J. Am. Chem. Soc. **1986**, *108*, 4561–4567

nm. Capillary GC monitoring on a 50-m OV 101 column, operated at column, injector, and detector temperatures of 110, 150, and 175 °C, respectively, with a carrier gas (N_2) flow of 0.8 mL/min, showed that consumption of the divinyl ether **2** was completed after 60 min, but only higher molecular weight products were formed.

Control Experiments. Photostability of the Photoproducts of Epoxy Ketone 1. Aliquots of 2 mL of 0.005–0.01 M solutions of the authentic photoproducts of the epoxy ketone **1** in *n*-pentane were irradiated independently at 300 nm for 225 min with 1-hexanol as internal standard. The concentrations of the substrates were monitored by capillary GC (for conditions cf. quantitative photolysis). A significant decrease of concentration could not be observed for any of the photoproducts of epoxy ketone **1**.

Photostability of Epoxide 6 in the Photolysate of Divinyl Ether 2. A sample of 30.0 mg (0.238 mmol) of divinyl ether **2** and 20.0 mg (0.159 mmol) of authentic epoxide **6**[15] in 10 mL of absolute acetonitrile was purged with nitrogen for 10 min and irradiated at 254 nm. The concentrations of **2** and **6** were monitored by capillary GC, using a 50-m OV 101 column operated at column, injector, and detector temperatures of 70, 150, and 175 °C, respectively, with a carrier gas (N_2) flow of 1.0 mL/min. After 100 min of irradiation, the decomposition of the divinyl ether **2** was completed, whereas only a slight decrease in the concentration of the epoxide **6** could be observed. In a second run a solution of 50.0 mg (0.396 mmol) of divinyl ether **2** in 5 mL of absolute acetonitrile was purged with nitrogen for 10 min and photolyzed to 64% consumption of the starting material (ca. 25 min). To the photolysis mixture 50.0 mg (0.396 mmol) of the epoxide **6** was added and the photolysis continued. Again a rapid decay of the divinyl ether **2** was observed, whereas epoxide **6** was inert. In a third run, 40.0 mg (0.317 mmol) of epoxide **6** in 20 mL of absolute aceonitrile was irradiated for 1 h. By means of coinjection of this solution with the photolysate of divinyl ether **2**, the absence of decomposition products of epoxide **6** was established.

Photostability of 2,5-Dimethyl-4-hexen-3-one[10] (3) in the Photolysate of Divinyl Ether 2. A sample of 7.46 mg (0.0591 mmol) of divinyl ether **2** and 11.4 mg (0.0903 mmol) of enone **3** was dissolved in 5 mL of absolute aceonitrile. An aliquot of 2 mL was purged with nitrogen for 10 min and irradiated at 254 nm. The concentrations of **2** and **3** were monitored by capillary GC (for conditions cf. above photostability experiment). After 75 min of irradiation, 61% of divinyl ether **2** was consumed, whereas the concentration of the enone **3** remained unchanged.

Photostability of 2,2,3,3-Tetramethylbutanedial, Isobutyraldehyde, and Isobutylene in the Photolysate of Divinyl Ether 2. The shapes of the concentration vs. time profiles (for recording conditions cf. yield of pentenal **5**) of these photoproducts indicated that secondary photolysis did not occur in the presence of excess divinyl ether **2**.

Formation of 3,5-Dimethyl-4-hexen-2-one. A solution of 35.0 mg (0.277 mmol) of ene epoxide **6** in 20 mL of acetone was irradiated at 300 nm for 80 min until 75% conversion of the ene epoxide **6** to its isomeric 3,5-dimethyl-4-hexen-2-one.[16] By means of capillary GC coinjection (for conditions cf. yield of pentenal **5**) of this solution with the photolysate of divinyl ether **2**, the absence of the enone as a photoproduct of divinyl ether **2** was confirmed.

Absence of 2,5-Dimethyl-2,4-hexadiene in the Photolysate of Divinyl Ether 2. Capillary GC coinjection (for conditions cf. yield of pentenal **5**) of the photolysate of divinyl ether **2** with an authentic sample of 2,5-dimethyl-2,4-hexadiene established that it was not formed as a photoproduct.

Quantum Yield (ϕ_{-S}) of Epoxy Ketone 1. Aliquots of 2.4 mL of solutions of epoxy ketone **1** (0.0340 M) and of cyclopentanone (0.0338 M) in *n*-pentane with 1-hexanol as internal standard were photolyzed at 300 nm under identical irradiation conditions, the decay of the substrates being monitored by capillary GC (for conditions cf. quantitative photolysis of epoxy ketone **1**). The relative decay rates of the two ketones were determined from the initial slopes of their concentration vs. time profiles. When the known ϕ_{-S} of cyclopentanone ($\phi_{-S} = 0.28$)[11] was employed, the ϕ_{-S} of epoxy ketone **1** was found to be 0.29 ± 0.03.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

Registry No. 1, 97455-13-5; **2**, 764-51-2; **3**, 13905-13-0; **4**, 97455-14-6; **6**, 13295-59-5; 2,4,4-trimethylcyclopenten-3-one, 71221-73-3; 2,2,5-trimethylcyclopentanone, 4573-09-5; 3,3,5,5-tetramethylcyclopentenone, 81396-36-3; 3,3,5,5-tetramethylcyclopentenone 2,4-dinitrophenylhydrazone, 102521-12-0; methyl isopropyl ketone, 563-80-4; acetone, 67-64-1.

Stereospecific Photoreduction of Polycyclic α,β-Unsaturated Ketones[1]

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Contribution from the Department of Chemistry, New York University, New York, New York 10003. *Received September 12, 1985*

Abstract: The photolysis of 4a-methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (**1**) in isopropyl alcohol (*i*-PrOH) is found to give lumiketone rearrangement product **5** and reduction product **8** via the enone triplet π,π^* excited state. Other reduction products, **6**, **7**, and **9**, arise from the triplet n,π^* excited state. The lower limit of the energy of the triplet state E_{n,π^*} is estimated to be ~67 kcal/mol above the ground state and that of the relaxed triplet π,π^* excited state is ~61 kcal/mol. Reduction of the C=C bond on the enone chromophore from both excited states is stereospecific, with the twisted π,π^* triplet leading exclusively to cis-fused bicyclic ketone and the planar n,π^* triplet to the trans-fused isomer. The results from the photolysis of 4a-methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (**4**) are consistent with these findings.

It is well-established[2,3] that 4,4-disubstituted α,β-unsaturated cyclohexenones rearrange to yield bicyclo[3.1.0]hexan-2-ones (lumiketones) upon UV excitation. It has been proposed[4] that this photorearrangement generally occurs via a twisted π,π^* excited state of the enone. However, Zimmerman et al.[5] proposed that a triplet n,π^* excited state is the reacting intermediate in the photorearrangement of 4-methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (**1**).

Two different modes of photoreduction of α,β-unsaturated cyclohexenones have been observed. Reaction directly at the C=O chromophore leads to a ketyl radical by abstraction of a hydrogen atom onto the electrophilic carbonyl oxygen of a $^3n,\pi^*$ state. This ketyl radical can either combine with another one of its kind to

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[1] Photochemistry of Ketones in Solution. 76. For part 75, see: Schuster, D. I.; Wang, L. *J. Am Chem. Soc.* **1985**, *107*, 7045.

[2] Dauben, W. G.; Spitzer, W. A.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3674.

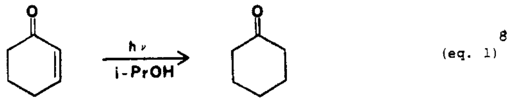
[3] Schuster, D. I.; Brown, R. H.; Resnick, B. M. *J. Am. Chem. Soc.* **1978**, *100*, 4504.

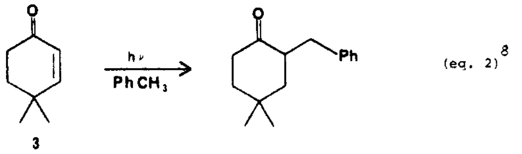
[4] Schuster, D. I. In *Rearrangement in Ground and Excited States*; De Mayo, P., Ed.; Academic: New York, 1980; Vol. III, Essay 17.

[5] Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 1965.

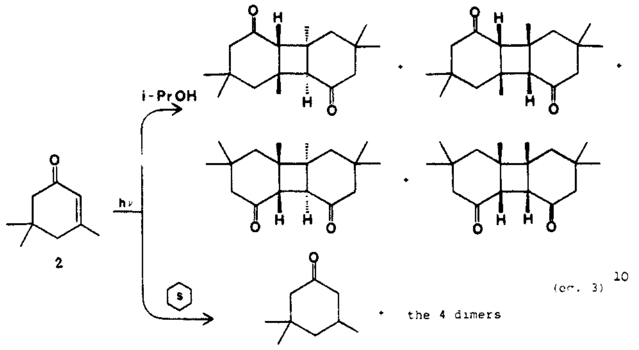
0002-7863/86/1508-4561$01.50/0

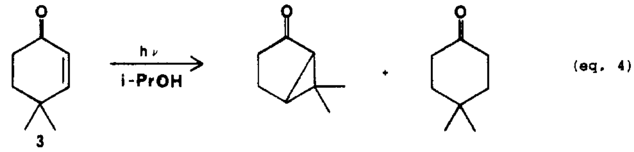
afford pinacol-type product[5,6] or can yield an alcohol by abstraction of a second hydrogen atom.[7] Reduction across the C═C bond initiated by H-abstraction onto the carbon atom accounts for the other mode of photoreduction. Products from this reaction include the cyclohexanone arising from addition of two hydrogen atoms across the C═C bond (eq 1)[8] and solvent adducts (eq 2).[9] Either





or both of the triplet n,π* or π,π* excited states may be responsible for the latter mode of reduction. For instance, photoreaction of isophorone (**2**) in polar solvents gives only [2 + 2] cycloaddition dimers, but in nonpolar solvents, in which the ^{3}n,π* excited state is stabilized,[2] a saturated cyclic ketone was also obtained in addition to the dimers[10] (eq 3). However, in the case of 4,4-dimethylcyclohex-2-enone (**3**), it has been postulated that photoreduction arises mainly from the triplet π,π* excited state[2,9] (eq 4). This is supported by the observation[9] that irradiation of **3**

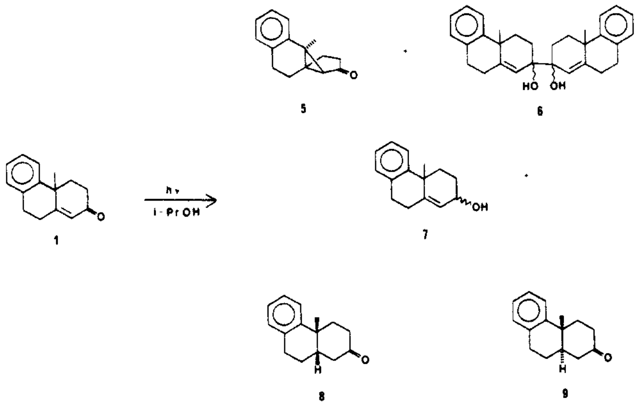


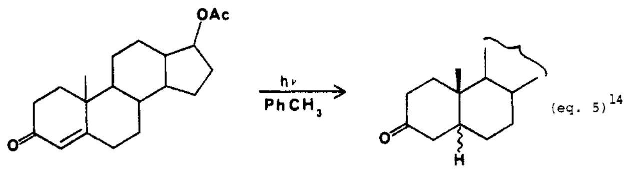


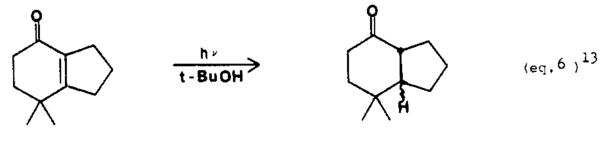
in isopropyl alcohol-*O-d* gives 75% of the cyclohexanone without deuterium incorporation. If the reduction occurred chiefly via the ^{3}n,π* excited state, a higher percentage of the cyclohexanone would be expected to contain deuterium at its α-position.[9] Furthermore, photolysis of **3** in toluene afforded only 2-benzylcyclohexanone (eq 2), indicating that reduction of the C═C bond proceeds via the ^{3}π,π* excited state of enone **3**.

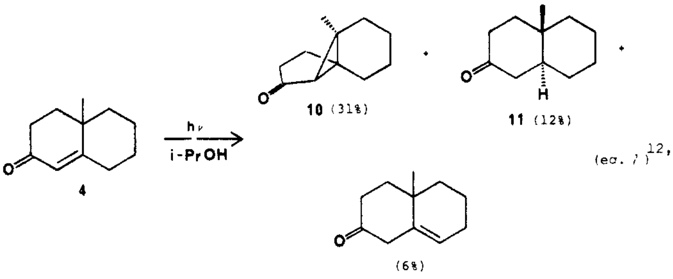
In spite of numerous examples of this reaction in the literature, the stereochemistry of photoreduction of the C═C bond in appropriate α,β-unsaturated cyclohexenones has not received much attention (see eq 5–7).[12-14] Furthermore, for the case given in eq 7, the product structure was apparently misassigned (see later discussion).

Scheme I









In order to better understand the unique behavior of compound **1**, an α,β-unsaturated ketone which was reported to give lumiketone rearrangement from a triplet n,π* excited state,[5] the photochemistry of this compound was reinvestigated.[16] This compound is also a good model for studying the stereochemistry associated with photoreduction of the C═C bond. 4a-Methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (**4**) was also studied, and the results are compared with those obtained from photoexcitation of **1**.

Results

(A) 4a-Methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (1). Upon direct irradiation of **1** at 350 nm in isopropyl alcohol (*i*-PrOH), five products (**5–9**) could be isolated (Scheme I). Each of the compounds has spectral properties identical with those of authentic samples synthesized independently.[16] The ratio of **5** to **6** was determined previously[5] to be about 5 in three photolysis

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(6) Butenandt, A.; Karlson-Peschmann, L.; Failer, G.; Schiedt, U.; Bickert, E. *Justus Liebigs Ann. Chem.* **1952**, *575*, 123.

(7) Schaffner, K. *Tetrahedron* **1974**, *30*, 1891.

(8) Nūnez, I. M. Ph.D. Dissertation, New York University, 1982.

(9) Schuster, D. I.; Nūnez, I. M.; Chan, C. B. *Tetrahedron Lett.* **1981**, *22*, 1187.

(10) Chapman, O. L.; Nelson, P. J.; King, P. W.; Trecker, D. J.; Griswold, A. A. *Rec. Chem. Prog.* **1967**, *28*, 167.

(11) Nann, B.; Gravel, D.; Schorta, R.; Wehrli, H.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1963**, *46*, 2473.

(12) Belluš, D.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta* **1969**, *52*, 971.

(13) Hussain, S. Ph.D. Dissertation, New York University, 1979.

(14) No stereochemistry was assigned to this reduction product. A mixture of isomers with bridgehead hydrogen both cis and trans to the angular methyl group was said to be formed.[12] Nann et al.[11] claimed that the trans isomer was formed in 20% yield when testosterone was irradiated in ethanol. The assignment of stereochemistry was based on the independent synthesis of the same ketone by reduction of testosterone with Pd/C under hydrogen atmosphere.[15] Nevertheless, the product of this synthetic route is more likely to have the cis configuration (see discussion in Results section).

(15) Butenandt, A.; Tscherning, K.; Hanisch, G. *Ber. Dsch. Chem. Ges.* **1935**, *68*, 2097.

(16) For a preliminary report, see: Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928 and references therein.

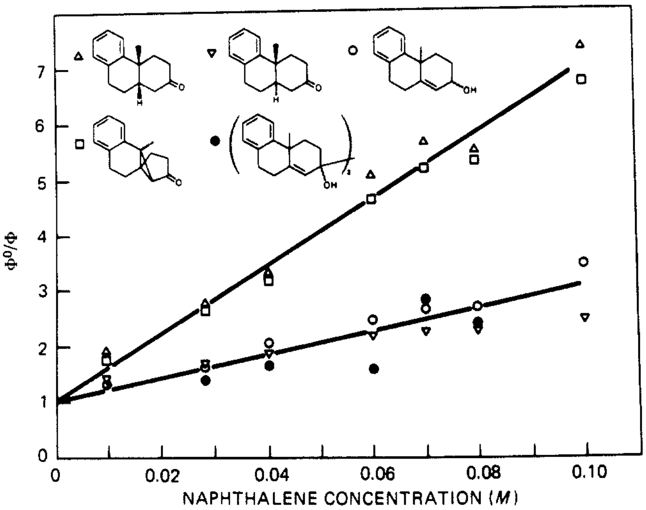

Figure 1. Stern–Volmer plots for quenching the photochemistry of 4a-methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (**1**) by naphthalene in isopropyl alcohol.

runs in *i*-PrOH, and the mass balance after irradiation of **1** in *i*-PrOH was reported to be in the range of 80–90%.[5] The proportion of the products from a typical photolysis experiment in the present work was calculated to be about 50:10:1:25:10 (**5**:**6**:**7**:**8**:**9**) from their GLC peak areas.[17] It is not likely that there are other major products besides those reported here.

Compounds **5**–**9** are all primary products since they do not interconvert upon irradiation in *i*-PrOH in separate runs, but do undergo photodecomposition. Furthermore, all of these compounds arise from triplet excited states, as shown by sensitization experiments using acetophenone or 4-methoxyacetophenone which produce no major change in the GLC peak ratio of products. Triphenylene sensitization also affords **5** and **7**–**9**; compound **6** was not detected due to limitations in the analytical method.[18]

Quenching experiments, using either naphthalene or phenanthrene, were done by irradiating *i*-PrOH solutions of phenanthrone **1** (~0.2 M) at 350 nm. The Stern–Volmer plot using naphthalene clearly indicates that there are two different excited states responsible for product formation (Figure 1). Formation of the photoproducts was unaffected by biphenyl, in accord with the results reported by Zimmerman at al.[5] When another quencher, *cis*-piperylene, with a lower triplet energy (E_T = 56.9 kcal/mol[19]) was used, a nonlinear Stern–Volmer plot was obtained. Similar quenching results have been observed by Nũnez in the quenching of 4,4-dimethylcyclohex-2-enone by *cis*-piperylene.[8] Pienta[20] also reported curvature in piperylene quenching of 2-cyclohexenone. Triplet energy transfer from enone **1** to *cis*-piperylene occurred, as shown by formation of *trans*-piperylene. The ratio of *cis*- and *trans*-piperylene was 1.3, a value expected for the steady-state triplet photosensitization of the diene.[21] The nonlinear quenching is most likely due to rapid consumption of the quencher, since products with longer GLC retention times were observed[20,22] as well as triplet energy transfer.

The effect of the concentration of **1** on the quantum yield of product formation was also studied to explore the possibility that

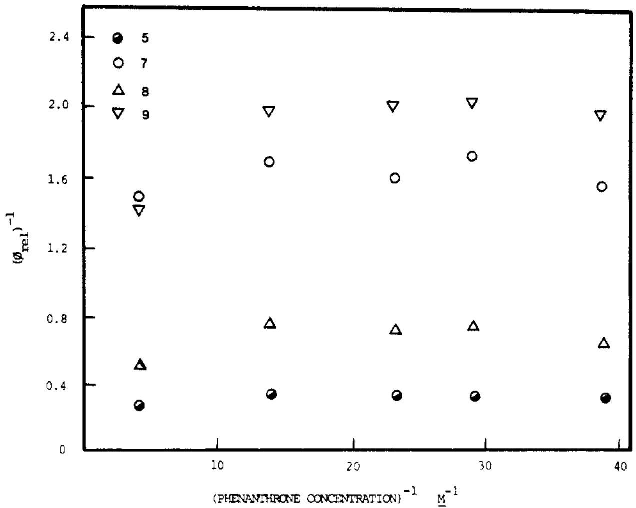

Figure 2. Double reciprocal plot of the relative quantum yield for formation of photoproducts from enone **1** vs. the enone concentration.

excimers might be precursors to the observed products, as suggested by Pienta and McKimmey.[23] If excimer formation were a prerequisite for all the other photochemical processes,[23] the kinetic picture would be as shown in Scheme II. The quantum

Scheme II

$$\begin{array}{lr}
\mathbf{1} \rightarrow {}^1(\mathbf{1})^* & (I_0) \\
{}^1(\mathbf{1})^* \rightarrow {}^3(\mathbf{1})^* & (k_{isc}) \\
{}^3(\mathbf{1})^* \rightarrow \mathbf{1} & (k_d) \\
{}^3(\mathbf{1})^* \rightarrow \mathbf{1} + h\nu & (k_p) \\
\mathbf{1} + {}^3(\mathbf{1})^* \rightarrow {}^3(\mathbf{1}\text{-}\mathbf{1})^* & (k_{ex}) \\
{}^3(\mathbf{1}\text{-}\mathbf{1})^* \rightarrow \text{product} & (k_r) \\
{}^3(\mathbf{1}\text{-}\mathbf{1})^* \rightarrow \mathbf{1} + \mathbf{1} & (k_{d'}) \\
{}^3(\mathbf{1}\text{-}\mathbf{1})^* \rightarrow \mathbf{1} + \mathbf{1} + h\nu' & (k_{em})
\end{array}$$

yield of formation of any product, ϕ_r, would then be given by

$$\phi_r = \phi_{isc}\phi_{ex}k_r/(k_r + k_{d'} + k_{em})$$

$$= \phi_{isc}\left(\frac{k_{ex}[1]}{k_{ex}[1] + k_p + k_d}\right)\left(\frac{k_r}{k_r + k_{d'} + k_{em}}\right)$$

$$\frac{1}{\phi_r} = \frac{1}{\phi_{isc}}\left(1 + \frac{k_p + k_d}{k_{ex}[1]}\right)\left(1 + \frac{k_{d'} + k_{em}}{k_r}\right)$$

A linear relationship between the reciprocal of the quantum yield of product formation and the reciprocal of the enone concentration should then be obtained. The slope of the plot should be equal to $(1/\phi_{isc})[1 + (k_{d'} + k_{em})/k_r](k_p + k_d)/k_{ex}$. Figure 2 shows a plot of the reciprocal of the relative quantum yield of photoproducts vs. the reciprocal of phenanthrone concentration. The relative quantum yields are obtained by multiplying the yields of each product (determined by GLC) by $I_{0'}/I_0$, where I_0 and $I_{0'}$ represent the light absorbed by the most concentrated solution and any of the other less concentrated solutions, respectively. The plot indicates that the quantum efficiency of product formation is basically enone concentration independent within the concentration range studied (0.025–0.200 M). Unfortunately, it is not possible to study this effect at higher enone concentrations due to solubility problems. The present results, however, suggest that the products are not formed in this system via excimers, as proposed by Pienta for 2-cyclohexenone.[23]

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[17] Pinacol **6** cannot be detected by the GLC method but can be quantitatively determined by HPLC analysis. The value of the ratio of **6** to lumiketone **5** is adapted from Zimmerman et al.[5]

[18] This reaction, however, could involve sensitized formation of singlet rather than triplet states of **1**, on the basis of findings of Smith and Agosta. Smith, A. B., III; Agosta, W. A. *J. Chem. Soc., Chem. Commun.* **1970**, 466.

[19] Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197.

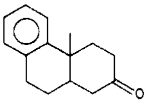
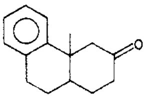
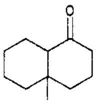
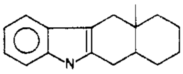
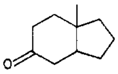
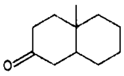
[20] Pienta, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2704.

[21] Hammond, G. S.; Leermakers, P. A.; Turro, N. J. *J Am. Chem. Soc.* **1961**, *83*, 2396.

[22] These products probably arise from the reaction of **1** and *cis*- and/or *trans*-piperylene, since no product with the same retention time was observed in the photolysis experiments in the absence of *cis*-piperylene.

[23] Pienta, N. J.; McKimmey, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 5501.

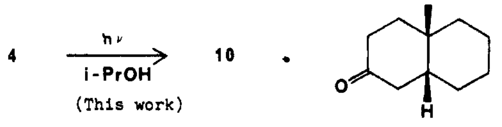
Table I. Chemical Shift of Angular Methyl Protons in Various Cis- and Trans-Fused Polycyclic Systems

compound	NMR signal, δ	
	cis	trans
	1.32 1.40	1.22[a] 1.32[b]
	1.30	1.11[b]
	1.05	0.80[c]
	1.05	0.88[d]
	1.12	0.95[e]
	0.97 1.33 1.18	1.18[f] 1.15[d] 1.06[a]

[a] Values were obtained with CCl_4 as solvent in the present work. [b] Reference 29. Values were obtained in $CDCl_3$. [c] Marshall, J. A.; Hochstetler, A. R. *J. Am. Chem. Soc.* **1969**, *91*, 648. [d] Miller, F. F.; Lohr, R. A., Jr. *J. Org. Chem.* **1979**, *43*, 3388. Solvent was not specified. [e] Stork, G.; Shiner, C. S.; Winkler, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 310. [f] Reference 12.

It has been shown with 4-methyl-4-phenylcyclohex-2-enone[24] and other similar systems[12,25,26] that changes in solvent polarity result in large changes in product ratios. This has been ascribed to a solvent effect on the ordering of the energy levels of the triplet n,π* and the π,π* excited states. Similar experiments were performed on phenanthrone **1**, using cumene, *i*-PrOH, *i*-PrOH–benzene (1:1), and *i*-PrOH–methanol (1:1). No major differences were seen in product ratios by GLC analysis among these four solvent systems.

(B) 4a-Methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (4). Compound **4** represents another model polycyclic enone system related to **1**. Irradiation of **4** in *i*-PrOH was reported to result in the mixture of compounds shown in eq 7.[12,27] The reported stereospecific reduction of **4** to give the trans-fused ketone **11** was of particular interest. We therefore repeated the photolysis of enone **4** in *i*-PrOH. The products isolated by column chromatography were identified as **10** and the *cis*-octahydronaphthalenone **12** (eq 8); only a trace amount of the *trans*-octahydronaphthalenone **11** could be detected in the present study by ^1H NMR spectroscopy. As discussed below, the discrepancy between our results and the earlier report is due to a misassignment of the structure of the product by the earlier workers.[12]



12

(eq. 8)

Thus, ketones **11** and **12** were independently synthesized according to published procedures,[28-31] and the isolated products were identified by NMR, IR, and mass spectroscopy. Spectra of model compounds (see Table I) show that angular methyl protons have a greater downfield chemical shift in cis-fused rather than trans-fused ring systems, in agreement with our structure assignment. The cis stereochemistry assigned to the photoproduct **12** is further supported by ^{13}C NMR spectroscopy. The angular methyl carbon displays a chemical shift of δ 27.0 with respect to Me_4Si, while the methyl carbon of the other isomer, **11**, has a value of δ 15.2. It has been proposed[32] that closely spaced hydrogens tend to shield the carbon bearing them as a result of steric interaction. The compound which bears a more upfield angular methyl group should thus be the trans-fused isomer where more severe nonbonded H–H interaction can be expected.

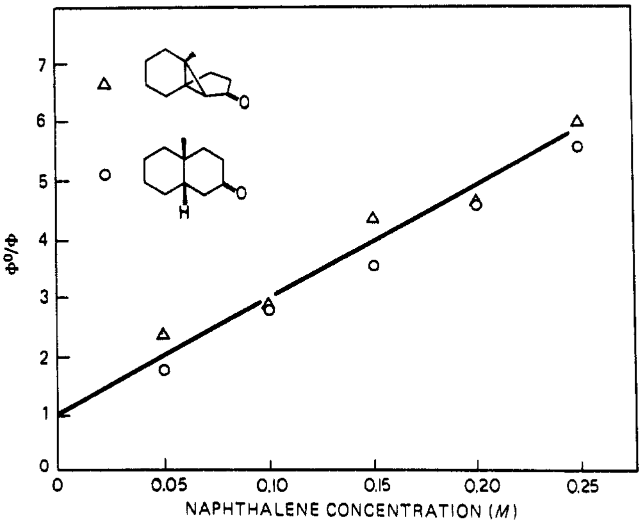


Figure 3. Stern–Volmer plot for quenching the photochemistry of 4a-methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (**4**) by naphthalene in isopropyl alcohol.

11

12

Furthermore, it was shown that the two reduced ketones do not interconvert. This eliminates the possibility that **11** somehow isomerized to **12** during the purification process. Interconversion of **11** and **12** by light was not observed in control experiments in which *i*-PrOH solutions of either **11** or **12** were irradiated until ~30% of the material had reacted.

The results of a quenching experiment using naphthalene are displayed in Figure 3. It reveals that both products, **10** and **12**, arise from only one excited state, presumably a triplet π,π* excited state as suggested by Belluš et al.,[12] or (less likely) from two triplet states undergoing rapid thermal equilibration.

Discussion

As pointed out in the introduction, photorearrangement of α,β-unsaturated cyclohexenones is thought to arise generally from the triplet π,π* excited state, while the triplet n,π* excited state is believed to be responsible for photoreduction at the carbonyl group to give pinacol and/or allylic alcohol as major products. This generalization seems to apply as well to the photochemistry

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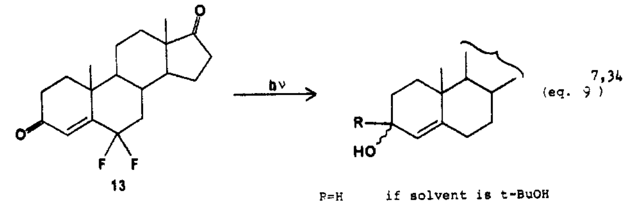
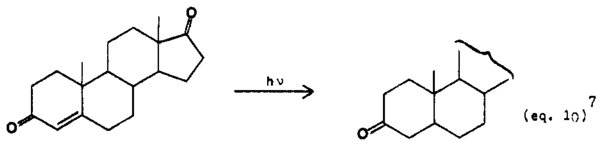
of phenanthrone **1** with the added wrinkle that we now find that both triplets in this system lead to reduction of the C=C moiety. In contradiction to the earlier conclusion by Zimmerman et al.[5,33] that photoproducts **5** and **6** both arise from the triplet n,π* excited state, our quenching and sensitization experiments establish unequivocally that these products arise from two distinct triplet excited states (Figure 1) which are not in thermal equilibrium at room temperature.[16]

An uncommon photoreduction product, allylic alcohol **7**, has been obtained in this work. There is only one other report of formation of an allylic alcohol, on photolysis of cyclohexenone **13** (eq 9), while the analogous steroidal enone **14** gives only reduction of the C=C bond (eq 10).[7] In general, the β-carbon of α,β-unsaturated cyclohexenones has a higher π-electron density in the ^{3}n,π* excited state relative to both the ground and the triplet π,π* excited states, according to calculations.[35] The two electronegative fluorine atoms at the γ-carbon atom of **13** would therefore be expected to stabilize the ^{3}n,π* state of the steroid and consequently enhance its reactivity. Therefore, the allylic alcohol was concluded to be formed from the triplet n,π* excited state.[34] This would suggest that **7** probably also arises from a triplet n,π* excited state. Since both **6** and **7** are quenched to the same extent by either naphthalene or phenanthrene, they clearly arise from a common excited state, namely, the triplet n,π* state.



13

R=H if solvent is t-BuOH
R=PhCH$_2$ if solvent is PhCH$_3$

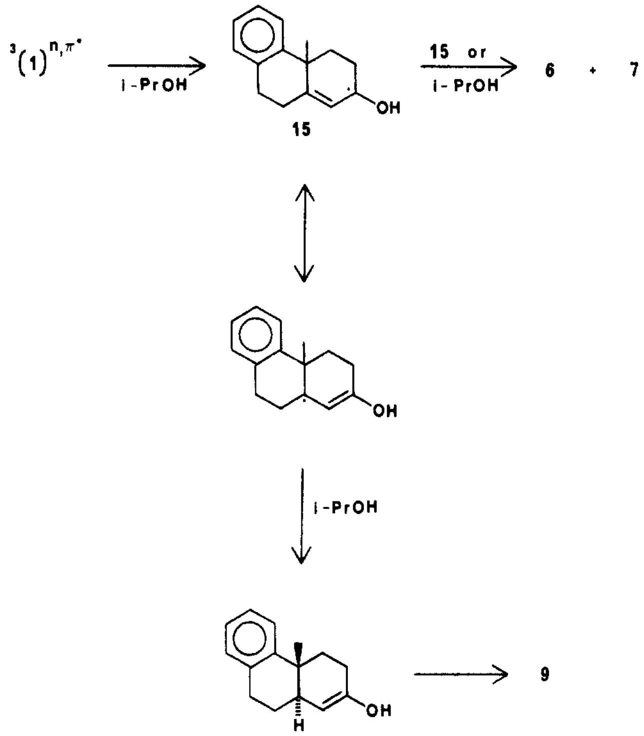


14

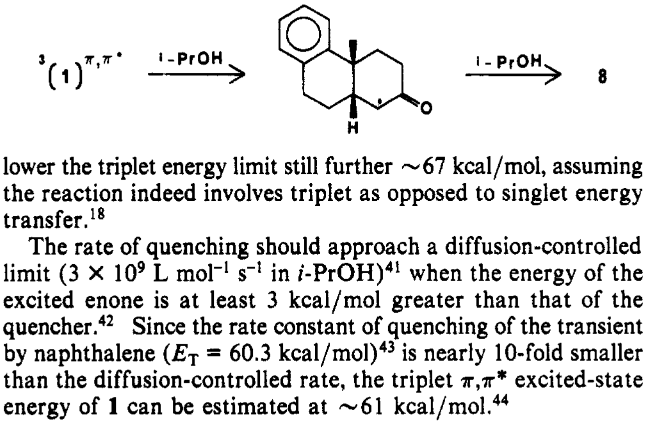
We conclude that lumiketone **5** is formed via a relaxed triplet π,π* excited state of enone **1**. This is supported by the agreement of $k_q\tau_T$ values obtained from the Stern–Volmer plot in Figure 1 (53 M^{-1}) and from direct laser flash studies of phenanthrone **1**.[36] The transient produced via short-pulse excitation of phenanthrone **1** has a lifetime, τ_T, or 145 ns in *i*-PrOH, and the directly measured rate constant k_q for triplet energy transfer to naphthalene is 4×10^8 M^{-1} s^{-1}. The product of these two values gives a $k_q\pi_T$ of 58 M^{-1},[37] in excellent agreement with the value measured in steady-state experiments. The transient detected in the flash photolysis study of cyclohexenone is believed to be a twisted triplet π,π* excited state, on the basis of its lifetime and rate constants for quenching by oxygen and by naphthalene.[36,38]

Wagner[39] suggested that biphenyl has a triplet excitation energy of 69.5 kcal/mol. Since this quencher has no effect on product formation upon photoexcitation of phenanthrone **1**, an upper limit to the energy of both the π,π* and n,π* triplet excited states of **1** can be estimated to be ~69.5 kcal/mol. The results of the sensitization experiment with triphenylene (E_T = 67.2 kcal/mol)[40] lower the triplet energy limit still further ~67 kcal/mol, assuming the reaction indeed involves triplet as opposed to singlet energy transfer.[18]

Scheme III



Scheme IV



The rate of quenching should approach a diffusion-controlled limit (3×10^9 L mol^{-1} s^{-1} in *i*-PrOH)[41] when the energy of the excited enone is at least 3 kcal/mol greater than that of the quencher.[42] Since the rate constant of quenching of the transient by naphthalene (E_T = 60.3 kcal/mol)[43] is nearly 10-fold smaller than the diffusion-controlled rate, the triplet π,π* excited-state energy of **1** can be estimated at ~61 kcal/mol.[44]

The 0,0 band of the $S_0 \rightarrow S_{n,\pi^*}$ absorption spectrum of **1** is ~370 nm, corresponding to 77.3 kcal/mol, while the $S_{n,\pi^*} \rightarrow T_{n,\pi^*}$ splitting in α,β-unsaturated ketones typically has a value of ~4.5 kcal/mol, as demonstrated by acrolein.[47] This sets E_T of the n,π* excited state of **1** at ~72.8 kcal/mol. Bond relaxation through elongation can further stabilize this triplet n,π* excited state, as indicated by the calculations of Devaquet.[48] A lowering of the energy of this particular triplet state from 72.8 to 67 kcal/mol as suggested above is, therefore, not unreasonable. The conclusion that the two excited triplet energy levels (i.e., E_{π,π^*} and E_{n,π^*}) in cyclohexenone **1** are separated by ≥6 kcal/mol is supported by the observation that changes in solvent polarity have no effect on the ratio of the photoproducts.

The Stern–Volmer quenching plot (Figure 1) reveals an interesting point. Even though the reduced ketones **8** and **9** are both

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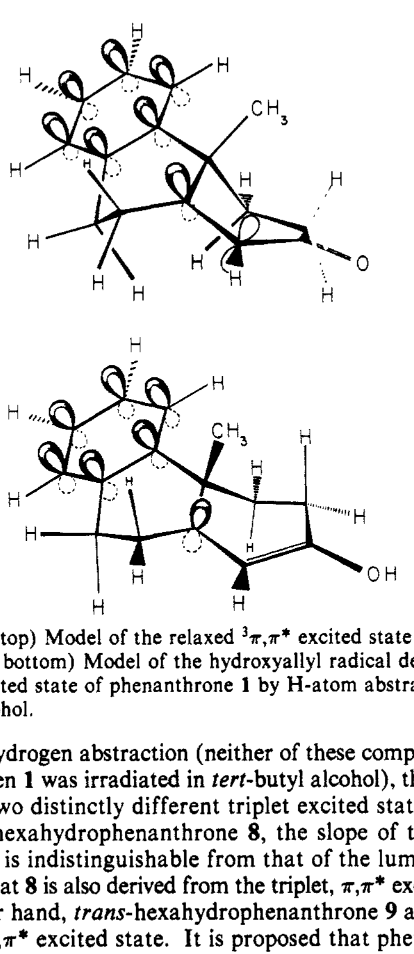
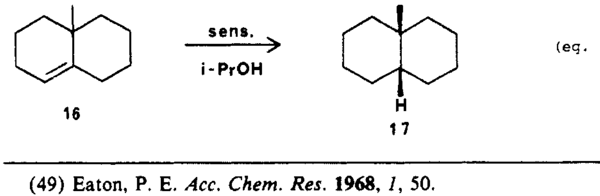


Figure 4. (a, top) Model of the relaxed $^3\pi,\pi^*$ excited state of phenanthrone **1**. (b, bottom) Model of the hydroxyallyl radical derived from the ^{3}n,π^* excited state of phenanthrone **1** by H-atom abstraction from isopropyl alcohol.

formed by hydrogen abstraction (neither of these compounds was obtained when **1** was irradiated in *tert*-butyl alcohol), they clearly arise from two distinctly different triplet excited states. In the case of *cis*-hexahydrophenanthrone **8**, the slope of the Stern–Volmer plot is indistinguishable from that of the lumiketone **5**, suggesting that **8** is also derived from the triplet, π,π^* excited state. On the other hand, *trans*-hexahydrophenanthrone **9** arises from the triplet n,π^* excited state. It is proposed that phenanthrone **1** in its n,π^* triplet excited state abstracts a hydrogen atom from the solvent to give allylic ketyl radical **15**, which either combines with another radical **15** to form pinacol **6** or abstracts a second hydrogen atom from the solvent to afford alcohol **7**. However, a hydrogen atom can also be abstracted by the β-carbon to yield the vinyl alcohol, which then tautomerizes to phenanthrone **9** (Scheme III).

As pointed out in our preliminary communication,[16] as the phenanthrone molecule **1** in its triplet π,π^* excited state twists around the C=C bond[3,49] the β-carbon becomes more pyramidal.[50] Thus, the approach of the hydrogen donor from the face anti to the angular methyl group is hindered, as displayed in Figure 4a, and the triplet π,π^* excited state will be reduced mainly to compound **8**, as shown in Scheme IV. On the other hand, the triplet n,π^* excited state on abstraction of a hydrogen atom gives radical **15**, which will attain a geometry as depicted in Figure 4b in which the angular methyl group lines up with the p-orbital at the radical center. The approach of a hydrogen donor to the radical site will now be preferred on the side anti to the angular methyl substituent. It is also interesting to note that octalin **16** yields product **17** with a cis-fused A/B ring configuration upon triplet-sensitized excitation in *i*-PrOH (eq 11).[53] A twisted C=C bond was also employed to rationalize the stereospecificity of this reaction.[54]



(eq. 11)[53]

In order to show the generality of the observation that the triplet π,π^* excited state gives rise exclusively to reduced ketone with cis-fused A/B rings, naphthalenone **4** was photolyzed in *i*-PrOH. The predominant reduction product (i.e., **12**) indeed has cis-fused rings. Quenching studies reveal that this product arises from the same triplet excited state as lumiketone **10**, namely a triplet π,π^* excited state (Figure 3).

Conclusion

The examples provided by photoreduction of polycyclic enones **1** and **4** demonstrate that reduction of the C=C bond of fused cyclohexenones of this type can arise from either ^{3}n,π^* and/or $^3\pi,\pi^*$ excited states. Furthermore, the reaction from each state in these systems appears to be stereospecific. The twisted triplet π,π^* exited state yields product with the two bridgehead substituents in a cis relationship, while the planar n,π^* triplet gives the corresponding trans isomer. Whether such stereospecificity will prove true for sterically less encumbered cyclohexenones or other types of cyclic enones remains to be explored.

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were recorded on a Hitachi-Perkin-Elmer Model R-20B high-resolution 60-MHz NMR spectrometer, using tetramethylsilane (99.9+% NMR Grade, Aldrich) as an internal standard. ^{13}C NMR spectra were recorded on a Varian Associates Model XL-100 NMR spectrometer with a Nicolet Fourier transform accessory, and the signals were measured relative to the central peak of the $CDCl_3$ triplet. IR spectra were taken on a Perkin-Elmer Model 735 spectrophotometer. Mass spectra were obtained on a Du Pont Model 21-492 double-focusing mass spectrometer, and UV absorptions were measured on a Perkin-Elmer Coleman 124D double beam spectrophotometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5710A gas chromatograph equipped with a $^1/_8$ in. × 6 ft column (10% SP2300 on 80/100 mesh Chromosorb P). High-pressure liquid chromatographic analyses were carried out on a Waters Associates Model 510 analytical HPLC with a reverse-phase column also supplied by Waters Associates. The eluent was DMF–H_2O (5:1). The preparative HPLC work was accomplished on a Waters Associates Model 500 chromatograph with a PrepPak-500/silica column from Waters Associates, using 10% EtOAc in hexanes as the eluent.

(A) **Syntheses.** Most of the compounds described below have been prepared previously (references as given). In these cases, allowing for differences in solvents, spectral data obtained were in good agreement with those reported in the literature. Therefore, only fragmentary spectral data are reported below.

4a-Methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (1). This compound was prepared according to the procedure in the literature.[5] The product obtained was purified by preparative HPLC followed by recrystallization from ether before being used in photolysis experiments: mp 87–90 °C (lit.[5] 89–90 °C); ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 3 H), 6.05 (s, 1 H); IR (CCl_4) 1675 cm^{-1}, UV (*i*-PrOH) λ_{max} 315 (ϵ 62), 234 (ϵ 18 620) nm.

3,4-Benzo-2-methyltricyclo[5.3.0^{1,7}.0^{2,7}]decan-10-one (5). This compound was readily obtained from the irradiation of phenanthrone **1**[5] and was purified by column chromatography using 5% ethyl acetate in benzene as eluent: mp 80–84 °C (lit.[5] 86–87 °C); ^{1}H NMR (CCl_4) δ 1.48 (s, 3 H); IR (neat) 1710 cm^{-1}; MS (*m/e*) 212.2 (M^+).

4,4′,4a,4a′,9,9a′,10,10a′-Octahydro-4a,4a′-dimethyl-2,2′-biphenanthrene-2,2′(3*H*,3′*H*)-diol (6). Reductive coupling of phenanthrone **1** using sodium amalgam to give pinacol **6** was performed according to the procedure suggested by Squire.[55] Thus, sodium amalgam prepared from 6.0 g of sodium metal was added to a mixture of *i*-PrOH (75 mL) and acetic acid (75 mL). Phenanthrone **1** (1.1 g) was then added over a period of 40 min. The solution was then poured into 600 mL of water to give a yellow precipitate, which was dissolved in hot benzene. After filtration the solution was concentrated. Column chromatography on silica gel using 5% $CHCl_3$ in benzene and then 5% ethyl acetate in benzene as eluent yielded a light yellow solid. Recrystallization from ethyl acetate gave a white solid: mp 217–219.5 °C (lit.[5] 219–222.5 °C); IR (KBr) 3320 cm^{-1}; MS (*m/e*) 426 (M^+).

4a-Methyl-2,3,4,4a,9,10-hexahydro-2-phenanthrenol (7). Reduction of the C=C bond in the α,β-unsaturated ketone was accomplished according to the procedure in the literature.[56] Phenanthrone **1** (2.12 g) was dissolved in 3.5 mL of freshly dried THF. The solution was chilled

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in an ice bath, and 9-BBN solution (containing 0.011 mol of 9-borabicyclo[3.3.1]nonane) was added dropwise over 0.5 h. The final solution was stirred in the cold for another 2 h and at room temperature for another 1 h. After the addition of 1 mL of methanol, the solvent was evaporated under reduced pressure. Pentane (50 mL) was then added, followed by 0.7 mL of 2-aminoethanol. The combined organic extracts were dried and concentrated. A portion of this product was purified by silica gel column chromatography, and the fraction containing pure **7** was collected and identified by spectroscopic methods: IR (neat) 3300 (OH), 3010, 2990, 2900, 2840, 1490, 1450, 1170, 1070, 865 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 3 H), 1.50–2.55 (m, 7 H), 3.00 (m, 2 H), 4.15 (s br, 1 H), 5.45 (s br, 1 H), 6.95–7.25 (m, 4 H); MS (*m/e*) 144.1, 181.2, 199.1, 214.1 (M$^+$).

***cis*-4a-Methyl-3,4,4a,9,10,10a-hexahydro-2(1*H*)-phenanthrone (8).** Phenanthrone **1** was reduced according to the procedure suggested by Wenkert and Stevens.[57] Thus, in a three-necked round-bottom flask, 0.9 g of 5% Pd/C was stirred under hydrogen with the slow addition of 25 mL of absolute EtOH solution of **1** (4%). The reaction was discontinued when no further hydrogen uptake was apparent, and the reaction mixture was filtered. The filtrate was concentrated and purified by column chromatography, using 20% ether in hexanes as eluent. The first fraction contained the pure desired product, which is a colorless liquid with a sweet odor. This liquid upon cooling in the refrigerator afforded a colorless soid with a melting point probably between 0 and −10 °.[57] The total yield was 60% on the basis of the starting material used: ^{1}H NMR (CCl_4) δ 1.35 (s, 3 H); IR (neat) 1710 cm^{-1}; MS (*m/e*) 214.2 (M$^+$).

***trans*-4a-Methyl-3,4,4a,9,10,10a-hexahydro-2(1*H*)-phenanthrone (9).** Reduction of phenanthrone **1** was accomplished by adding dropwise 50 mL of anhydrous ether solution of 1.43 g of phenanthrone **1** to 300 mL of liquid ammonia, which contained 0.71 g of dissolved lithium metal.[31] Solid NH_4Cl (14.28 g) was then added after 40 min. The ammonia was allowed to evaporate overnight, the white residue was dissolved in a 1:1 $CHCl_3$–water mixture, and the aqueous layer was extracted with additional chloroform. The combined organic layers were then washed with dilute HCl, then with saturated aqueous $NaHCO_3$ solution, and again with water. The final greenish yellow solution was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The crude product was further purified by chromatography on a silica gel column to afford 0.64 g of the desired product. The second portion of the column contained mainly unreacted starting material. Recrystallization of the solid from the first portion with petroleum ether (30–60 °C) gave a white solid: mp 104–105.5 °C (lit.[58] 107–108 °C); ^{1}H NMR (CCl_4) δ 1.22 (s, 3 H); IR (neat) 1720 cm^{-1}; MS (*m/e*) 214.2 (M$^+$).

4a-Methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (4). The acid-catalyzed annulation, described by Heathcock et al.,[59] of 22.5 g of 2-methylcyclohexanone and 18 g of methyl vinyl ketone in 50 mL of benzene was achieved by adding 0.5 mL of concentrated H_2SO_4 to the solution with stirring. The mixture was warmed to reflux over a period of 1 h under nitrogen. The water was removed from the reaction solution by a Dean–Stark trap. The final solution was then diluted with 50 mL of 5% aqueous KOH (w/w) solution. The upper layer was dried, and the solvent was evaporated under reduced pressure. The reddish brown residue was vacuum-distilled twice to give 13.4 g of colorless enone: bp 80–82 °C/0.3 mmHg (lit.[60] 82–83 °C/0.5 mmHg); total yield 41% (lit.[59] 49%); NMR ($CDCl_3$) δ 1.30 (3 H, CH_3), 5.61 (1 H, vinyl H); IR (neat) 1620, 1680 cm^{-1}; UV (95% EtOH λ_{max} 312 (ε 56), 237 (ε 15 800) nm.

2-Methyltricyclo[5.3.0^{1,7}.0^{2,7}]decan-10-one (10). This compound was readily obtained through irradiation of naphthalenone **4** in *tert*-butyl alcohol according to Zimmerman et al.[5] The desired product was separated from the unreacted starting material by preparative GLC ($^1/_4$ in. × 12 ft 20% XE-60 on Chromosorb W column; column temperature 160 °C): ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 3 H); IR (neat) 1705 cm^{-1}; MS (*m/e*) 164.2 (M$^+$).

***trans*-4a-Methyl-3,4,4a,5,6,7,8,8a-octahydro-2(1*H*)-naphthalenone (11).** A naphthalenone **4** solution (1.55 g of the enone in 80 mL of anhydrous ether) was added dropwise into 450 mL of liquid ammonia containing 1.0 g of dissolved lithium metal. The solution was stirred for another 40 min after the addition. Solid NH_4Cl (20 g) was added, and the ammonia was allowed to vaporize at room temperature. The white residue was dissolved in a 1:1 mixture of chloroform and water. The product was isolated according to the procedure described for the preparation of **9**. Pure product was obtained as colorless liquid by either preparative GLC ($^1/_4$ in. × 12 ft 20% XE-60 on Chromasorb W; column temperature 180 °C) or standard column chromatography (silica gel support and 1% ether–hexanes as eluent): ^{1}H NMR (CCl_4) δ 1.06 (s, 3 H); IR (CCl_4) 1715 cm^{-1}; MS (*m/e*) 166.2 (M$^+$).

***cis*-4a-Methyl-3,4,4a,5,6,7,8,8a-octahydro-2(1*H*)-naphthalenone (12).** The naphthalenone **4** solution (0.5 g of **4** in 1 mL of absolute ethanol) was injected into a suspension of the 5% Pd/C catalyst in ethanol. The mixture was stirred until no further hydrogen absorption was observed. The black suspension was filtered, and the solvent was evaporated to give a colorless liquid. The product then crystallized to form a white solid upon cooling: mp 38–41 °C (lit.[61] 46 °C); ^{1}H NMR (CCl_4) δ 1.18 (s, 3 H); IR (neat) 1720 cm^{-1}; MS (m/e) 166.2 (M$^+$).

(B) Photolysis of Enones 1 and 4. Preparative photolyses of both **1** and **4** were done by irradiating an *i*-PrOH solution of either ketone (0.2 M for **1** and 0.1 M for **4**) in a quartz immersion well apparatus which housed a 450-W Hanovia high-pressure mercury arc lamp with quartz filter. The photolyses were done under a positive pressure of nitrogen. The solvent was evaporated, and the products were identified either by co-injections with authentic samples into the chromatographic instruments or by spectroscopic methods after isolations.

Quenching experiments were performed by adding different amounts of quencher to a stock solution of enone of known concentration. Irradiations were performed on 1.0–2.0-mL aliquots of these solutions in a Rayonet photochemical reactor equipped with 16 lamps (350 nm) and a Rayonet merry-go-round apparatus. Each of the solutions was placed in a Pyrex test tube and purged with nitrogen for 15 min before exposure to UV light. A fixed volume from each photolysate was pipetted into a sample vial containing a constant amount of internal standard solution. These solutions were then analyzed by both GLC and HPLC. Each portion was injected at least 5 times, and the data were averaged. The relative quantum yield ϕ_0/ϕ for each photoproduct was obtained from the average GLC peak area ratio of product to standard in the absence and presence of the quencher.

Enough acetophenone, *p*-methoxyacetophenone, and triphenylene were used in the triplet sensitization experiments to absorb more than 90% of the incident light. All sensitizers were either distilled or recrystallized before use. All sensitized irradiations were performed by using 300-nm lamps in a Rayonet photochemical reactor, and the photolysates were analyzed by GLC and HPLC. The product distributions were similar to those obtained upon direct photoexcitation of the enones.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant CHE-7819750.

Registry No. 1, 6606-34-4; **4**, 826-56-2; **5**, 6606-35-5; **6**, 7363-88-4; **7**, 81457-34-3; **8**, 70524-91-3; **9**, 1686-50-6; **10**, 5771-64-2; **11**, 938-07-8; **12**, 938-06-7.

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