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Photochemistry of 1,5-Hexadien-3-ones: Wavelength-Dependent Selectivity in Intramolecular Enone–Olefin Photoadditions†

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Abstract: The photochemistry of ten 1,5-hexadien-3-ones in methanol is studied over the wavelength range of 313–366 nm, by using monochromatic light. With the goal of understanding the unusual wavelength-dependent selectivity observed for 5-methyl-1,5-hexadien-3-one (**1**), quantum yield measurements, structure reactivity studies, triplet sensitization, and quenching experiments are performed. While six of the ten dienones studied show selectivities that are independent of irradiation wavelength from 313 to 366 nm, four of the dienones exhibit wavelength-dependent selectivities that are similar to that observed in **1**, thus establishing that **1** is not unique, as previously believed. Triplet sensitization studies suggest that the wavelength dependence results, largely, from a single-state α-cleavage reaction that competes with triplet cycloaddition. A variety of triplet quenchers were ineffective at inhibiting these reactions. Some possible mechanisms are discussed.

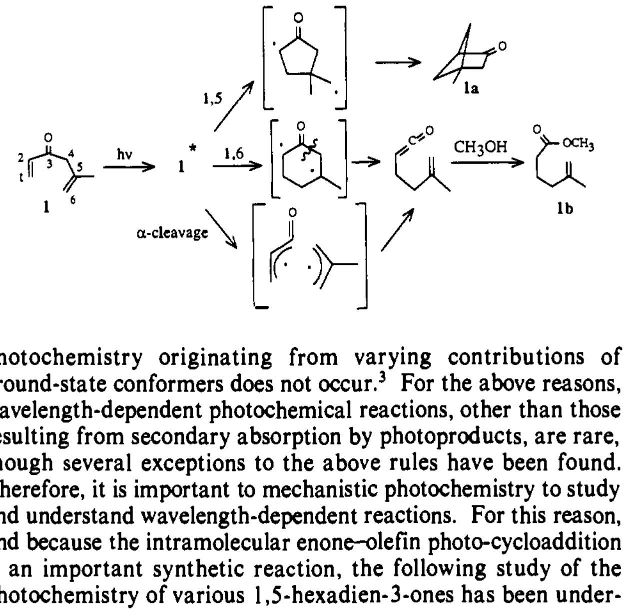
Introduction

The intramolecular [2+2] photoaddition of an enone to an olefin is one of the most utilized photochemical reactions in synthetic organic chemistry.[2] The wide use of this reaction results, in large part, from the fact that the regiochemical outcome with a variety of systems is predictable and reliable due to the large body of empirical data accumulated.[2] Although many of the factors controlling the selectivity in the inter- and intramolecular [2+2] photocycloadditions have been explored, relatively little attention has been given to the effect of irradiation wavelength in these photoreactions.[3] Indeed, an important but seldom recognized element of this reliability has been the fact that the selectivity observed with enone–olefin photocycloadditions is usually independent of irradiation wavelength over the synthetically useful range of 250–400 nm, provided that one is careful to avoid secondary photochemistry.

An important exception was noted by Agosta and co-workers in the case of 5-methyl-1,5-hexadien-3-one (**1**).[4,5] It was reported that *chemical yields* of the [2+2] cycloadduct **1a** (Scheme I) and the rearranged methanol adduct **1b** were 43% and 27%, respectively, when $\lambda > 340$ nm light was used, while yields were 0% and "low", respectively, with ~313-nm light, suggesting a dramatic wavelength dependence in the photochemistry of **1**. Irradiation of **1**-*6,6-d_2* led to a mixture of **1b**-*6,6-d_2* and **1b**-*4,4-d_2*, the ratio of **1b**-*6,6-d_2* to **1b**-*4,4-d_2* being larger at $\lambda \approx 313$ nm than at $\lambda > 340$ nm. It was suggested[4] that formation of **1b**-*6,6-d_2* resulted from a wavelength-dependent α-cleavage reaction in **1**, while **1b**-*4,4-d_2* was formed by both α-cleavage and 1,6-closure of the excited dienone (Scheme I). While the above studies clearly establish a wavelength dependence in the photochemistry of **1**, the use of product yields rather than quantum yields allows conclusions about relative efficiencies but not absolute efficiencies of the various photochemical processes occurring in **1** at the two wavelength ranges studied. A report[4] that formation of **1a** and **1b** from **1** could not be triplet sensitized or quenched was also unusual, since intramolecular enone–olefin photocycloadditions generally proceed through sensitizable triplet excited states.[6]

In general, upon direct photochemical excitation of an organic molecule in solution, the initially formed excited singlet undergoes internal conversion and vibrational relaxation to a vibrationally equilibrated first excited singlet state faster than intersystem crossing (ISC), photochemical reaction, or radiative decay. In such cases, photochemistry occurs from the same equilibrated excited state, regardless of the excitation wavelength.[3] Furthermore, conformational equilibration in the excited state is often faster than photochemistry, in which case wavelength-dependent photochemistry originating from varying contributions of ground-state conformers does not occur.[3] For the above reasons, wavelength-dependent photochemical reactions, other than those resulting from secondary absorption by photoproducts, are rare, though several exceptions to the above rules have been found. Therefore, it is important to mechanistic photochemistry to study and understand wavelength-dependent reactions. For this reason, and because the intramolecular enone–olefin photo-cycloaddition is an important synthetic reaction, the following study of the photochemistry of various 1,5-hexadien-3-ones has been undertaken.

Scheme I



Results and Discussion

Preparation of Dienones. Three general synthetic approaches were used in the synthesis of the dienones (details are provided in the Experimental Section): (1) The first approach entailed reaction of an α,β-unsaturated aldehyde with the appropriate allylic Grignard reagent, to provide the α,β-$\beta'\gamma'$-unsaturated alcohol, which was oxidized to the desired dienone.[5,7] (2) The second approach relied on [2,3] Wittig rearrangement of a suitably

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† Dedicated to Professor Kurt Schaffner on the occasion of his 60th birthday.

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Table I. Quantum Yields for the Indicated Photoproducts at Various Wavelengths and Product Ratios from Triplet Sensitization[a,b]

	313 nm	334 nm	350 nm	366 nm	sensitized
1a	0.0039	0.0034	0.0030	0.0032	see Table II
1b	0.0080	0.0036	0.0020	0.0012	
2a	0.046	0.14	0.11	0.13	**2a**:**2b** = 266:1[c]
2b	0.0021	0.0027		0.00071	
3a[e]	0.0056	0.0081	0.0089	0.0099	**3a**:**3b**:**3c**:**3d** = 30:110:0:1[d]
3b[e]	0.021	0.030	0.033	0.037	
3c[e]	0.016	0.014	0.0091	0.0058	
3d[e]	0.0067	0.0054	0.0042	0.0025	
5a	0.0008			0.0008	**5a**:**5b** = 11:1[c]
5b	0.011	0.013		0.010	
6a	0.27	0.25	0.25	0.20	**6a**:**6b**:**6c** = 5.5:2.6:1.0[c]
6b	0.13	0.12	0.11	0.096	
6c	0.048	0.043	0.039	0.033	
7a	0.16	0.26	0.24	0.23	**7a**:**7b** = 1.0:1.4[c]
7b	0.25	0.36	0.33	0.32	
8a	0.7	0.8	0.8	0.5	**8a**:**8b** = 49:1[c]
8b	0.02	0.02	0.02	0.01	
9a	0.39	0.42	0.39	0.36	
10a	0.09	0.07		0.07	

[a] Indicated value is average of at least two runs. [b] Estimated error is 10–20%. [c] Xanthone sensitized. [d] *p*-Methoxyacetophenone sensitized. [e] From irradiation of **3**.

substituted bis-allylic ether,[8] to afford the desired α,β-$\beta'\gamma'$-unsaturated alcohol, which was oxidized to the dienone. (3) The third approach utilized 1,3-dithiane methodology.[9] Peterson olefination of the appropriate cycloalkanone with 2-(trimethylsilyl)-1,3-dithiane afforded the thioketene acetal. Allylic deprotonation of the thioketene acetal and alkylation with the appropriate allylic halide, followed by oxidative hydrolysis of the dithiane, provided the desired dienone.

For quantum yield measurements, analytically pure dienone samples were obtained by either preparative GC or HPLC.

Quantum Yield Measurements for 5-Methyl-1,5-hexadien-3-one (1). The study commenced with **1**, since it is only this dienone that has been reported to show wavelength-dependent photochemistry. Quantum yields were determined for formation of ketone **1a** and ester **1b** in methanol at room temperature, from 313 to 366 nm (Table I). The [2+2] cycloaddition adduct **1a** is formed with a quantum efficiency that is nearly invariant over the wavelength range from 313 to 366 nm ($\phi = 0.0034 \pm 0.0004$). In contrast, the quantum yield for formation of ester **1b** shows a dramatic 7-fold variation, from 0.0080 to 0.0012, over the same range. It can, therefore, be concluded that the change in selectivity in the photochemistry of **1** with wavelength results from a change in the absolute efficiency of ester formation, consistent with Agosta's proposal that an α-cleavage reaction becomes increasingly important at shorter wavelengths.[4]

Inspection of the data in Table I reveals the low efficiency for the formation of **1a** and **1b** from **1**. This is most likely due to the well-known free-rotor effect.[10] It is important to note that extreme care is required to avoid undesirable secondary photochemistry in these systems at short irradiation wavelengths. Inspection of the UV absorption spectrum for **1a** reveals small tailing of the absorbance all the way out to wavelengths >300 nm. Determination of the quantum yield for disappearance of **1a** at 280 nm yielded a value of 0.09, approximately 60 times more efficient than its quantum yield of formation at this wavelength. The high quantum efficiency for the photodestruction of **1a** coupled with the low optical density of **1** at 290–300 nm ($\epsilon < 50$) precluded accurate quantum yield measurements at wavelengths below 313 nm. It is interesting to note, however, that even at very low conversion, where secondary photochemistry is unlikely, quantum yields for both **1a** and **1b** began to drop at wavelengths below 313 nm, as will be discussed below. The present study focused on the range from 313 to 366 nm.

Table II. Yields of **1a** and **1b** upon Sensitization of **1** to Complete Conversion

		% yield	
sensitizer	E_T (kcal/mol)	**1a**	**1b**
none (direct)		46	21
xanthone	74	35	9
p-methoxyacetophenone	72	48	18
thioxanthone	66	0	0
acetone	79	0	0
propiophenone	75	7	2
m-methoxyacetophenone	72	8	4
benzophenone	69	0	0

The apparent discrepancy between the formation of **1a** at 313 nm in the present study compared with Agosta's observation that no **1a** is formed at ~313 nm is undoubtedly due to a combination of the high-energy radiation allowed to pass through the filter solution and the irradiation to high conversion, both resulting in secondary photochemistry in the latter study.[4]

Sensitization Studies on 1. In order to further probe the nature of the excited state(s) involved in the photochemistry of **1**, various triplet sensitizers were employed. At the onset of this aspect of the general study, the report[4] that **1** could not be triplet sensitized to produce **1a** and **1b** was particularly intriguing, since enone–olefin cycloadditions are generally triplet reactions.[6] Thus, a more complete range of triplet sensitizers was explored (Table II). Only two of the sensitizers studied, xanthone and *p*-methoxyacetophenone, efficiently produced **1a** and **1b** via triplet energy transfer to **1**.

At first glance, the exclusive sensitization with xanthone and *p*-methoxyacetophenone appeared to be a function of the high triplet energies of these compounds. However, acetone and propiophenone have equal or higher triplet energies than xanthone and *p*-methoxyacetophenone but do not yield any significant amount of **1a** or **1b**. Upon closer consideration of the sensitizer triplets, it was noted that, for both xanthone and *p*-methoxyacetophenone, the lowest lying triplets are $\pi\pi^*$.[11,12] With xanthone, it is known that polar solvents accentuate both the intensity and lifetime of the $\pi\pi^*$ triplet state. This solvent effect on the $\pi\pi^*$ triplet state of xanthone was studied in detail by Huber, who showed that, in nonpolar 3-methylpentane, the $n\pi^*$ and $\pi\pi^*$ triplets of xanthone have lifetimes of 25 and 120 ms, respectively.[12] In methanol–water, the lowest triplet state is $\pi\pi^*$, with a lifetime of 0.9 s, while the $n\pi^*$ triplet was not detectable.[12] The enhanced triplet lifetime of xanthone in methanol should increase its ability to transfer its triplet energy to **1**, a feature that appears to be required for the sensitized activation of **1**.

The remaining sensitizer entries in Table II all produce lowest $n\pi^*$ triplets upon irradiation except for thioxanthone, which is $\pi\pi^*$. Although little or none of the 1,5- or 1,6-closure products are formed when these $n\pi^*$ sensitizers are used, the starting dienone **1** is consumed. The high reactivity of $n\pi^*$ triplets of ketones is well documented[13] and may account for the consumption of **1**. The reduced reactivity of triplet $\pi\pi^*$ states toward hydrogen atom abstraction,[14] coupled with the enhanced lifetime of its $\pi\pi^*$ triplet in methanol, therefore qualifies xanthone (and other $\pi\pi^*$ sensitizers, e.g., *p*-methoxyacetophenone) as an excellent triplet energy transfer agent for the sensitization of **1**. Finally, the ineffectiveness of the $\pi\pi^*$ sensitizer thioxanthone is attributed its low triplet energy (E_T = 66 kcal/mol), thus placing the triplet

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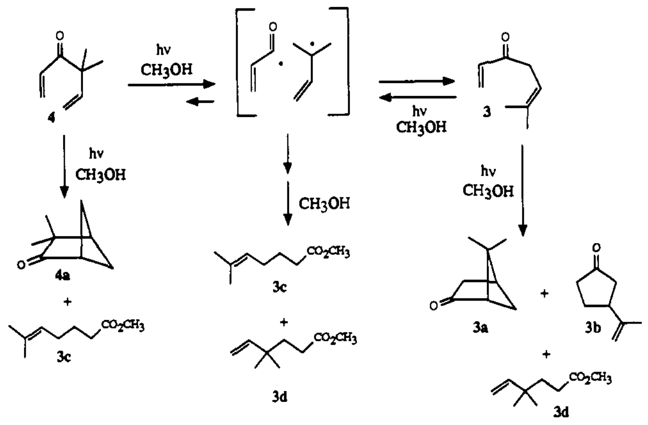
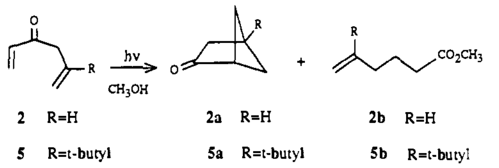
Scheme II



energy of 1 between 72 and 66 kcal/mol.

Quenching Studies on 1. The positive results obtained in the sensitization of 1 prompted a closer look at quenching the reactive triplet possibly produced upon direct irradiation of 1. Agosta and co-workers noted that 2,3-dimethyl-1,3-butadiene (0.27–4.5 M) did not quench the photochemistry of 1 upon direct irradiation.[4] In addition to 1 M 2,3-dimethyl-1,3-butadiene, 1 M *cis*-piperylene, 0.25–1 M phenylacetylene, and 0.1–1 M biphenyl were tested as triplet quenchers in the present study. In no case was quenching observed.

Photochemistry of 1,5-Hexadien-3-one (2). It has been reported that ketone **2a** was the only product obtained when **2** was irradiated at λ > 340 nm in methanol/benzene.[5] In the present study, irradiation of **2** at λ = 366 nm in methanol afforded ketone **2a** and ester **2b** in a ratio of ca. 180:1. Since the yield of **2b** was so low, identification and location of **2b** was facilitated by injecting a GC standard of independently synthesized **2b** to determine its retention time (see experimental section). In contrast to the 366-nm results, irradiation at λ = 313 nm in methanol afforded **2a** and **2b** in a ratio of 22:1.



The quantum yield of **2a** was constant at 0.13 ± 0.02 from 366 to 334 nm, but dropped significantly to 0.046 at 313 nm (Table I). The quantum yield for ester **2b** increased 4-fold from 0.000 54 at 366 nm to 0.0023 at 334 nm. Little change was seen in the ester quantum yield between 334 and 313 nm (Table I). With several of the dienones in the present study, a drop-off of quantum yields below 313 nm was encountered, as mentioned above for dienone **1**. The drop-off observed between 334 and 313 nm for formation of **2a** may be due to the same phenomena (see below) but shifted to higher wavelength, since the quantum yield of **2a** is constant from 366 to 334 nm. Finally, triplet sensitization using xanthone in methanol provided **2a** and **2b** in a ratio of ca. 270:1 (Table I).

The dramatic decrease in the ratio of **2a** to **2b** at shorter wavelengths suggests that **2** is mechanistically related to **1** and that **1** is not a unique case as previously believed. Though consistent with a wavelength-dependent α-cleavage reaction in **1** and **2**, the ability to regiochemically distinguish between α-cleavage and 1,6-closure is desired.

Photochemistry of 6-Methyl-1,5-heptadien-3-one (3). Dienone **3** appeared to be an ideal case for study, since the two terminal methyl groups serve as a convenient marker by which to observe α-cleavage (Scheme II), much as the deuterium label used by Agosta.[4] Although no variation in wavelength has been previously investigated, irradiation of **3** using a broad-band light source was observed to produce α-cleavage ester **3c**, as well as ester **3d** (which can potentially be formed by both α-cleavage and 1,6-closure) and enone **3b**, which results from disproportionation of the 1,5-closure intermediate.[7]

In the present study, irradiation of **3** at 366 nm in methanol yielded products **3a**–**3d**, with quantum yields indicated in Table I. Similar to results obtained with **1**, quantum yields of esters **3c** and **3d** increase by about 3-fold on going from 366 to 313 nm, unambiguously establishing the presence of a wavelength-dependent α-cleavage reaction. In contrast to **1a** and **2a**, the quantum yields of the 1,5-closure products **3a** and **3b** decreased by nearly a factor of 2 over the same range. The decrease in quantum yield of **3a** and **3b** may result from an increase in the competition by α-cleavage and/or an unobserved process at shorter wavelengths.

Triplet sensitization with *p*-methoxyacetophenone in methanol resulted in formation of **3a**, **3b**, and **3d** but no detectable α-cleavage ester **3c** (Table I), suggesting that the α-cleavage originates from the singlet excited state. As encountered with acyclic dienones **1**, **4**, and **5**, irradiation of **3** in acetone resulted in disappearance of starting material without formation of any **3a**–**d**. With **3**, as with all other dienones in the present study, degassed and nondegassed samples gave identical results, suggesting that oxygen is not an effective triplet quencher for these reactions.

Qualitative Photochemistry of 4,4-Dimethyl-1,5-hexadien-3-one (4). As with **3**, the methyl groups in **4** serve as convenient markers to observe α-cleavage (Scheme II). Irradiation of dienone **4** in methanol afforded the ketone (1,5-closure) product **4a**, as well as esters **3c** and **3d**. Interestingly, dienone **3** was formed as a primary photoproduct, which resulted in formation of **3a** and **3b** (and additional amounts of **3c** and **3d**) as secondary photoproducts. Compounds **3** and **3d** are primary products from α-cleavage of **4**. Dienone **4** also showed wavelength-dependent product ratios, with the ratio of esters **3c** and **3d**, dienone **3**, ketone **3a**, and enone **3b** to ketone **4a** each being higher at λ = 280–320 nm (**4a**:α-cleavage products ≈ 1:6) than at λ > 340 nm (**4a**:α-cleavage products ≈ 1:3). The relationship between the photochemistry of **3** and **4** is summarized in Scheme II. As with previous cases mentioned above, bicyclic ketone products **3a** and **4a** were not observed in previous studies.[7]

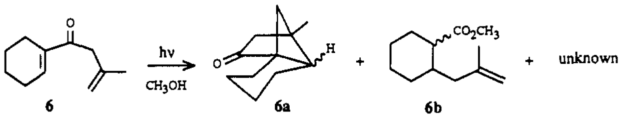
Photochemistry of 5-*tert*-Butyl-1,5-hexadien-3-one (5). The report[5] that irradiation of **5** in methanol at λ > 340 nm afforded ketone **5a** and ester **5b**, in analogy to the chemistry of **1**, prompted the present study of **5** over the wavelength range from 313 to 366 nm to determine if a wavelength dependence is operative in **5** similar to that observed with **1**.

Solutions of **5** in methanol were irradiated at 313, 334, and 366 nm. Quantum yields for ester **5b**, in contrast to **1b**, are independent of irradiation wavelength (Table I), with a value of 0.011 ± 0.001. The low quantum yield for ketone **5a** precluded its accurate measurement. However, comparing results with broad-band radiation (λ > 340 nm versus λ ≈ 280–320 nm), it was determined that, at low conversion, the ratio of **5a** to **5b** is ~0.07 at both wavelength ranges. Thus, the quantum yield for **5a** is estimated to be 0.0008 from 313 to 366 nm. As with **1a**, **5a** is highly prone to undergo secondary photochemistry at short wavelengths.

Dienone **5** showed a similar sensitivity to the choice of sensitizer as **1**. For example, xanthone and *p*-methoxyacetophenone efficiently sensitized formation of **5a** and **5b** in the same ratio as direct irradiation, while propiophenone consumed starting material with no formation of **5a** and **5b**.

Quantum yields obtained with **5** in the presence of 1 M *cis*-piperylene and 2,3-dimethylbutadiene were close to those without quencher present. Small amounts of products were formed in the presence of quencher other than **5a** and **5b**, possibly from chemical reaction between the quencher and **5**, precluding quantitative conclusions as to whether or not quenching by triplet energy transfer had occurred.

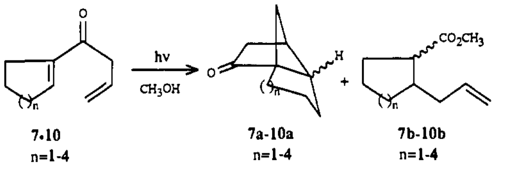
Photochemistry of 1-(1-Cyclohexenyl)-3-methyl-3-buten-1-one (6). Irradiation of dienone **6** in methanol afforded [2+2] cycloadducts **6a**, esters **6b**, and an unidentified product **6c** (see the Experimental Section for a discussion of **6c**). From 313 to 366 nm, all products showed quantum yields that were independent of irradiation wavelength (Table I): **6a**, $\phi = 0.24$; **6b**, $\phi = 0.11$; **6c**, $\phi = 0.040$. The high quantum efficiency obtained with **6** (and **7–9**) relative to **1–5** is attributed to the inability of **6** to undergo significant twisting about the α–β double bond due to the rigidity of the six-membered ring.



In contrast to **1–5**, dienone **6** was efficiently sensitized by sensitizers with either lowest $\pi\pi^*$ or lowest $n\pi^*$ states. Thus, propiophenone, xanthone, *m*-methoxyacetophenone, *p*-methoxyacetophenone, benzophenone, and triphenylene efficiently sensitized formation of **6a–6c** in the same ratio as obtained on direct irradiation of **6**. Apparently, due to the high quantum efficiency for triplet 1,5- and 1,6-closure in **6**, destruction by $n\pi^*$ sensitizers does not effectively compete with product formation as it does with dienones **1–5**. Thioxanthone and 2-acetonaphthone failed to sensitize the reaction of **6**, placing the triplet energy of **6** at about 65–67 kcal/mol.

Attempts to quench the photochemistry of **6** with 0.08–2.4 M *cis*-piperylene, 0.9 M 2,3-dimethylbutadiene, and 0.8–1.8 M biphenyl were unsuccessful. Quantum yields were the same in the presence and absence of these triplet quenchers.

Photochemistry of 1-(1-Cycloalkenyl)-3-buten-1-ones 7, 8, 9, and 10. Irradiation of dienones **7**, **8**, **9** and **10** in methanol afforded products with quantum yields that were independent of irradiation wavelength from 313 to 366 nm (Table I). Dienone **7** provided ketone **7a** ($\phi = 0.25$)[15] and esters **7b** ($\phi = 0.34$). Dienone **8** afforded ketones **8a** ($\phi = 0.6$) and esters **8b** ($\phi = 0.019$). Dienone **9** yielded only ketones **9a** ($\phi = 0.39$) and none of the ester product. Similarly, dienone **10** provided only ketones **10a** ($\phi = 0.07$). Triplet sensitization of **7** and **8** with xanthone afforded photoproducts in the same ratio as on direct irradiation (sensitization of **9** and **10** was not studied).



An interesting regiochemical trend, noted by Agosta and co-workers,[5] is the increase in the ratio of 1,5- to 1,6-closure products on going from dienone **7** to dienone **8**. The present data, including previously unknown dienones **9** and **10**, conform to this trend, the cause of which is not understood but may be related to the higher flexibility of the larger rings.

Mechanistic Considerations. Dienones **5–10**, upon irradiation over the range from 313 to 366 nm showed quantum yields (and product ratios) that were independent of irradiation wavelength, within experimental error of 10–20%. Furthermore, triplet sensitization afforded products in the same ratios as direct irradiation in **5–8**. In light of these observations, the following conventional mechanism is proposed to explain the photochemistry of **5–10**.

Irradiation at wavelengths longer than 313 nm results in excitation to the S_1 ($n\pi^*$) state, followed by vibrational equilibration and intersystem crossing at rates that exceed any photochemistry from S_1. After intersystem crossing and vibrational equilibration of the resulting triplet, 1,5- and/or 1,6-closure leads to ketone and/or ester, respectively. The inability to triplet quench these reactions is attributed to very short dienone triplet lifetimes.[16]

A second, less appealing, possibility for dienones **5–10** is excitation to S_1 followed by vibrational relaxation to an equilibrated S_1 state that undergoes 1,5- and 1,6-closure prior to intersystem crossing. The inability to triplet quench would be easily rationalized, but the ability to triplet sensitize would require the coincidence that the dienone triplet formed upon sensitization afforded photoproducts in the same ratio as produced from the S_1 photochemistry.

As mentioned above, in several cases, it was observed that the quantum yields dropped at wavelengths shorter than 313 nm and, in the case of **2** and **7**, below 334 nm, even at very low conversions where secondary photochemistry or light absorption by photoproducts is negligible. It is proposed that this results from some direct excitation to (and nonproductive reaction from) S_2 at shorter wavelengths. This hypothesis is supported by inspection of the UV spectra of dienones **1–10**, which show an $n\pi^*$ maximum between 315 and 340 nm. After a brief drop in extinction coefficient toward the low-wavelength edge of the $n\pi^*$ peak, the extinction coefficient begins to rise rapidly on the high-wavelength edge of the $\pi\pi^*$ peak, without ever approaching zero in the valley between peaks. Thus, at some point near 300–320 nm, a significant fraction of the absorbed light must result in excitation to S_2. It was for this reason, and because of the propensity of the [2+2] ketone products to undergo secondary photochemistry, that the present study was limited to the 313–366-nm range. No attempt was made to establish the presence of a nonproductive reaction from S_2.

In contrast to **5–10**, dienones **1–4** show wavelength-dependent selectivities between 313 and 366 nm, which suggest the involvement of a more complicated set of circumstances. The two most likely possibilities follow.

(1) After excitation to S_1, the electronically and vibrationally excited dienone undergoes an α-cleavage reaction in competition with vibrational relaxation and intersystem crossing.[3,17] That fraction that crosses to the triplet manifold can then undergo 1,5- and 1,6-closure. Such a mechanism is consistent with the triplet sensitization results, especially with dienone **3**, which produced α-cleavage ester **3c** upon direct irradiation but not upon triplet sensitization. In addition, triplet sensitization of **1**, **2**, and **4** results in 1,5-closure product to ester ratios that are higher than obtained on direct irradiation, as would be expected if some of the ester produced upon direct irradiation resulted from a singlet-state α-cleavage and some from triplet 1,6-closure.

The failure to observe any wavelength-dependent ester formation in **6**, **7**, and **9** could conceivably be due to the fact that the quantum yields for 1,5- and 1,6-closures in these dienones are so high, making detection of a low quantum yield (and low chemical yield) competing α-cleavage experimentally difficult. However, such a process in dienones **5**, **8**, and **10** should be more readily observed. For example, if a wavelength-dependent α-cleavage was operative in **5** that was of comparable magnitude to that found in **1**, the observed wavelength-independent ester quantum yield of 0.011 would increase to about 0.02 at 313 nm.

In light of these observations, especially the fact that only the smaller dienones **1–4** exhibit evidence for the proposed wavelength-dependent α-cleavage, it is tempting to propose that the α-cleavage rate in **1–10** is related to the number of vibrational modes over which the excess vibrational energy can distribute itself before dissipating to the environment. As related by RRK theory,[18] the more vibrational modes there are in a molecule, the lower is the probability that a given amount of excess vibrational energy will accumulate in a particular mode required for reaction. Though any excess vibrational energy should be dissipated on the order of 10^{-12} s, a fast unimolecular reaction might compete under favorable conditions.[3] The low quantum yields observed for the α-cleavage reactions in this study require that such a process only be minimally competitive with vibrational equilibration.

(2) A second possibility is that the observed wavelength effect is due to the participation of more than one conformation of a given dienone.[3] For example, if two conformations of a given

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(15) With **7**, only one diastereomer of **7a** was obtained, as reported in ref 5.

(16) Reference 14, pp 243–264.

(17) (a) For a review of enone photochemistry, including a discussion of singlet versus triplet α-cleavage reactions, see ref 2c. (b) For an example of chemical reaction in competition with vibrational equilibration, see: Becker, R. S.; Dolan, E.; Balke, D. E. *J. Chem. Phys.* **1969**, *50*, 239.

(18) (a) Rice, O. K.; Ramsperger, H. C. *J. Am. Chem. Soc.* **1927**, *49*, 1617; **1928**, *50*, 617. (b) Kassel, L. S. *J. Phys. Chem.* **1928**, *32*, 225.

dienone exist in solution, each with a slightly different UV absorbance spectrum, then variation of the irradiation wavelength will change the ratio of the two conformations, which are raised to S_1. Provided that photochemistry is faster than conformational equilibration in the excited state (which is usually not the case) and that the conformation that undergoes a relative increase in absorbance upon higher energy excitation is more reactive toward α-cleavage, a wavelength effect such as that seen with **1**–**4** would be expected. No evidence for or against such a "conformational control" mechanism is available from the above data but will be the aim of future study.

Summary

Four examples of wavelength-dependent selectivity in intramolecular enone–olefin photoadditions have been identified. The data suggest that the dependence is primarily due to an increase in the quantum efficiency of a singlet-state α-cleavage reaction at shorter wavelengths that competes with 1,5- and 1,6-closure. The α-cleavage reaction leads to ester formation, while 1,5- and 1,6-closure lead to ketone cycloadduct and ester, respectively.

Those dienones with low quantum yields for reaction showed an unusual sensitivity to the choice of triplet sensitizer, being destroyed by those with lowest $n\pi^*$ triplets, while undergoing efficient sensitization by those with lowest $\pi\pi^*$ triplets.

From a synthetic standpoint, these results underscore the importance of carefully filtered light (both to avoid secondary destruction of the [2+2] cycloadduct and to avoid unwanted dienone α-cleavage) and suggest the use of sensitized irradiation for cases where α-cleavage might compete with desired cycloaddition.

Experimental Section

General Methods. All synthetic transformations were run under a nitrogen atmosphere. Methanol and acetone were spectrometric grade. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Toluene and hexamethylphosphoric triamide (HMPA) were distilled from CaH_2. *n*-BuLi was used as a 1.5–1.8 M hexane solution. All sensitizers and quenchers were used as received with no further purification. Preparative irradiations, sensitization, and quenching experiments were performed by using a Rayonet Photochemical Reactor (RPR) equipped with 18 bulbs. Bulbs used were either 350 nm (major emission at 366 nm; 320–400 band-pass) or 300 nm (260–340 band-pass). Preparative HPLC was conducted by using a Whatman Partisil 10 column. For preparative GC, either an SE-30 or a carbowax 20M column was used. Elemental analyses were performed by the Microanalytical Laboratory and mass spectral analyses by the Mass Spectrometry Facility, both operated by the College of Chemistry, University of California, Berkeley.

Quantum Yield Measurements. Quantum yields were measured by using a Photon Technologies Inc. electronic actinometer[19] calibrated with standard potassium ferrioxalate actinometry[20] at each wavelength studied. The light source was a 1000-W Conrad-Hanovia Xe–Hg lamp with a monochromator, resulting in a bandwidth of 2 nm. Before use, purity of starting material was established by GC (>98%). Dienone samples (10^{-2}–10^{-3} M) were degassed with nitrogen and irradiated in standard quartz cuvettes at room temperature. Irradiations were carried out to 2–10% conversion of the dienone. The amounts of products formed were measured by using a capillary gas chromatograph equipped with either an SE-30 or Carbowax 20M capillary column, in the following way. After the desired amount of irradiation, a volumetrically prepared aliquot of an internal standard was added to the irradiated solution. For each product formed, the sensitivity of the FID detector was calibrated relative to the internal standard (tetradecane, hexadecane, methyl isoamyl ketone, or cycloheptanone) with products isolated from the preparative irradiations. Thus, the absolute amount of product formed could be ascertained from the GC analysis of the irradiated solution containing the internal standard. Each irradiation mixture was analyzed with between 4 and 12 separate injections.

5-Methyl-1,5-hexadien-3-one (1). Dried magnesium turnings (1.75 g, 0.072 mol) were added to a dry, N_2-flushed, 250-mL, three-necked, round-bottom flask equipped with a magnetic stirrer, addition funnel, and low-temperature thermometer. THF (25 mL) was added to the flask, and the temperature of the solution was lowered to −10 °C. Approximately 0.4 mL of 3.6 mL (3.26 g, 36 mmol) of dry methallyl chloride was added, slowly via syringe, to initiate the reaction. A crystal of I_2 was added to signal initiation upon its color disappearance. The remainder of the chloride in 50 mL of THF was added, slowly, over approximately 5 h. Addition of 0.5 mL of the Grignard reagent to a small amount of 1,10-phenanthroline in 0.5 mL of THF under N_2 gave a brown solution that was titrated to a light green end point with 0.015 mL of *n*-butanol. The calculated yield of methallyl Grignard was 25 mmol (69%). A solution of 2 mL (1.68 g, 30 mmol) of acrolein in 50 mL of dry THF was added, with stirring, to the Grignard reagent at 0 °C. The resulting clear, colorless THF solution was filtered from the excess magnesium and acidified with 5% HCl and the THF layer removed and dried twice with Na_2SO_4 and then $MgSO_4$. The aqueous phase was extracted with 3 × 25 mL of ether, dried as above, and added to the initial THF layer. The THF was removed by using a rotary evaporator and the remaining liquid distilled (55 °C (15 Torr)) to give 2.4 g (71%) of the alcohol: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.9 (m, 1 H), 5.1 (m, 2 H), 4.85 (s, 1 H), 4.2 (m, 1 H), 2.2 (d, 2 H), 1.88 (s, 1 H), 1.76 (s, 3 H); IR (film) 3400, 3100, 1660, 1000, 930, 900 cm^{-1}.

A solution of 1.14 g (10 mmol) of 5-methyl-1,5-hexadien-3-ol in 20 mL of ether and 10 mL of H_2O was added to a 100-mL round-bottom flask. The solution was cooled to 0 °C, and 12 mL of freshly prepared Jones reagents (10 mL of H_2O, 2.7 g of CrO_3, 2.2 mL of 18 M H_2SO_4) were added, slowly, via a controlled addition funnel (or syringe pump) with vigorous magnetic stirring. After addition, the solution was allowed to warm to room temperature with continued stirring. The ether layer was removed and the aqueous layer extracted with 2 × 25 mL of ether. The combined ether extracts were washed twice with 25 mL of H_2O and dried over $MgSO_4$. The ether was removed by using a rotary evaporator to yield 770 mg (69%) of a yellow liquid. Dienone **1** was isolated in analytical purity by preparative GC: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (m, 1 H), 6.26 (m, 1 H), 5.81 (m, 1 H), 4.95 (s, 1 H), 4.80 (s, 1 H), 3.27 (s, 2 H) 1.75 (s, 3 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 198.3, 139.2, 135.7, 128.7, 115.1, 49.3, 22.6; IR (film) 3100, 1710, 1690, 1410, 1098, 1000, 970, 905 cm^{-1}; UV max (CH_3OH) $\pi\pi^*$ 209, $n\pi^*$ 337 nm (ϵ 50). Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.20; H, 9.21.

1,5-Hexadien-3-one (2). To 180 mL of THF and allylmagnesium chloride (50.0 mL, 86.0 mmol; Aldrich THF solution) cooled to 0 °C was added acrolein (4.9 g, 86.8 mmol) in 50 mL of THF, dropwise over 50 min. The solution was stirred for 1 h and then warmed to room temperature. Water (100 mL) was cautiously added, followed by 400 mL of ether. The mixture was acidified with 10% HCl. The ether layer was washed with 100 mL of water and 100 mL of saturated Na_2SO_3, dried ($MgSO_4$), and concentrated. The residue was distilled under aspirator vacuum to afford 5.4 g of 1,5-hexadien-3-ol (58%): ^{1}H NMR δ 5.92–5.68 (m, 2 H), 5.29–5.00 (m, 4 H), 4.11 (s, 1 H), 2.26 (m, 2 H), 1.73 (d, 1 H).

Diethyl ether (18 mL), water (9.0 mL), and 1.0 g of 1,5-hexadien-3-ol were stirred at 0 °C. Jones reagent (8.4 g of CrO_3, 20 mL of water, 3.4 mL of 18 M H_2SO_4) was added, dropwise over 30 min with a syringe pump. The cooling bath was removed and the mixture allowed to stir for an additional 5 min. The mixture was extracted with 50 mL of pentane and washed with two 25-mL portions of water and 25 mL of saturated aqueous sodium bicarbonate. The volume was reduced to a few milliliters, but the dienone solution was not concentrated further due to its high volatility; the dienone was isolated as needed by preparative GC: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.44–6.21 (m, 2 H), 6.04–5.84 (m, 2 H), 5.23–5.12 (m, 2 H), 3.37 (m, 2 H); IR (film) 3090, 3020, 2980, 2918, 1676, 1640, 1626, 1398, 1320, 1182, 1086, 980, 960, 915, 820 cm^{-1}; HRMS for C_6H_8O, calcd 96.0575, found 96.0575; UV max (CH_3OH) $n\pi^*$ 324 nm (ϵ 49).

5-Hexenoic Acid, Methyl Ester (2b). 5-Hexenoic acid anhydride[21] (3.9 g, 18.6 mmol) was added to 4.0 mL of methanol and sodium methoxide (2.1 g, 38.9 mmol), and the mixture was heated at 50 °C for 30 min. The mixture was extracted with five 5.0-mL fractions of pentane. Pure **2b** was obtained by preparative GC: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.78 (m, 1 H), 5.10–4.97 (m, 2 H), 3.68 (s, 3 H), 2.33 (t, 2 H), 2.10 (q, 2 H), 1.77 (m, 2 H); IR ($CDCl_3$) 3090, 2960, 1730, 1648, 1442, 1178, 906, 730 cm^{-1}; MS, *m/z* (relative intensity) 128 (2), 74 (100).

6-Methyl-1,5-heptadien-3-ol. Sodium hydride (0.17 mol) was washed with two 40-mL pentane fractions and then dried under vacuum. DMSO (85 mL) was added, and the mixture was heated at 70–75 °C for 1.5 h (until hydrogen evolution had ceased).[22] The mixture was cooled to 25

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°C and charged with a small amount of triphenylmethane as indicator. While maintaining the temperature at 25 °C with external cooling, the red anion solution was treated, dropwise, with 2-methyl-3-buten-1-ol until the red color was gone (16 mL, 0.16 mol). Allyl bromide (21.8 g, 0.18 mol) was added, dropwise. The mixture solidified after a few minutes, requiring additional DMSO to homogenize the mixture. The mixture was added to 100 mL of pentane with the aid of 100 mL of water. The organic layer was washed with three 25-mL water fractions, dried ($MgSO_4$), and concentrated. The residue was distilled at reduced pressure to afford 6.2 g of 1-(2-propenoxy)-1,1-dimethyl-2-propene (31%): ^1H NMR (250 MHz, $CDCl_3$) δ 6.00–5.79 (m, 2 H), 5.34–5.10 (m, 4 H), 3.87 (d, 2 H), 1.33 (s, 6 H).

The above ether (6.2 g, 49 mmol) in 50 mL of THF was cooled to −78 °C. *n*-BuLi (41 mL, 69 mmol) was added, dropwise. After 6.3 h at −78 °C, the mixture was warmed to 0 °C and stirred for 1.5 h, acidified with 10% HCl, and extracted with 150 mL of ether. The organic layer was washed with three 50-mL water fractions, dried ($K_2CO_3/MgSO_4$), and concentrated to provide 5.9 g (95%) of crude alcohol, which was used without further purification. An analytical sample was prepared by preparative GC: ^1H NMR (250 MHz, $CDCl_3$) δ 5.99–5.80 (m, 1 H), 5.30–5.09 (m, 3 H), 4.15 (q, 1 H), 2.27 (t, 2 H), 1.76 (s, 3 H), 1.65 (s, 3 H); IR (film) 3360, 3080, 2970, 2912, 2860, 2720, 1846, 1720, 1672, 1642, 1438, 1420, 1372, 1102, 1034, 982, 912, 862, 812, 765 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.84; H, 11.11.

6-Methyl-1,5-heptadien-3-one (3). 6-Methyl-1,5-heptadien-3-ol (1.0 g, 7.9 mmol) in 18 mL of ether and 9 mL of water was stirred at 0 °C as Jones reagent (2.1 g of CrO_3, 9.1 mL of H_2O, 1.7 mL of 18 M H_2SO_4) was added, dropwise, over 20 min. The mixture was warmed to 25 °C over 10 min and taken into 50 mL of pentane, washed with two 20-mL water fractions, dried (K_2CO_3), concentrated, and chromatographed on silica gel to provide 0.50 g of the dienone **3** (51%), which gave the same ^1H NMR and IR data as those previously reported.[7] In addition, UV max (CH_3OH) $n\pi^*$ 328 nm (ϵ 123).

4,4-Dimethyl-1,5-hexadien-3-ol. To 3-methyl-2-buten-1-ol (20.0 g, 0.23 mol) in 34 mL of hexane were added allyl bromide (28.1 g, 0.23 mol) and benzyltriethylammonium chloride (2.6 g, 11.4 mmol). The mixture was cooled to 0 °C, and 50 mL of saturated aqueous sodium hydroxide was added in one portion.[23] The mixture was warmed to room temperature over 1 h and stirred overnight. The organic layer was separated, the aqueous layer was extracted with 100 mL of pentane, and the combined organic layers were washed with three 20-mL portions of water, dried ($MgSO_4$), and concentrated. The residue was distilled under aspirator vacuum to afford 25.9 g of 1-(2-propenoxy)-3-methyl-2-butene (89%): ^1H NMR (500 MHz, $CDCl_3$) δ 5.93 (m, 1 H), 5.38–5.13 (m, 3 H), 3.96 (m, 4 H), 1.73 (s, 3 H), 1.68 (s, 3 H); IR (film) 3085, 3020, 2980, 2920, 2860, 1678, 1648, 1450, 1378, 1074, 918 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.14; H, 11.18.

To the above ether (10.0 g, 79.2 mmol) in 80 mL of THF at −83 °C was added *n*-BuLi (65.3 mL, 0.11 mol). The mixture was warmed overnight to 25 °C. Then, 300 mL of ether and 100 mL of water were added, and the mixture was acidified with 10% HCl. The aqueous layer was extracted with an additional 100 mL of ether, and the combined organic layers were washed with 75 mL of water and 75 mL of saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated to provide crude 4,4-dimethyl-1,5-hexadien-3-ol in quantitative yield, with spectra in agreement with published values.[7]

4,4-Dimethyl-1,5-hexadien-3-one (4). 4,4-Dimethyl-1,5-hexadien-3-ol (1.0 g, 7.9 mmol) in 18 mL of ether and 9 mL of water was cooled to 0 °C, and Jones reagent (4.2 g of CrO_3, 10 mL of H_2O, 3.4 mL of 18 M H_2SO_4) was added with a syringe pump over 25 min. The cooling bath was removed and the mixture stirred for an additional 5 min. The mixture was extracted with 100 mL of pentane. The organic layer was washed with 50 mL of saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated to provide 0.72 g of dienone **4** (71%), with spectra in agreement with published values.[7] In addition, UV max (CH_3OH) $n\pi^*$ 332 nm (ϵ 87).

5-*tert*-Butyl-1,5-hexadien-3-one (5). To 2,3,3-trimethyl-1-butene (13.8 g, 0.14 mol) in 345 mL of carbon tetrachloride was added *N*-bromosuccinimide (75.0 g, 0.42 mol). The mixture was refluxed under irradiation from a tungsten lamp until ^1H NMR of aliquots indicated completion of the reaction. The solution was filtered and concentrated. The solution was filtered and concentrated. The residue was distilled under aspirator vacuum to afford 8.8 g of 1-bromo-2-*tert*-butyl-2-propene (35%): ^1H NMR (500 MHz, $CDCl_3$) δ 5.27 (s, 1 H), 5.19 (s, 1 H), 4.05 (s, 2 H), 1.17 (s, 9 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 153.21, 115.59, 35.79, 32.79, 29.72.

The above bromide (1.0 g, 5.6 mmol), benzyltriethylammonium chloride (0.07 g, 0.31 mmol), 1.5 mL of hexane, and 1.2 mL of saturated aqueous sodium hydroxide were stirred at 0 °C as allyl alcohol (0.33 g, 5.7 mmol) was added.[23] The mixture was warmed to room temperature over 1 h and stirred overnight. The mixture was extracted with 20 mL of pentane. The organic layer was washed with 5 mL of water, dried ($MgSO_4$), and concentrated to provide 0.60 g of 1-(2-propenoxy)-2-*tert*-butyl-2-propene (69%): ^1H NMR (250 MHz, $CDCl_3$) δ 6.05–5.87 (m, 1 H), 5.36–5.03 (m, 4 H), 4.04 (s, 2 H), 4.01 (d, 2 H), 1.11 (s, 9 H); IR (film) 3080, 2958, 2862, 1640, 1460, 1360, 1078, 905 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.45; H, 11.67.

The above ether (0.60 g, 3.9 mmol) in 4 mL of THF at −84 °C was treated with *n*-BuLi (4.0 mL, 6.8 mmol), dropwise over 10 min. The solution was stirred at −75 to −85 °C for 9 h, then warmed to 0 °C, and stirred for an additional 1 h. The solution was acidified with 10% HCl and extracted with 20 mL of ether. The organic layer was washed with 5 mL of water and 5 mL of saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated to yield a 0.31-g (52%) mixture of the desired 5-*tert*-butyl-1,5-hexadien-3-ol as well as some 2-*tert*-butyl-1,5-hexadien-3-ol in a ratio of 1.5 to 1. This mixture was carried on directly.

The above mixture of alcohols (0.31 g, 2.0 mmol) in 10 mL of ether and 5 mL of water at 0 °C was treated over 20 min with Jones reagent (0.84 g of CrO_3, 5.0 mL of H_2O, 0.7 mL of 18 M H_2SO_4). The cooling bath was removed and the mixture stirred for an additional 10 min. The mixture was extracted with 30 mL of pentane. The extract was washed with 25 mL of water and 25 mL of saturated aqueous sodium bicarbonate and dried ($K_2CO_3/MgSO_4$). The solvent was removed, and the two dienone isomers were separated by HPLC to afford 0.10 g of pure dienone **5** (33%), with ^1H NMR and IR spectra in agreement with published values.[5] In addition, UV max (CH_3OH) $n\pi^*$ 325 nm (ϵ 51).

1-(1-Cyclopentenyl)-3-buten-1-ol. To a refluxing solution consisting of 30 mL of toluene, HMPA (9.9 g, 0.055 mol), and lithium bromide (4.8 g, 0.055 mol) was added *cis*-2,3-epoxycyclohexanol (2.8 g, 0.025 mol), dropwise, over a period of 30 min.[24] The mixture was cooled in an ice bath and poured into a separatory funnel with 110 mL of ether. The lithium HMPA complex settled and was drained off. The organic layer was washed with three 10-mL portions of water, dried ($MgSO_4$), and briefly rotary evaporated to remove ether, affording a toluene solution of 1-cyclopentenecarboxaldehyde, which was used directly.

THF (15 mL) and allylmagnesium chloride (0.03 mol, Aldrich THF solution) were stirred at 0 °C. The toluene solution of cyclopentenecarboxaldehyde was added dropwise over a period of 45 min. The mixture was allowed to warm to 25 °C and stir for an additional 1.5 h. The mixture was slowly poured onto 100 g of ice. The resulting mixture was extracted with three 40-mL ether portions and filtered to remove insoluble salts. The aqueous layer was extracted with 30 mL of ether, and the combined organic fractions were washed with three 30-mL water fractions, dried ($MgSO_4$), and concentrated to yield the alcohol (1.8 g, 52%), with spectra in agreement with those previously reported.[24]

1-(1-Cyclopentenyl)-3-buten-1-one (7). Dienone **7** was prepared from the above alcohol by the published procedure, providing IR and ^1H NMR spectra in agreement with those published.[5] In addition, UV max (CH_3OH) $n\pi^*$ 315 nm (ϵ 140) was obtained for **7**.

2-(1-Cyclohexenyl)-2-(2-methyl-2-propenyl)-1,3-dithiane (11). 2-Cyclohexylidene-1,3-dithiane[25] (**12**) (8.0 g, 39.9 mmol) in 120 mL of THF and 32 mL of HMPA was cooled to −60 °C, treated, dropwise, with *n*-BuLi (30.3 mL, 52.1 mmol), and allowed to warm to 15 °C over 4 h. The mixture was cooled to −60 °C, and 3-iodo-2-methylpropene (9.9 g, 54.4 mmol) was added, dropwise, over 20 min and allowed to warm to 25 °C overnight. The mixture was taken into 200 mL of ether, washed with three 30-mL fractions of water, dried ($MgSO_4$), concentrated, and chromatographed on silica gel to yield 6.5 g of **11** (64%): ^1H NMR (250 MHz, $CDCl_3$) δ 6.26 (s, 1 H), 4.89 (s, 1 H), 4.80 (s, 1 H), 2.93–2.53 (m, 6 H), 2.26–1.78 (m, 6 H), 1.77 (s, 3 H), 1.71–1.44 (m, 4 H); IR (film) 3088, 2940, 2870, 1650, 1440, 1430, 1378, 1282, 1030, 895 cm^{-1}; HRMS for $C_{14}H_{22}S_2$, calcd 254.1163, found 254.1160.

1-(1-Cyclohexenyl)-3-methyl-3-buten-1-one (6). Dithiane **11** (6.4 g, 25 mmol) in 135 mL THF and 135 mL of 95% ethanol was stirred at 57 °C. A solution of silver nitrate (9.0 g, 53 mmol) in 20 mL of water was added dropwise over 2 min and allowed to stir for 50 min.[26] The mixture was poured into 150 mL of saturated aqueous NaCl solution and extracted with 200 mL of ether. The ether layer was filtered, washed with 150 mL of water, dried ($MgSO_4$), and concentrated. Purification using silica gel chromatography afforded 0.85 g of the dienone **6** (21%): ^1H NMR (250 MHz, $CDCl_3$) δ 6.94 (m, 1 H), 4.89 (d, 1 H), 4.74 (d, 1 H), 3.35 (s, 1 H), 2.23 (m, 4 H), 1.74 (d, 3 H), 1.61 (m, 4 H); IR (film) 3090, 2945, 2875, 1670, 1645, 1440, 1380 cm^{-1}; UV max (CH_3-

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OH) $n\pi^*$ 317 nm (ϵ 104). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.16; H, 10.02.

2-(1-Cyclohexenyl)-2-(2-propenyl)-1,3-dithiane (13). A solution of **12** (3.6 g, 18.0 mmol) and HMPA (14 mL) in 46 mL of THF was cooled to −78 °C. *n*-BuLi (13.1 mL, 19.8 mmol) was added, dropwise, and the mixture was allowed to warm to 25 °C over 3 h and then cooled again to −78 °C. Allyl bromide (22 mL, 25 mmol) was added, dropwise, to the red solution. The mixture immediately became yellow and was warmed to 25 °C after 30 min and stirred overnight. The mixture was added to 150 mL of ether, washed with four 14-mL portions of water, dried ($MgSO_4$), and concentrated to yield crude **13**. Purification using silica gel chromatography provided 2.6 g of **13** (55%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.20 (m, 1 H), 5.71 (m, 1 H), 5.11 (m, 2 H), 2.93–2.53 (m, 6 H), 2.24–1.77 (m, 6 H), 1.59 (m, 4 H); IR (film) 3100, 2920, 2870, 2680, 1655, 1435, 1355, 1285, 1250, 1145, 1105, 1090, 1000, 920, 880, 800 cm^{-1}. Anal. Calcd for $C_{13}H_{20}S_2$: C, 64.95; H, 8.38. Found: C, 65.06; H, 8.51.

1-(1-Cyclohexenyl)-3-buten-1-one (7). Dithiane **13** (0.62 g, 2.6 mmol) in 13 mL of THF and 13 mL of 95% ethanol was stirred at 50 °C as silver nitrate (0.92 g, 5.4 mmol) in 1.9 mL of water was added, dropwise over 5 min. After stirring for 30 min at 50 °C, the mixture was filtered into 90 mL of saturated aqueous sodium chloride. The solution was extracted with 75 mL of ether. The ether layer was dried ($MgSO_4$), concentrated, and chromatographed on silica gel, yielding 0.14 g of dienone **7** (36%) having spectra in agreement with those published for **7**.[5]

2-(1-Cycloheptenyl)-2-(2-propenyl)-1,3-dithiane (14). To 2-cycloheptylidene-1,3-dithiane[25] (4.1 g, 19 mmol) in 40 mL THF and 16 mL of HMPA at −60 °C was added *n*-BuLi (16.1 mL, 25 mmol), dropwise, over 30 min. The mixture was warmed to 0 °C over 3 h and then cooled to −60 °C. Allyl bromide (3.6 g, 30 mmol) was added, dropwise, and the solution warmed to room temperature over 3 h and stirred overnight. The mixture was taken up in 200 mL of ether, washed with three 100-mL portions of water, dried ($MgSO_4$), and concentrated to yield 5.6 g of crude **14**. Purification using silica gel chromatography afforded 3.1 g (63%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.38 (t, 1 H), 5.73 (m, 1 H), 5.13 (m, 2 H), 2.86 (m, 2 H), 2.62 (m, 4 H), 2.35 (t, 2 H), 2.23 (q, 2 H), 2.00–1.88 (m, 2 H), 1.77 (m, 2 H), 1.48 (m, 4 H): IR (film) 3070, 2915, 2850, 1675, 1638, 1420, 1270, 980, 905 cm^{-1}; HRMS for $C_{14}H_{22}S_2$, calcd 254.1163, found 254.1163.

1-(1-Cycloheptenyl)-3-buten-1-one (9). Dithiane **14** (1.5 g, 5.9 mmol) in 30 mL of THF and 30 mL of 95% ethanol was stirred at 50 °C while silver nitrate (2.1 g, 12.4 mmol) in 4.3 mL of water was added, dropwise over 5 min. The mixture was stirred for 20 min at 50 °C, then combined with 100 mL of saturated aqueous sodium chloride, and filtered. The filtrate was extracted with three 50-mL portions of pentane, dried (Na_2SO_4), filtered, and concentrated. Purification using silica gel chromatography provided 0.20 g of **9** (21%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.12 (t, 1 H), 5.96 (m, 1 H), 5.12 (m, 2 H), 3.43 (m, 2 H), 2.51 (m, 2 H), 2.35 (m, 2 H), 1.78 (m, 2 H), 1.64–1.40 (m, 4 H); IR (film) 3095, 2940, 2865, 1670, 1640, 1450, 1180, 990, 915 cm^{-1}; UV max (CH_3OH) $n\pi^*$ 314 nm (ϵ 61). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.22; H, 9.66 (single peak on capillary GC).

2-Cyclooctylidene-1,3-dithiane (15). To 2-(trimethylsilyl)-1,3-dithiane[25] (11.8 g, 61 mmol) in 100 mL of THF at −35 °C was added *n*-BuLi (39 mL, 67 mmol), over 5 min. The mixture was allowed to warm to 0 °C over 4 h and then cooled to −65 °C. Cyclooctanone (9.2 g, 73 mmol) in 20 mL THF was added, over 10 min, and the mixture was warmed to 25 °C overnight. The mixture was taken up in 200 mL of ether, washed with four 30-mL portions of water, dried ($MgSO_4$), and concentrated to give crude thioketene acetal, which contained much 2-(trimethylsilyl)-1,3-dithiane and cyclooctanone. The residue was distilled under vacuum to afford several mixed fractions as well as 6.0 g of pure 2-cyclooctylidene-1,3-dithiane (43%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.88 (t, 4 H), 2.48 (t, 4 H), 2.13 (m, 2 H), 1.69 (m, 4 H), 1.49 (m, 6 H); IR (film) 2915, 2845, 2670, 1690, 1560, 1465, 1440, 1415, 1345, 1300, 1275, 1240, 905, 840 cm^{-1}; HRMS for $C_{12}H_{20}S_2$, calcd 228.1006, found 228.1006.

1-(1-Cyclooctenyl)-3-buten-1-one (10). A solution of **15** (6.0 g, 26 mmol), 20 mL of HMPA, and 66 mL of THF was cooled to −78 °C. *n*-BuLi (17.0 mL, 29 mmol) was added over 10 min, and the mixture was allowed to warm to 25 °C over 4 h and then cooled to −78 °C. Allyl bromide (4.1 g, 34 mmol) was added over 15 min, and then the reaction mixture was warmed overnight to 25 °C. The mixture was taken into 200 mL of ether, washed with three 30-mL portions of water, dried ($MgSO_4$), and concentrated. Purification using silica gel chromatography afforded 3.6 g of 2-(1-Cyclooctenyl)-2-(2-propenyl)-1,3-dithiane (**16**) (52%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 (t, 1 H), 5.71 (m, 1 H), 5.09 (m, 2 H), 2.81 (m, 2 H), 2.68 (m, 4 H), 2.36 (m, 2 H), 2.20 (m, 2 H), 2.03–1.83 (m, 2 H), 1.55 (br s, 8 H); IR (film) 3090, 2920, 2860, 2810, 2680, 1695, 1645, 1470, 1450, 1425, 1300, 1280, 1210, 1070, 985, 910, 740 cm^{-1}.

Dithiane **16** (1.6 g, 6.1 mmol) in 30 mL of THF and 30 mL of 95% ethanol was heated to 50 °C, and silver nitrate (2.1 g, 12.4 mmol) in 4.0 mL of water was added, rapidly. The mixture was stirred at 50 °C for 30 min, filtered into 50 mL of saturated aqueous sodium chloride, and extracted with 100 mL of ether. The organic layer was washed with two 15-mL water portions, dried ($MgSO_4$), and concentrated to yield 0.96 g of crude dienone **10** (59%). Purification using HPLC provided **10**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (t, 1 H), 5.94 (m, 1 H), 5.10 (m, 2 H), 3.43 (d, 2 H), 2.42 (m, 2 H), 2.32 (m, 2 H), 1.61 (m, 2 H), 1.48 (m, 2 H), 1.41 (m, 4 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 198.66, 143.13, 142.18, 132.09, 117.68, 42.17, 29.02, 28.94, 27.43, 26.43, 25.98, 23.45; IR (film) 3090, 3050, 2930, 2862, 1670, 1638, 1470, 1450, 1380, 1320, 1290, 1190, 1175, 1090, 990, 910 cm^{-1}; UV max (CH_3OH) $n\pi^*$ 317 nm (ϵ 96); HMRS for $C_{12}H_{18}O$, calcd 178.1358, found 178.1355.

Preparative Photochemistry. Each dienone studied was irradiated on a preparative scale to allow isolation, characterization, and GC calibration of the photoproducts. No attempt was made to quantify these irradiations, since subsequent detailed quantum yield studies were undertaken and are reported for each dienone.

5-Methyl-1,5-hexadien-3-one (1). In a Pyrex tube, 0.19 g of **1** and 100 mL of methanol were irradiated through a uranium glass filter with the 350-nm bulbs in the RPR. Preparative GC afforded known ketone **1a** and known ester **1b**. **1a**:[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.75 (t, 1 H), 2.02 (t, 2 H), 1.89 (m, 2 H), 1.62 (m, 2 H), 1.26 (s, 3 H); IR ($CDCl_3$) 1760 cm^{-1} (C═O). **1b**:[4] ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.71 (s, 1 H), 4.66 (s, 1 H), 3.65 (s, 3 H), 2.29 (t, 2 H), 2.02 (t, 2 H), 1.75 (t, 2 H), 1.69 (s, 3 H); IR (film) 3100, 2960, 1750, 1660, 1450, 890 cm^{-1}.

1,5-Hexadien-3-one (2). In the 350-nm RPR, 0.20 g of dienone **2** in 40 mL of pentane was irradiated through uranium glass. The solution was concentrated to about 0.5 mL, and ketone **2a** was isolated by using preparative GC: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.82 (m, 2 H), 2.22 (m, 2 H), 2.13 (m, 2 H), 1.62 (m, 2 H); IR (film) 3000, 2890, 1760, 1422, 1294, 1270, 1228, 1154, 1014, 862, 802, 754 cm^{-1}; MS, *m*/*z* (relative intensity) 96.07 (54), 67.10 (100).

A second tube containing 0.20 g of **2** in 100 mL of pentane/methanol (25:1) was irradiated through Pyrex by using the 300-nm bulbs in the RPR. The solution was concentrated to about 0.5 mL. In addition to **2a**, ester **2b** was isolated by preparative GC and identified by comparison of its ^{1}H NMR spectrum and GC retention time on two different capillary columns with independently synthesized and characterized **2b** (see above).

6-Methyl-1,5-heptadien-3-one (3). Irradiation, through uranium glass, of 0.25 g of dienone **3** in 90 mL of methanol provided known esters **3c** and **3d**,[7] known enone **3b**,[7] and known ketone **3a**,[27] which were separated by using a combination of preparative HPLC and GC. Spectra obtained for the four products agreed with published values.

4,4-Dimethyl-1,5-hexadien-3-one (4). In 250 mL of methanol, 0.50 g of dienone **4** was irradiated through Pyrex glass by using the 300-nm bulbs in the RPR. With a combination of preparative HPLC and GC, products **3a**–**3d** and ketone **4a** were isolated: **4a** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.77 (m, 1 H), 2.43 (m, 1 H), 2.10 (m, 2 H), 1.88 (m, 2 H), 1.15 (s, 6 H); IR ($CDCl_3$) 2965, 1738, 1460, 1210 cm^{-1}; MS, *m*/*z* (relative intensity) 124 (23), 81 (100).

5-*tert*-Butyl-1,5-hexadien-3-one (5). In 50 mL of methanol, 0.10 g of dienone **5** was irradiated through uranium glass by using the 350-nm bulbs in the RPR to afford known ketone **5a** and known ester **5b** after separation by preparative HPLC. Spectra agreed with published values.[5]

1-(1-Cyclohexenyl)-3-methyl-3-buten-1-one (6). In 200 mL of methanol, 0.40 g of dienone **6** was irradiated through Pyrex by using the 350-nm bulbs in the RPR. Separation using preparative HPLC afforded three fractions. The first fraction contained trans ester **6b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74 (s, 1 H), 4.65 (s, 1 H), 3.65 (s, 3 H), 2.61 (m, 1 H), 2.18–1.30 (m, 11 H), 1.57 (s, 3 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 175.18, 143.80, 111.78, 51.00, 44.67, 38.78, 34.67, 27.91, 25.63, 23.81, 22.60, 21.94; IR (film) 3080, 2940, 2862, 1740, 1650, 1450, 1440, 1375, 1242, 1160, 1042, 890, 732 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 71.71; H, 9.90 (contained trace residual solvent).

The second fraction was a mixture of two compounds, which were separated by preparative GC, providing pure samples of cis ester **6b** and an unidentified product (**6c**). **6b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.72 (s, 1 H), 4.71 (s, 1 H), 3.65 (s, 3 H), 2.12–1.19 (m, 12 H), 1.68 (s, 3 H); IR (film) 3080, 2940, 2860, 1742, 1652, 1450, 1440, 1256, 1200, 1158, 728 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 72.59; H, 10.00. **6e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03–1.86 (m, 4 H), 1.72–1.62 (m, 2 H), 1.54–1.36 (m, 3 H), 1.23–1.07 (m, 3 H), 1.17

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(s, 3 H), 0.91 (m, 1 H); ^{13}C NMR (DEPT) (500 MHz, CDCl$_3$) δ 203.45 ($C{=}O$), 65.64 (quart.), 59.89 (quart.), 38.68 (CH), 37.83 (CH$_2$), 35.32 (CH$_2$), 32.62 (CH$_2$), 25.95 (CH$_2$), 24.94 (CH$_2$), 23.88 (CH$_2$), 11.90 (CH$_3$); IR (film) 2940, 2890, 1795, 1450 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.34; H, 9.83. These data are consistent with the structure shown below for **6c**.

6c (proposed)

The third HPLC fraction was the minor ketone isomer **6a**: ^{1}H NMR (250 MHz, CDCl$_3$) δ 2.16–1.97 (m, 3 H), 1.77–1.18 (m, 9 H), 1.29 (s, 3 H), 1.06–0.87 (m, 1 H); ^{13}C NMR (DEPT) (500 MHz, CDCl$_3$) δ 215.96 ($C{=}O$), 62.74 (quart.), 57.13 (CH), 50.28 (CH$_2$), 46.02 (quart.), 43.07 (CH$_2$), 24.69 (CH$_2$), 24.33 (CH$_2$), 23.32 (CH$_2$), 22.09 (CH$_2$), 18.68 (CH$_3$); IR (film) 2940, 2872, 1758, 1450, 1312, 1050 cm^{-1}; HRMS for $C_{11}H_{16}O$, calcd 164.1206, found 164.1201.

The fourth HPLC fraction contained the major ketone isomer **6a**: ^{1}H NMR (250 MHz, CDCl$_3$) δ 2.42–2.03 (m, 3 H), 1.61–1.15 (m, 9 H), 1.13 (s, 3 H), 1.00–0.85 (m, 1 H); ^{13}C NMR (DEPT) (500 MHz, CDCl$_3$) δ 214.40 ($C{=}O$), 59.64 (quart.), 51.00 (CH), 49.94 (CH$_2$), 41.09 (quart.), 39.89 (CH$_2$), 22.88 (CH$_2$), 21.70 (CH$_2$), 21.63 (CH$_2$), 21.13 (CH$_2$), 15.78 (CH$_3$); IR (film) 2938, 2872, 1760, 1448, 1240, 1048 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found C, 79.78; H, 9.83.

1-(1-Cyclopentenyl)-3-buten-1-one (7). With use of the 350 nm bulbs in the RPR, 70 mg of **7** in 45 mL of methanol was irradiated through uranium glass. Separation using preparative HPLC afforded **7a** and **7b**. Spectra of **7a** agreed with those previously reported.[5] Compound **7b** also showed spectra in agreement with those previously reported,[5] though in the previous study the stereochemistry was not specified. In the present study, both *cis*- and *tran*-**7b** were isolated (ratio ~1:2 by GC). *cis*-**7b**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.74 (m, 1 H), 4.96 (m, 2 H), 3.61 (s, 3 H), 2.82 (m, 1 H), 2.12 (m, 2 H), 2.00–1.60 (m, 7 H). *trans*-**7b**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.74 (m, 1 H), 4.98 (m, 2 H), 3.63 (s, 3 H), 2.28 (m, 1 H), 2.21–1.60 (m, 9 H).

1-(1-Cyclohexenyl)-3-buten-1-one (8). In the RPR, with use of the 350-nm bulbs, 0.27 g of dienone **8** in 100 mL of methanol was irradiated through a uranium glass filter. Separation using preparative HPLC resulted in isolation of three products, ketone **8a** and ester **8b**, which had spectra in agreement with those previously reported.[5]

1-(1-Cycloheptenyl)-1,5-hexadien-3-one (9). In the RPR, with use of the 350-nm bulbs, 0.20 g of dienone **9** in 40 mL of methanol was irradiated through uranium glass. Separation using preparative HPLC provided ketones **9a**. Major isomer: ^{1}H NMR (250 MHz, CDCl$_3$) δ 2.57–2.50 (m, 1 H), 2.38 (t, 1 H), 2.26–2.17 (m, 3 H), 1.95–1.84 (m, 5 H), 1.24 (m, 4 H), 1.19–0.83 (m, 2 H); IR (film) 2920, 2870, 1753, 1454, 1000, 754 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.82; H, 10.00. Minor isomer: ^{1}H NMR (250 MHz, CDCl$_3$) δ 2.58 (m, 1 H), 2.37–2.28 (m, 1 H), 2.24–2.01 (m, 3 H), 1.85–1.49 (m, 6 H), 1.41–1.13 (m, 3 H), 1.06–0.87 (m, 2 H); IR (CDCl$_3$) 2932, 2862, 1760, 1452, 1270, 1082, 1000, 902, 732 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.80; H, 9.86.

1-(1-Cyclooctenyl)-3-buten-1-one (10). In 45 mL of methanol, 0.23 g of dienone **10** was irradiated through uranium glass by using the 350-nm bulbs in the RPR. Purification using preparative HPLC afforded ketones **10a**. Major isomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.51 (m, 1 H), 2.37 (m, 1 H), 2.24 (m, 2 H), 2.21–2.13 (m, 1 H), 1.90 (m, 1 H), 1.82–1.25 (m, 12 H); ^{13}C NMR (DEPT) (500 MHz, CDCl$_3$) δ 215.00 ($C{=}O$), 66.29 (quart.), 56.22 (CH), 44.89 (CH$_2$), 40.41 (CH$_2$), 35.92 (CH), 29.02 (CH$_2$), 27.10 (CH$_2$), 25.54 (CH$_2$) 22.61 (CH$_2$), 22.41 (CH$_2$), 21.97 (CH$_2$); IR (CDCl$_3$) 2924, 1755, 1450, 1065, 726 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.96; H, 10.14. Minor isomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.57 (m, 1 H), 2.29 (m, 1 H), 2.23–2.06 (m, 2 H), 1.98 (m, 1 H), 1.80 (M, 1 H), 1.66–1.03 (m, 12 H); ^{13}C NMR (DEPT) (500 MHz, CDCl$_3$) δ 215.24 ($C{=}O$), 67.73 (quart.), 53.67 (CH), 44.17 (CH$_2$), 38.82 (CH$_2$), 34.09 (CH), 28.68 (CH$_2$), 27.82 (CH$_2$), 25.81 (CH$_2$), 25.72 (CH$_2$), 24.82 (CH$_2$), 22.57 (CH$_2$); IR (CDCl$_3$) 2926, 2878, 1758, 1462, 1272, 1065, 728 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.98; H, 10.11.

Triplet Sensitization. In all sensitization experiments, unless otherwise mentioned, two degassed samples were irradiated simultaneously under identical conditions. The first sample consisted of a dienone solution with no added sensitizer; the second sample consisted of the dienone solution and added sensitizer, in concentrations such that the sensitizer to dienone absorbance ratio was greater than 9:1.

Dienone 1 with Propiophenone. Propiophenone (5.6×10^{-4} mol) was added to 3 mL of methanol containing 1.1×10^{-5} mol of **1**. The solution was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 1 with Xanthone. Xanthone (3×10^{-5} mol) was added to 1 mL of methanol containing 6.5×10^{-6} mol of **1**. The solution was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 1 with *p*-Methoxyacetophenone. *p*-Methoxyacetophenone (1×10^{-4} mol) was added to 1 mL of methanol and 6.5×10^{-6} mol of **1**. The solution was irradiated through Pyrex by using the 300-nm bulbs in the RPR.

Dienone 1 with Thioxanthone. Thioxanthone (4.7×10^{-6} mol) was added to 1 mL of methanol and 2.7×10^{-6} mol of **1**. The solution was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 1 with Acetone. A 2.1×10^{-3} M solution of **1** in spectrometric grade acetone was irradiated through Pyrex by using the 300-nm bulbs in the RPR.

Dienone 1 with Benzophenone. Benzophenone (2.3×10^{-3} mol) was added to 2 mL of methanol and 7.1×10^{-6} mol of **1**. This solution was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 1 with *m*-Methoxyacetophenone. *m*-Methoxyacetophenone (2.7×10^{-5} mol) was added to 1 mL of methanol and 2.7×10^{-6} mol of **1**. The solution was irradiated through Pyrex by using the 300-nm bulbs in the RPR.

Dienone 2 with Xanthone. A solution of 4.8×10^{-5} mol of xanthone and 1.3×10^{-5} mol of **2** in 3 mL of methanol was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 3 with *p*-Methoxyacetophenone. A solution of 1 mL of methanol containing 5×10^{-6} mol of **3** and 9.8×10^{-4} mol of *p*-methoxyacetophenone was irradiated through Pyrex by using the 300-nm bulbs in the RPR.

Dienone 4 with Xanthone. A solution of 3 mL of methanol containing 1.5×10^{-6} mol of **4** and 3.6×10^{-5} mol of xanthone was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 5 with Xanthone. A solution of 1 mL of methanol containing 3.8×10^{-6} mol of **5** and 2.3×10^{-5} mol of xanthone was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 5 with *p*-Methoxyacetophenone. A solution of 0.5 mL of methanol containing 1.7×10^{-6} mol of **5** and 2.3×10^{-5} mol of *p*-methoxyacetophenone was irradiated through Pyrex by using the 300-nm bulbs in the RPR.

Dienone 5 with Propiophenone. A solution of 1 mL of methanol containing 3.8×10^{-6} mol of **5** and 3.7×10^{-4} mol of propiophenone was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 6 with Xanthone. A 3-mL methanol solution containing 1.1×10^{-6} mol of **6** and 3.6×10^{-5} mol of xanthone was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 6 with 2-Acetonaphthone. A 3-mL methanol solution containing 1.1×10^{-6} mol of **6** and 5.9×10^{-5} mol of 2-acetonaphthone was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 6 with Triphenylene. A 3-mL methanol solution containing 1.1×10^{-6} mol of **6** and 1.9×10^{-5} mol of triphenylene was irradiated through Pyrex glass by using the 300-nm bulbs in the RPR.

Dienone 6 with Benzophenone. A solution of 2.8 mL of hexane and 0.2 mL of methanol containing 7.6×10^{-7} mol of **6** and 1.2×10^{-4} mol of benzophenone was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 6 with Thioxanthone. A solution of 2.8 mL of hexane and 0.2 mL of methanol containing 7.6×10^{-7} mol of **6** and 8.1×10^{-5} mol of thioxanthone was irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 7 with Xanthone. In 3 mL of methanol, 1.7×10^{-6} mol of **7** and 9.8×10^{-5} mol of xanthone were irradiated through uranium glass by using the 350-nm bulbs in the RPR.

Dienone 8 with Xanthone. In 3 mL of methanol, 2.9×10^{-5} mol of **8** and 9.8×10^{-5} mol of xanthone were irradiated through uranium glass by using the 350-nm bulbs in the RPR.

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