Articles

Wavelength-Dependent Photochemistry of 4-Methoxybicyclo[3.1.0]hexenones[†]

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Wavelength-dependent photochemistry of a series of 4-methoxybicyclo[3.1.0]hexenones is mechanistically investigated. Upon excitation of the symmetry-forbidden S_1 $n \rightarrow \pi^*$ state, photoisomerization is exclusively observed. By comparison of the direct and sensitized quantum yields for this particular process, the T_1 $\pi \rightarrow \pi^*$ state, which is populated via efficient intersystem crossing as shown by phosphorescence experiments, is proven to be the reactive state. A pathway via external cyclopropane bond cleavage followed by racemization of the formed triplet biradicals reasonably accounts for the observed photostationarity. Excitation of the electric dipole allowed S_2 $\pi \rightarrow \pi^*$ state initiates phenol formation. The T_2 $n \rightarrow \pi^*$ state, which could not be sensitized, gives a type-B oxyallyl zwitterion via internal cleavage as could be shown by intermolecular as well as intramolecular trapping experiments. The observed data are in good agreement with computational studies.

Introduction

Wavelength-dependent photochemistry[1] is a rarely observed phenomenon, which can be of particular interest in terms of selective synthesis, one of the most challenging topics in organic chemistry today. During the past decade, Schultz and co-workers[2] have demonstrated the synthetic use of photorearrangements of cross-conjugated cyclohexadienones (type A) as well as bicyclo[3.1.0]hexenones (type B), reactions first observed in the rearrangements of α-santonin[3] and mechanistically interpreted by Zimmerman and Schuster.[4] Recently, the type-B rearrangement has been studied in a crystalline cage.[5] These photochemical rearrangements have been reviewed in great detail.[6]

Focusing on the rearrangements of the bicyclo[3.1.0]hexenones bearing a methoxy substituent in the 4-position, both photoisomerization and phenol formation have been observed.[2a,7] The first process was suggested to originate from a $\pi \rightarrow \pi^*$ triplet via external cyclopropane bond cleavage, whereas the latter was supposed to occur from a $n \rightarrow \pi^*$ triplet via internal cleavage.[8] In the latter sequence, a zwitterionic species was proposed as a key intermediate. In terms of wavelength-dependent photochemistry, only Miller[9] indicated partition of more than one excited singlet state in order to explain observed side reactions.

Recently, Dauben et al.[10] have found wavelength-dependent photochemical behavior in the methyl ester series (**1**−**3a**) and, therefore, gave rise to further mechanistic investigation. Since we sought specific evidence to establish the multiplicity and character of the excited states and their relationship to external and internal bond cleavage processes, a detailed mechanistic study of the photochemistry of the bicyclic enones **2** and **3** (Scheme 1) was undertaken.

Results and Discussion

Photophysics. Analysis of the UV spectra of **2a**,**b** as well as **3a**,**b** revealed the characteristic enone absorption pattern of a weak, low-energy $n \rightarrow \pi^*$ transition corresponding to the S_1 state followed by an intense band due to the electric dipole allowed $\pi \rightarrow \pi^*$ transition to the S_2

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[†] In memory of William G. Dauben (1919−1997).

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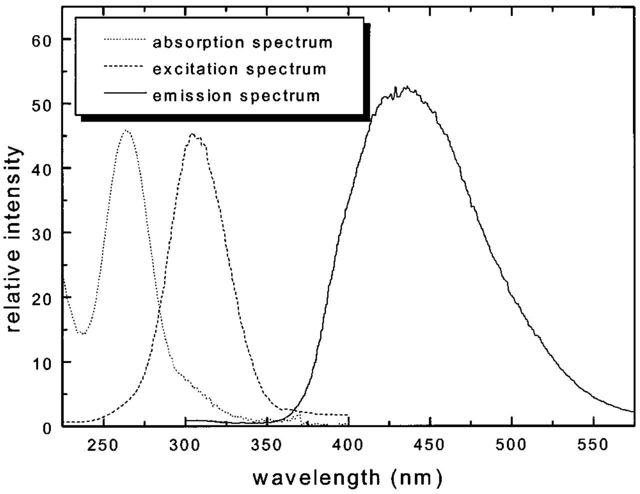
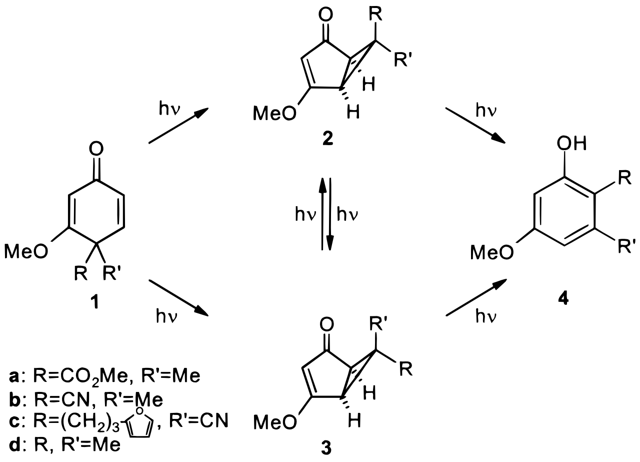


Figure 1. Spectral overlay for compound **2a** (absorption spectrum (reduced for graphic reasons) in methanol at 298 K with $\lambda_{max} = 264$ nm, phosphorescence excitation spectrum at $\lambda_{em} = 430$ nm in ethanol at 77 K with $\lambda_{max} = 305$ nm, and phosphorescence emission spectrum at $\lambda_{exc} = 300$ nm in ethanol at 77 K with $\lambda_{max} \approx 433$ nm).

Scheme 1



state. The nature of the S_2 state was additionally confirmed by observation of bathochromic shifts in the range of 10 nm upon changing the solvent from cyclohexane to methanol.

No fluorescence could be detected at room temperature in solution and at low temperature in ethanol matrices, indicating fast depopulation of the singlet excited states by intersystem crossing (ISC) as verified by phosphorescence measurements. In these experiments, a broad phosphorescence emission was observed, which is usually associated with a $\pi\rightarrow\pi^*$ triplet electronic configuration.[11] The triplet energies were determined to be ~65 kcal/mol by phosphorescence.

The most intriguing spectroscopic feature is a large red shift of ~40 nm between the absorption spectrum and the phosphorescence excitation spectrum depicted in Figure 1.

This mismatch evolves from the participation of two different excited singlet states in this particular photophysical process. The excitation spectrum represents the symmetry-forbidden S_1 state, which populates the emitting triplet state T_1 more efficiently than the allowed S_2 state (absorption maximum). Thus, we assume that internal conversion (IC) from S_2 to S_1 is relatively slow compared to ISC from S_1 to T_1. This fact can be rationalized by the poor symmetry overlap between $^1(\pi\rightarrow\pi^*)$ and $^1(n\rightarrow\pi^*)$ on one hand and by spin–orbit coupling of $^1(n\rightarrow\pi^*)$ and $^3(\pi\rightarrow\pi^*)$ according to El Sayed's rules[12] on the other hand.

Direct Irradiation. Turning to the photochemical behavior, direct irradiation of **1a**,**b** by excitation into the S_1 shoulder using an Uranium filter gave exclusively photoisomerization products, i.e., bicyclo[3.1.0]hexenones **2a**,**b** and **3a**,**b**. After longer irradiation times, a photostationary state was approached, and phenol **4a** was detected in small amounts. The fact that no **4b** was observed reflects the high migration tendency of the ester compared to the cyano substituent.[2a,b,13] The poor type-B photochemistry indicates a very inefficient ISC (El Sayed's rules apply) from S_1 to T_2, which is of $n\rightarrow\pi^*$ nature and initiates the phenol formation.

By employing a Corex filter to excite the S_2 state, the efficiencies of both isomerization and phenol formation increased due to higher absorption. Hence, both phenols **4a** and **4b** were detected, although **4b** was formed only in small quantities, presumably due to the low migratory aptitude of the cyano group. It is obvious that epimerization occurs from S_1, or a state derived from S_1, and phenol formation originates from S_2 or a state derived most efficiently from S_2.

Sensitized Irradiation. To investigate the multiplicity of the reactive excited states, sensitization studies were undertaken. According to the measured triplet energies, xanthone ($\pi\rightarrow\pi^*$, 74 kcal/mol)[14] and benzophenone ($n\rightarrow\pi^*$, 69 kcal/mol)[14] were chosen as triplet sensitizers. Theoretical analysis of the triplet–triplet energy transfer (TTET) for these particular systems on the basis of an appropriate model suggested by Mirbach et al.[15] indicates generation of the $\pi\rightarrow\pi^*$ triplet of the substrate in all cases and is consistent with the phosphorescence studies. Indeed, sensitization gave exclusively interconversion of the endo and exo epimers (**2a**,**b** and **3a**,**b**), implying that T_1 is as the reactive state for photoisomerization. Thioxanthone ($\pi\rightarrow\pi^*$, 65 kcal/mol)[14] did not lead to any product formation, implicating inefficient TTET due to the low triplet energy of the sensitizer.[16] In contrast, attempts to quench the triplet excited state of the substrate using 1,3-cyclohexadiene, which would yield diene dimers,[17] failed.

To account for the observed isomerization products, it is quite reasonable that the $\pi\rightarrow\pi^*$ triplets of **2** and **3** undergo scission of the external cyclopropane bond[2a] to give triplet biradicals, which after rotation around the C(1)–C(6) bond (**5**) or C(5)–C(6) bond (**6**) and subsequent spin flip lead to isomerization of the starting material (Scheme 2). In the photochemistry of cyclopropyl ketones, the bond which better overlaps with the π-system of the carbonyl group is usually the one that is prefer-

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Scheme 2

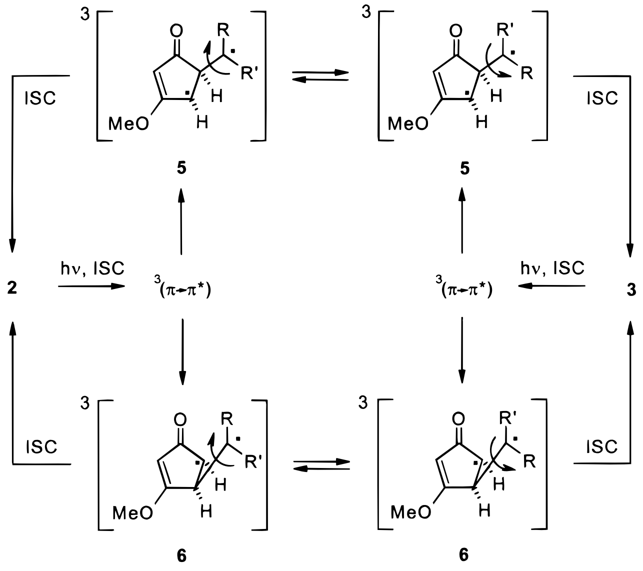


Table 1. Direct and Sensitized Quantum Yields for Photoisomerization[a]

	$\Phi_{2a\rightarrow 3a}$	$\Phi_{3a\rightarrow 2a}$
direct[b]	0.2	0.2
313 nm	0.04	0.2
366 nm		
sensitized[c]	0.188 (0.261)	0.156 (0.092)
xanthone	0.102 (0.102)	0.141 (0.076)
benzophenone		

	$\Phi_{2b\rightarrow 3b}$	$\Phi_{3b\rightarrow 2b}$
direct[d]	0.059	0.115
313 nm	0.062	0.104
334 nm	nr[e]	nr
366 nm		
sensitized[f]	0.047 (0.084)	0.079 (0.116)
xanthone	0.027 (0.039)	0.066 (0.021)
benzophenone		

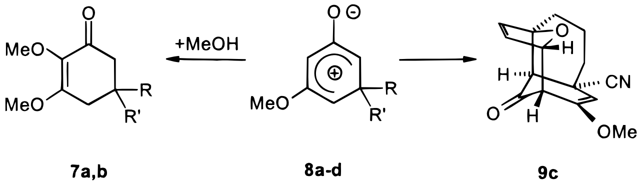
[a] In benzene, numbers in parentheses correspond to acetonitrile. [b] Reference 9. [c] Method b. [d] In acetonitrile. [e] No reaction. [f] Method a.

entially broken.[18] Furthermore, Hixson[19] and Garin[20] independently provided evidence to support a triplet-state mechanism for the isomerization of related compounds.

Quantum Yield Measurements. Quantum yields for photoisomerization on direct and triplet-sensitized excitation are given in Table 1.

Comparison of the data for **2a**/**3a** and **2b**/**3b** is not possible because different experimental approaches and different solvents were employed. However, within experimental error, the triplet quantum yields for the isomerization match the direct quantum yields, which strongly suggests that this reaction originates from the T_1 state. Phenol formation is only detected at shorter wavelength[10] in the absence of sensitizer. The measured quantum yields are in good agreement with the observed ratios of the two epimers approaching the photostationary state. The observation that TTET from benzophenone is less efficient than from xanthone is attributed to both the lower triplet energy of the sensitizer and the poorer frontier orbital overlap in the donor–acceptor pair according to an exchange mechanism.[21] Observed solvent effects can be explained in terms of different triplet-state lifetimes especially of $^3(\pi\rightarrow\pi^*)$.[22]

Scheme 3



Trapping Experiments. Trapping experiments were carried out in order to investigate the reactive state responsible for phenol formation and to elucidate the existence of type-B oxyallyl zwitterionic intermediates[4,6] (Scheme 3).

Intermolecular trapping performed with **2** and **3** in neat methanol[23] using a Corex filter afforded **7b** almost exclusively, whereas **7a** could only be detected in small amounts by GC–MS. Repeat experiments carried out either with an Uranium filter or in the presence of sensitizer failed to yield any **7a** or **7b**.

In analogy to an intramolecular trapping experiment described in the literature,[13] we investigated the [4 + 3] cycloaddition[24] of a tethered furan to zwitterion **8c** to form **9c** as a function of the excitation wavelength and the presence of sensitizer. Surprisingly, the direct and sensitized runs did not show significant differences, but as expected, S_2 excitation led to dramatically increased yields of the trapping product. Therefore, the authors suggest that in **2c** and **3c** the T_2 $n\rightarrow\pi^*$ state, which is the precursor of zwitterion **8c**, is lowered in energy as a result of the appended furan moiety and becomes accessible to TTET from the sensitizer. Intramolecular energy-transfer processes from the furanyl system to the bicyclic enone unit cannot be ruled out.

The trapping experiments confirm the existence of zwitterionic intermediates during the course of the reaction and unambiguously indicate that T_2 is the reactive state for zwitterion and consequently phenol formation. Again, ISC ($S_2\rightarrow T_2$) should be favored according to El Sayed's rules.[12]

Computational Studies. In previous studies, it has been shown that semiempirical methods such as MNDO[25] and AM1,[26] that take doubly or multiply excited configurations into account, are well suited for calculating excitation energies and excited-state geometries.[27] On this particular level of theory, the computational results

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Table 2. Calculated Singlet and Triplet Transitions (λ_{exc}), Oscillator Strengths (f_{osc}), and Characters of the Excited States[a]

	2a	2b	2c	3a	3b	3c
S_1:						
λ_{exc} (nm)	277 (305)[b]	282 (300)	274	274 (310)	281 (313)	274
f_{osc}	0.27	0.06	0.33	0.18	0.08	0.38
character	37% $n \to \pi^*$	64% $n \to \pi^*$	70% $\pi_f \to \pi_f^*$[c]	54% $n \to \pi^*$	62% $n \to \pi^*$	69% $\pi_f \to \pi_f^*$
S_2:						
λ_{exc} (nm)	260 (273,[e] 270,[f] 263[g])[d]	266 (270, 267, 259)	266	263 (264, 260, 250)	266 (264, 262, 254)	269
f_{osc}	0.26	0.48	0.48	0.32	0.46	0.41
character	37% $\pi \to \pi^*$	65% $\pi \to \pi^*$	70% $\pi \to \pi^*$	55% $\pi \to \pi^*$	62% $\pi \to \pi^*$	69% $\pi \to \pi^*$
T_1:						
λ_{exc} (nm)	446 (~433)[h]	478 (~446)	492	446 (~443)	490 (~432)	493
character	70% $\pi \to \pi^*$	68% $\pi \to \pi^*$	71% $\pi_f \to \pi_f^*$	70% $\pi \to \pi^*$	68% $\pi \to \pi^*$	71% $\pi_f \to \pi_f^*$
T_2:						
λ_{exc} (nm)	278	294	429	281	292	438
character	70% $n \to \pi^*$	71% $n \to \pi^*$	71% $\pi \to \pi^*$	70% $n \to \pi^*$	70% $n \to \pi^*$	71% $\pi \to \pi^*$

[a] Numbers in parentheses refer to experimental data. [b] From phosphorescence excitation spectra. [c] Transition localized on the furanyl system. [d] From absorption spectra in: [e]methanol, [f]acetonitrile, [g]cyclohexane. [h] from phosphorescence emission spectra.

support the observed spectroscopic data (Table 2). The computational studies suggest a strong mixing of the two main configurations, i.e., $n \to \pi^*$ and $\pi \to \pi^*$, in the singlet excited states. The low-energy $\pi \to \pi^*$ states of the furan chromophore in **2c** and **3c** indicate the possibility of intramolecular energy-transfer processes.

Because the T_2 state could not directly be detected, additional computations were performed to gain further insight into the energetic requirements of the two competing photochemical pathways. The relative state energies of the proposed intermediates **5**/**6** and **8** were calculated in their respective minimum conformations. To simplify the stereochemistry arising from the endo and exo epimers, the model system **2d** (or **3d**) was studied. The calculated energy levels suggest that the triplet biradical species **5d** and **6d** should be almost equally involved in the isomerization process with a slight preference toward **5d**. The six-membered ring formed after internal cleavage adopts a planar geometry with a large contribution from the zwitterionic form **8d** in the ground state.[28] Comparison of the calculated energies of the excited states favors T_2 as the reactive state for zwitterion formation, while T_1 is assumed to be the entrance to an exocyclic cleavage route via **5d** and/or **6d** (Figure 2).

Proposed Mechanism. In summary, the photophysical and photochemical information, in combination with computational studies, points to a reasonable mechanism for the observed wavelength-dependent phenol formation as illustrated in Figure 3. It should be noted that the figure serves only illustrative purposes. The two competing photochemical processes are projected on two perpendicular reaction coordinates and the potentials of the individual states are shown qualitatively.

It is important to note that IC ($S_2 \to S_1$ and $T_2 \to T_1$) is symmetry forbidden, while ISC ($S_2 \to T_1$ and $S_1 \to T_2$) is El Sayed forbidden. This fact leads to a separation of the two different reaction pathways depending upon the applied excitation wavelength, i.e., population of the two reactive triplet excited states after El Sayed allowed ISC from the corresponding excited singlet states. Thus, either photoisomerization from the T_1 $\pi \to \pi^*$ state via external cyclopropane bond cleavage and formation of a triplet biradical species or zwitterion formation via internal cleavage from the T_2 $n \to \pi^*$ state, which after

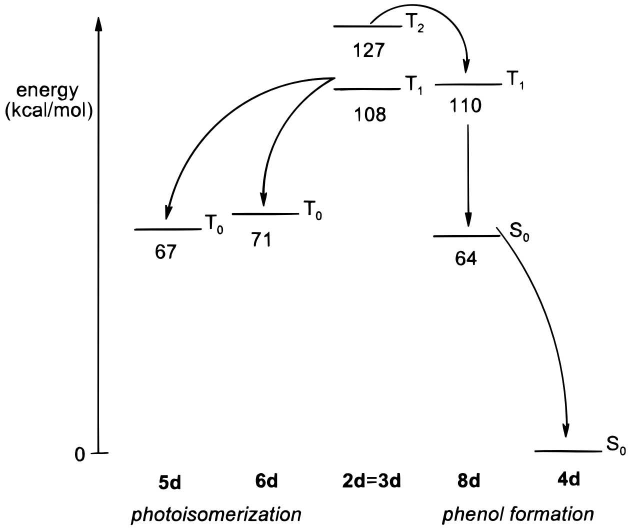

Figure 2. Computed energy diagram of intermediates and products of the model system **2d** = **3d** (arrows correspond to most likely processes; S_0 of **4d** was set to 0 kcal/mol).

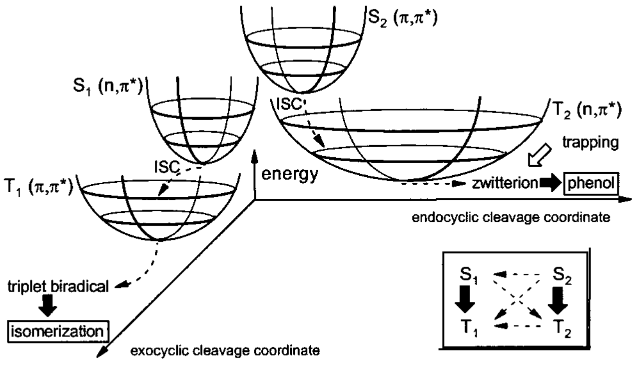

Figure 3. Illustration of the suggested mechanism to account for the observed wavelength-dependent photochemistry of 4-methoxybicyclo[3.1.0]hexenones (arrows correspond to the two major reaction pathways as shown in the box).

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[1.2]migration yields phenolic products, can occur in this particular system.

Conclusion

Wavelength-dependent photochemistry of 4-methoxybicyclo[3.1.0]hexenones has been demonstrated, and a reasonable mechanistic picture is suggested. The crucial factor for achieving wavelength dependency is the 4-methoxy substitution pattern, which dramatically lowers the $\pi \rightarrow \pi^*$ triplet state.[29] As a result, two competing processes, i.e., photoisomerization and phenol formation, become apparent. The product distribution, which is dictated by the population of the two different triplet excited states, depends mainly on efficiencies of ISC and IC starting from the excited singlet states. Herein, the wavelength dependency has its origin.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR were recorded at 300 and 400 MHz in $CDCl_3$ solutions calibrated with TMS. Gas chromatography was performed on a gas chromatograph equipped with a flame-ionization detector and a 25 m × 0.25 μm DB1-30N fused silica capillary column. HPLC was done using a 250 × 4.6 mm packed silica column with elution mixtures of hexanes and ethyl acetate. UV detection was employed. Response factors were developed against internal standards for GC and HPLC for each compound quantified. The estimated error of the response factors is ±5%. Flash chromatography was performed on 230−400 mesh silica gel applying medium pressure.[30] All solvents used in spectroscopy, in irradiation and trapping experiments, and in quantum yield measurements were of spectroscopic grade and used as received. Benzene was distilled over $LiAlH_4$ prior to use.

2,5-Cyclohexadienones (1) and Bicyclo[3.1.0]hexenones (2 and 3). 2,5-Cyclohexadienones (**1a**−**c**) were prepared via Birch reduction followed by allylic oxidation using a mixture of *tert*-butyl hydroperoxide and PDC[31] according to a procedure by Schultz.[2a] For **1c**, the furan tether was prepared in a five-step sequence starting from furfural.[32] Irradiation yielded the corresponding bicyclo[3.1.0]hexenones (**2a**−**c**, **3a**−**c**) already described previously.[2a] Characterization of phenol **4a** and trapping product **9c** were in good agreement with the literature.[2a,13] All compounds were chromatographed and recrystallized from hexane/ethyl acetate. **7a** could not be isolated, and only GC−MS analysis is available.

2-Cyano-5-methoxy-3-methylphenol (4b). A solution of **2b** (0.3 g, 1.8 mmol) in 10 mL of acetonitrile was purged with nitrogen for 10 min and irradiated with a 450 W Hanovia high-pressure mercury lamp equipped with a Corex filter until complete conversion (GC > 97%). Removal of the solvent in vacuo and column chromatography (silica gel, ether/hexane 4:1) gave **4b** as an oil (86 mg, 29% yield): ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H), 3.8 (s, 3H), 6.32 (d, $J = 2$ Hz, 1H), 6.39 (d, $J = 2$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 165.1, 159.6, 144.0, 116.0, 108.1, 99.1, 92.8, 54.1, 21.3; HRMS calcd for $C_9H_9NO_2$ 163.06333, found 163.06337.

2,3-Dimethyl-5-cyano-5′-methyl-2-cyclohexenone (7b). A solution of **2b** (0.25 g, 1.5 mmol) in 10 mL of methanol was degassed with nitrogen for 10 min and irradiated with a 450 W Hanovia Hg lamp equipped with a Corex filter until complete conversion (GC > 98%). Removal of the solvent in vacuo and column chromatography (silica gel, ether/hexane 4:1) gave **7b** as an oil (54 mg, 22% yield): ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 3H), 2.4 (d, $J = 17$ Hz, 1H), 2.58 (d, $J = 17$ Hz, 1H), 2.8 (q, $J = 17$ Hz, 1H), 3.66 (s, 3H), 4.03 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 189.9, 159.8, 136.4, 122.3, 61.0, 59.4, 46.9, 39.2, 32.5, 25.3; IR (film) 2956, 2200, 1675, 1623, 1150 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 270 nm (1700 L/mol cm); HRMS calcd for $C_{10}H_{13}NO_3$ 195.089 54, found 195.089 01.

Fluorescence and Phosphorescence Measurements. The chromatographed compounds were recrystallized twice from hexane/ethyl acetate, and no impurity (<0.1%) was detected by GC. At room temperature, the fluorescence experiments were carried out in a 1 cm quartz cuvette, whereas low-temperature experiments (77 K) were performed with ethanol glass matrices in quartz tubes. In the phosphorescence measurements, a perpendicular experimental arrangement with an internal chopper was used in order to eliminate fluorescence. The concentrations were adjusted to approximately 10^{-3} mol/L. The phosphorescence spectra were corrected with an obtained sensitivity−wavelength calibration function of the detector, and the background of a sample containing neat solvent was subtracted.

Direct and Sensitized Irradiations. Preparative irradiation experiments were carried out using a 450 W Hg lamp employing uranium ($\lambda_{50\%T} = 340$ nm, $\lambda_{10\%T} = 320$ nm) as well as Corex ($\lambda_{50\%T} = 290$ nm, $\lambda_{10\%T} = 270$ nm) filters. For analytical runs, constant light conditions were established and the runs were monitored by GC or HPLC. In sensitized experiments, the concentrations were adjusted to guarantee >99% absorption of the light by the sensitzer. All irradiations were performed under deaerated conditions (thoroughly degassing with dry nitrogen).

Direct and Triplet Quantum Yields. Direct quantum yields were measured by a PTI electronic actinometer[33] calibrated with standard potassium ferrioxalate actinometry[34] at each wavelength. A 1000 W Xe−Hg lamp equipped with a monochromator resulting in a bandwidth of 2 nm was used. Sample and actinometer cells were sequentially irradiated, and from the actinometer cell the photon flux was determined. The light flux remained constant. Quantification was done by GC. Biphenyl was used as internal standard. The samples (1 mM in benzene or acetonitrile) were irradiated to 2−5% conversion. Each irradiation mixture was analyzed with five separate injections, and the runs were repeated at least three times. Triplet quantum yield measurements were performed on solutions with sensitizer−compound absorbance ratios of ~100. Maximum TTET efficiency[16,35] was guaranteed by obtaining a quantum yield−sensitizer concentration−function (saturation curve) for each sensitizer and each compound. Two different experimental approaches were applied: in method a, the triplet quantum yields are determined analogous to the direct quantum yields, whereas in method b, an experimental arrangement consisting of a Rayonet reactor equipped with RPR-3500 Å lamps and a combination of a uranium filter and a solution filter[36] ($\lambda_{50\%T} = 360$ nm, $\lambda_{10\%T} = 375$ nm) in order to isolate the 350 nm Hg line was used. In method b, ferrioxalate actinometry was performed sequentially to the irradiation. All quantum yield determinations were carried out after rigorous purging with dry nitrogen. The estimated error is ±10%.

Trapping Experiments. Intermolecular and intramolecular trapping experiments were performed using a 450 W Hg lamp equipped with either a Corex or a uranium filter. Concentrations were ~10 mM, and in sensitized runs it was verified that >99% of the light was absorbed by the sensitizer. In the intermolecular experiments, neat methanol was used as solvent. Quantification was done by GC or HPLC, and degassed conditions were applied in all experiments.

Computations. Semiempirical calculations were done

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using AM1[26] using CIS and CISD methods. All geometries were fully optimized.

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Supporting Information Available: Copies of NMR spectra (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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