenyl)butan-2-one (8). Enone **8** was prepared following the published procedure,[10] with only slight modifications. The enone was obtained as a colorless oil, bp 80–84 °C (7.7–8.0 mm), and was purified prior to photolysis by the following methods: (a) preparative GLC on 20% XE-60 on 60–80 mesh Chromosorb W or 30% Carbowax 20M on 60–100 mesh Chromosorb P; (b) HPLC on a microporasil column using 5% ether in hexane as elutant; (c) column chromatography on fluorisil using pentane as the eluting solvent; (d) column chromatography on silica gel using 2% ether in hexane as the eluting solvent. The spectral properties of **8** are as follows: IR (neat) 2950, 2850, 1715, 1640, 1360, 1340, 960 cm^{-1} (lit.[10] 1714 cm^{-1}); ^{1}H NMR δ 5.65 (m, 1 H), 2.05 (s, 3 H), 1.90–2.50 (m), 1.25 (s, 6 H) (lit.[10] 5.63 (m, 1 H), 1.99 (s, 3 H), 1.90–2.50 (m), 1.23 (s, 6 H)); MS *m/e*, 152 (M^+), 109, 93, 91, 66 (100%), 55, 43, 28: UV $\lambda_{max}{}^{C_6H_{12}}$ 298 nm (ϵ 118) (lit.[10] $\lambda_{max}{}^{C_6H_{12}}$ 300 nm (ϵ 118)).

Preparative-Scale Sensitized Irradiation of Enone 8. A 1-g sample of enone **8** in 150 mL UV-grade acetone in a Pyrex tube was purged with nitrogen for 15 min, and the tube was placed in a Rayonet RPR-204 Type RS preparative reactor containing four low-pressure U-shaped mercury lamps, with a maximum wavelength of 300 nm and a bandwidth of 30 nm. The tube was placed in a water-cooled jacket suspended in the center of the reactor, and the solution was agitated by nitrogen bubbled through it during the course of the irradiation. The photoreaction was allowed to proceed to ca. 30% conversion (at higher conversions additional peaks appeared on GLC analysis of the photolysate). After irradiation, the solvent was removed at reduced pressure on a rotary evaporator, leaving an oil containing **8**, **9**, and **10**. Analysis of the photolysate was accomplished by GLC on a 0.25 in. × 6 ft 10% SE-30 on 60–80 mesh Chromosorb P column at 100 °C with an He flow rate of 40 mL/min or by HPLC on a microporasil column using 5% ether in hexane as the eluting solvent. The ^{1}H NMR spectra of the products were as follows: ketone **9**, δ 3.41 (br s, 1 H), 2.06 (s, 3 H), 1.54 (s, 3 H), 1.66 (s, 3 H), 1.70–2.46 (m) (lit.[10] 3.37 (br m, 1 H), 2.00 (s, 3 H), 1.64 (br d, 6 H), 1.70–2.40 (m)); ketone **10**, 2.04 (s, 3 H), 1.50–2.40 (m), 1.10 (s, 3 H), 1.01 (s, 3 H) (lit.[10] 2.08 (s, 3 H), 1.50–2.10 (m), 1.08 (s, 3 H), 1.00 (s, 3 H)).

Quantum-Yield Measurements. Sample were irradiated with the output of an Osram HBO 200-W super-pressure mercury lamp, type L2/W2, after being passed through a Bausch and Lomb Model 33-86-25 UV grating monochromomator. A Corning 7-54 filter was used to remove visible light. A split-beam technique was utilized[56] in which the major portion of the beam passed directly into the cell and a minor portion was deflected to a cell containing the actinometer. The beam split ratio, determined several times during each run, was measured with actinometer solutions in both compartments. Potassium ferrioxalate actinometry[57,58] was used throughout this study. To reduce errors in the determination of the beam split ratio, we placed a light screen of transmittance 7.52% at 298 nm (OD 1.124) in front of the sample cell, so that the number of photons entering the cell was close to that impinging on the reference cell. The chemical yields of photoproducts were determined by GLC analysis on a $^1/_8$ in. × 6 ft 10% Carbowax 20M on 60–100 mesh Chromosorb P column, with *n*-tridecane as the internal standard, by using a temperature program in which the column temperature varied from 108 to 200 °C. Response factors of the products were determined in the usual manner by using known amounts of pure compounds and the standard. A minimum of five injections were made for each determination. A maximum error of 10% in the derived quantum yields is estimated, mostly derived from errors involved in the determination of the quantity of

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(56) Barile, G. C. Ph.D. Dissertation, New York University, 1977.

(57) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A*, **1956**, *235*, 518.

(58) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; pp 783–786.

photons adsorbed by the sample in each run.

Quenching Studies. The quencher 2,5-dimethyl-2,4-hexadiene (Chemical Sample Co.) was distilled, purified by GLC (20% XE-60 on 60–80 Chromosorb W), and passed several times through an alumina column until the sample presented no fluorescence above 330 nm. A neat sample of the purified diene presented a small UV absorption at 310 nm (OD 0.180). Studies of the effect of this diene on the formation of **9** on direct irradiation of **8** were carried out by using a Wild–Heerbrugg housing containing a 200-W Osram HBO super-pressure mercury lamp, with an OPTIQUIP Model 1022 power supply. The bottom of a Pyrex beaker was used to filter out light below 290 nm.

Differential quenching studies were carried out in a precision rotating turntable (Moses Co.) surrounding a water-cooled Pyrex-jacketed 450-W high-pressure mercury lamp. The turntable holds test tubes in cavities which are precisely bored so that each tube receives the same amount of light.

Measurements of Temperature Dependence. For the fluorescence measurements, the same and reference cuvette holders were jacketed for constant-temperature control. For low-temperature measurements, methanol cooled in a dry ice–isopropyl alcohol heat exchanger was circulated through the cell holders, and dry nitrogen was blown through the cavity of the spectrofluorimeter to prevent fogging of the sample cell due to condensation. The temperature of the sample was measured with a thermocouple with one end inserted in the reference cell. For measurements at 0 °C, methanol cooled in a constant-temperature bath was circulated through the jackets. For measurements at higher temperatures, water heated in the constant-temperature bath was circulated through the cell jackets.

For the quantum-yield measurements, the heating and cooling systems were identical with those described above. However, in the low-temperature measurement, the temperature could not be kept precisely constant since (a) the sample cell in this apparatus is not enclosed, and nitrogen had to be blown directly on to the cell face to prevent fogging, and (b) the long time period required for the measurements caused heating of the circulating pump, which in turn created problems in holding the bath at a constant temperature. The temperature reported in the first entry of Table IV is the average value observed during the experiment.

Xenon Perturbation Effects. A special cell, including a fluorescence cuvette and a degassing chamber, was designed and constructed (International Crystal Co.) to withstand gas pressures of up to 3 atm. The unit is connected to a ball joint through a Teflon valve prossessing solvent-resistant neoprene O-rings. A cyclohexane solution of the enone of interest is placed in the cell and is thoroughly degassed by several freeze–pump–thaw cycles, after which the valve is tightly closed. The cell is then attached at the ball joint to a glass manifold. A stopcock was blown onto a 1-L Xenon bulb above the break seal, and this unit was attached to the manifold, which was also connected to a vacuum line and a manometer. With the stopcock on the Xe bulb in the open position, the unit was evacuated. This stopcock was then closed, the seal to the Xe bulb was broken with a magnet, and a manometer reading was taken. The system was then isolated from the vacuum line, and Xe was admitted to the manifold, after which the stopcock at the Xe bulb was closed and another manometer reading was made. The valve was opened, admitting the Xe into the sample chamber, cooled in liquid nitrogen, until the desired decrease in pressure was noted on the manometer (the Xe was collected at this point in the frozen state), whereupon the valve on the sample cell was tightly closed. The pressure of Xe in the sample cell after the cell was allowed to warm to room temperature could be calculated from the three manometer readings, the volume of the sample cell, and the volume of the entire manifold.[59] The entire sample cell could be placed into the sample compartment of the spectrofluorimeter or the quantum-yield apparatus for the desired measurements.

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Registry No. 8, 39782-06-4; **9**, 39782-09-7; **10**, 39782-11-1; acetone, 67-64-1.

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(59) For further details on the procedure and calculations, see: Calcaterra, L. T. Ph.D. Dissertation, New York University, 1981.

(60) Schaffner and co-workers (private communication) have found that the dominant 1,3-SAS pathway of **6** (R = CD_3) is enantioselective, and involves either a fast primary geminate recombination of ^{1}RP to give unpolarized products or a symmetry-allowed concerted reaction.

Concerted Homolysis in Thermal Decomposition of Peresters from *α*-Hydroperoxydiazenes

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Abstract: Treatment of 2-(phenylazo)-2-propyl hydroperoxide with benzoyl chloride and pyridine in ether or in hydrocarbon at −5 °C afforded the unstable 2-(phenylazo)-2-propyl perbenzoate (**1**). Thermolysis of **1** in *p*-chlorotoluene, chlorobenzene, or deuteriochloroform followed first-order kinetics with rate constants $6.4 \pm 0.7 \times 10^{-4}\ \mathrm{s}^{-1}$, $4.5 \times 10^{-4}\ \mathrm{s}^{-1}$, and $5.1 \pm 0.7 \times 10^{-4}\ \mathrm{s}^{-1}$, respectively, at 10 °C. Those rate constants are about 10^8 times as large as the rate constant for thermolysis of *tert*-butyl perbenzoate, which is known to react by one-bond scission. The much higher reactivity of **1** implies that it reacts by a concerted mechanism, to form the benzoyloxy radical, acetone, and phenyldiazenyl radical as initial fragments. Attempts to prepare 2-(*tert*-butylazo)-2-propyl perbenzoate (**2**), from 2-(*tert*-butylazo)-2-propyl hydroperoxide by the analogous procedure, failed. That failure suggests that **2** decomposes still more rapidly than **1**, and the further enhancement of reactivity implies that **2** decomposes by concerted, 3-bond scission to yield benzoyloxy radical, acetone, nitrogen, and *tert*-butyl radical in the rate-determining step. The mechanisms of thermolysis of **1** and **2** are pertinent to the chemistry of *α*-hydroxydiazenes and *α*-hydroperoxydiazenes, for which concerted, induced decomposition pathways have been postulated earlier.

Fragmentations that produce more than two fragments from one molecule of substrate have long attracted the attention of mechanistic chemists. Since more than one bond is broken in such processes, the scissions can be either sequential or concerted. Well-studied systems that generally involve homolytic bond breaking include azo compounds, peresters, and diacyl peroxides, all of which can fall into either the stepwise or the concerted mechanistic category, depending on the substituents.

There is no information on the mechanisms followed by systems in which both the azo and the peroxide functions are present and contiguously located, as in an azo peroxide ($>\mathrm{C(OOR')N{=}NR}$) or an azo perester ($>\mathrm{C(OOC(O)R')N{=}NR}$). Decomposition of the former could involve concerted cleavage of a maximum of three bonds, to form R′O·, $>\mathrm{C{=}O}$, N_2, and R·. The latter has

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