J. Phys. Chem. A **2001,** *105,* 10329−10333

2,5-Dimethylphenacyl Esters: A Photoremovable Protecting Group for Carboxylic Acids[†]

Miroslav Zabadal,[‡] Anna Paola Pelliccioli,[§] Petr Klán,*,[‡] and Jakob Wirz*,[§]

Department of Organic Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, CZ-611 37 Brno,
Czech Republic, and Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80,
CH-4056 Basel, Switzerland

Received: January 19, 2001; In Final Form: July 13, 2001

Irradiation of 2,5-dimethylphenacyl (DMP) esters (**1a**−**c**) in benzene or cyclohexane solutions produces the corresponding free carboxylic acids (**2a**−**c**) in high chemical yields, along with 6-methyl-1-indanone (**3**). In methanol, 2-(methoxymethyl)-5-methylacetophenone (**4**) is formed as a coproduct. Quantum yields for the photorelease of the DMP group are higher in nonpolar solvents, $\phi \approx 0.2$, than in methanol, $\phi \approx 0.1$. The photoreaction is initiated by efficient photoenolization, $\phi \approx 1$. Three transient intermediates were identified by laser flash photolysis of **1a**, the triplet-state photoenol and the two ground-state photoenols of *Z* and *E* configuration. Release of the acids **2a**−**c** occurs predominantly from the *E* isomer, which has a lifetime of about 2 ms in methanol and 0.5 s in benzene solution. The present data are essential for potential applications of the DMP moiety as a photoremovable protecting group in organic synthesis or biochemistry ("caged compounds").

Introduction

Photoremovable protecting groups are of interest in organic synthesis and biochemistry.[1−3] Several substituted phenacyl compounds have been studied in the past decade. First reports[4−6] were followed by a series of papers by Givens and co-workers dealing with the *p*-hydroxyphenacyl chromophore.[7−13] Falvey et al. studied the photorelease of carboxylic acids, alcohols, and phosphates from the corresponding phenacyl esters in the presence of excited-state electron donor or hydrogen donor molecules.[14−18] Some of us recently proposed the 2,5-dimethylphenacyl (DMP) chromophore as a new photoremovable protecting group for carboxylic acids.[19] Direct photolysis of DMP esters at 254−366 nm led to the formation of the free acids in high yields. Moreover, the side products should be biologically benign so that the group may be useful for biochemical applications when a proper substitution allows a reasonable water solubility.

The primary photochemistry is related to that of other *ortho*-substituted aromatic ketones, which is now well understood.[20−25] In these systems, the excited triplet ketone undergoes fast intramolecular hydrogen abstraction to yield a biradicaloid species, the triplet enol. Decay of the latter results in the formation of two ground-state intermediates, the xylylenols of *Z* and *E* configurations, that reketonize with different kinetics. The *Z* isomer, which in part is also formed directly via hydrogen abstraction occurring in the singlet state of the ketone, has a lifetime similar to that of the triplet enol (<1 μs) and gives the starting compound via an intramolecular [1,5] H-shift. The *E* isomer, on the other hand, may persist up to seconds because its reketonization requires proton transfer through the solvent. Accordingly, its kinetics are very sensitive to the experimental conditions: traces of base shorten its lifetime because they make reketonization easier.[26] The *E* isomer may be trapped by dienophiles,[20] and it may undergo ring closure to form cyclobutenols.[27] In addition to this, when leaving groups are present in an appropriate position, efficient elimination reactions occur, as in the case of *o*-(2-substituted ethyl)benzophenone[28] or acetophenone[29] and of DMP chloride.[30−32] Here we report on the mechanism, efficiency, and release rates of DMP esters (**1a**−**c**, Scheme 1).

Results

Quantum Yield Measurements. Photolysis of DMP esters (**1a**−**c**) in benzene and methanol provides high chemical yields (85−95% isolated) of the corresponding acids (**2a**−**c**), as reported in a preliminary communication.[19] While 6-methyl-1-indanone (**3**) is formed as the only coproduct in benzene at low conversions, the reaction in methanol provides the solvolysis product 2-(methoxymethyl)-5-methylacetophenone (**4**) in addition to indanone **3**. These results parallel the photochemistry of DMP chloride (**1d**) reported by Bergmark, where the chloride ion was the leaving group.[30,31] Exhaustive irradiation of the ester solutions in methanol provided, besides **3** and **4**, several unidentified photodegradation products.

Quantum yields for the disappearance of starting material were determined using valerophenone as an actinometer[33,34] (Table 1). The reactions of compounds **1** in nonpolar benzene were found to be as efficient ($\phi = 0.18-0.25$) as that of the α-phenyl-*o*-nitrobenzyl protecting group.[35] However, an unexpected decrease in the quantum yields by a factor of ∼2 was found in methanol relative to benzene. This differs from the results of Bergmark,[31] who reported a quantum yield $\phi = 0.76$ for the photolysis of DMP chloride **1d** in methanol but only $\phi = 0.11$ in benzene. An explanation for the different behaviors of DMP chloride **1d** and DMP esters **1a**−**c** will be given in the Discussion. The acids produced by the photolysis of **1a,b** are poorly soluble in methanol and precipitated from the solution at higher reaction conversions (>35%). All data in Table 1 were obtained for low conversions (<20%).

[†] This work was presented at the PP2000 in Costa do Estoril, Portugal, honoring Professor Ralph Becker's contributions.

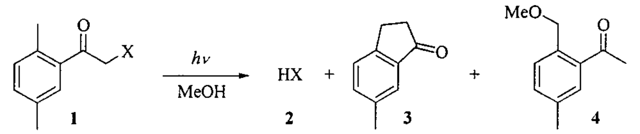
* To whom correspondence should be addressed. P.K.: E-mail klan@sci.muni.cz; phone +420-5-41129356; fax +420-5-41211214. J.W.: E-mail J.Wirz@unibas.ch; phone +41-61-2673842; fax +41-61-2673855.

[‡] Masaryk University.

[§] Universität Basel.

10.1021/jp010220e CCC: $20.00 © 2001 American Chemical Society
Published on Web 09/20/2001

Scheme 1[a]



[a] X = $-$OCOPh (**a**), $-OCOCH_2Ph$ (**b**), $-$OCOMe (**c**), and $-$Cl (**d**).

TABLE 1: Photochemistry of DMP Esters at >366 nm

X	solvent	ϕ^a
$-$OCOPh (**1a**)	benzene	0.23 ± 0.02
	methanol	0.09 ± 0.01
$-OCOCH_2Ph$ (**1b**)	benzene	0.18 ± 0.02
	methanol	0.11 ± 0.01
$-OCOCH_3$ (**1c**)	benzene	0.25 ± 0.01
	methanol	0.14 ± 0.02^b

[a] Quantum yields for ester degradation. Valerophenone was used as an actinometer.[33,34] [b] Irradiated at >300 nm. Error margins are standard errors of the means.

TABLE 2: Photochemistry of DMP Esters with Piperylene at >300 nm

X	solvent	piperylene (mol L^{-1})	ϕ^a
$-$OCOPh (**1a**)	benzene	0.00	0.23 ± 0.01
		0.10	0.20 ± 0.01
		0.25	0.16 ± 0.01
		0.50	0.12 ± 0.02
		2.00	0.07 ± 0.02
	methanol	0.00	0.09 ± 0.01
		0.10	0.06 ± 0.01
		0.25	0.04 ± 0.01
		0.50	0.03 ± 0.01
		2.00	0.01 ± 0.01
$-$OCOCH3 (**1c**)	cyclohexane	0.1	0.18 ± 0.02 (0.22)
	methanol	0.1	0.11 ± 0.01 (0.15)

[a] Quantum yields for ester degradation. The values in the parentheses are those measured without the piperylene addition (Table 1). Error margins are standard errors of the means.

Bergmark reported a product ratio of **3**/**4** = 0.68 for photolysis of **1d** in methanol solution.[30,31] In the course of a reinvestigation of this compound,[36] we found that HCl release affects the product ratio but not the quantum yield of disappearance of **1d**. We obtained a product ratio of **3**/**4** = 0.7 after exhaustive irradiation of a 5×10^{-3} M solution of **1d**, but that ratio increased to >0.9 when the irradiation was stopped at lower conversions. Bergmark had noted[30] that the formation of **4** was reduced when methanol was saturated with $NaHCO_3$. We support this finding, though not an associated reduction in the quantum yield. When 1 equiv of HCl gas is dissolved in methanol prior to irradiation, the ratio **3**/**4** is restored to 0.7 at very low conversions (<5%). Saturation of methanolic solutions with $NaHCO_3$ or HCl prior to irradiation had no significant influence on the quantum yields of **1a**. A ratio < 1.8 of the photoproducts (**3**/**4**) was obtained with each of the DMP esters **1a**−**c** at >366 nm. Quantum yields for the degradation of esters **1a**,**c** in the presence of piperylene are given in Table 2.

Laser Flash Photolysis. Transient absorption spectra of **1a** in air-saturated methanol solution showed the formation of three intermediates, a short-lived one, $\lambda_{max} \approx 340$ nm, and two longer-lived ones, $\lambda_{max} \approx 390$ nm, which are the wavelengths of maximum absorption of the expected triplet enol ^{3}**E** and of the photoenols, respectively (Figure 1).[23,26] In air saturated solution a fast decay ($\tau = 79$ ns) at 340 nm was followed by two slower first-order decays ($\tau = 8.3$ μs and 1.7 ms). At 390 nm there was a resolved initial increase in absorbance, whose rate constant (1.2×10^7 s^{-1}) matched the one of the fast decay at 340 nm. This also was followed by two slower decays (7.5 μs and 2.2 ms). Upon degassing, the lifetime of the short-lived transient increased at both wavelengths of observation (decay at 340 nm, growth at 390 nm; $\tau \approx 300$ ns), in keeping with its assignment to a triplet state. The lifetimes of the two longer-lived species were independent of oxygen concentration. In analogy with *o*-methylacetophenone,[23] the fast transient is assigned to the triplet enol, ^{3}**E**, and the two slower ones are assigned to the *Z* and *E* ground-state photoenols. The assignment of ^{3}**E** was confirmed by quenching studies with piperylene.[23,36]

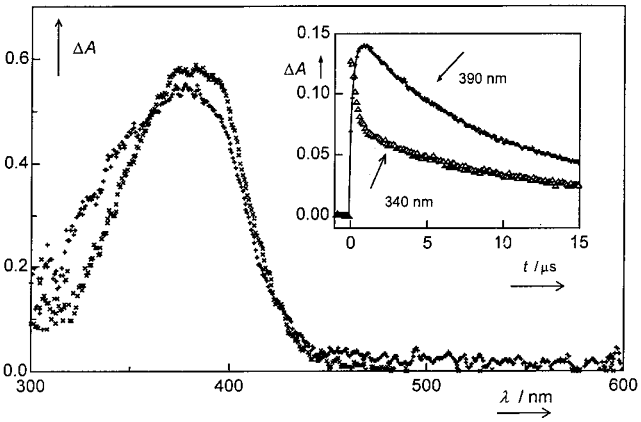


Figure 1. Difference absorption spectra of **1a** in MeOH, (+) 20 ns and (×) 300 ns after the laser pulse. The inset shows kinetic traces recorded at 340 and 390 nm.

Addition of the quencher did not affect the lifetime of ^{3}**E**, but its amount decreased progressively as the concentration of piperylene was increased. The energy of ^{3}**E** is too low for quenching by piperylene, whereas the precursor triplet ketone is readily quenched by it.[23] Similarly, the lifetimes of the *Z* and *E* were not changed by piperylene, but the amplitudes of these transients were reduced. Formation of the enols by the triplet pathway, ^{3}**1a** → ^{3}**E** → *Z* + *E*, is reduced by quenching of ^{3}**1**. Steady-state analysis leads to the Stern−Volmer relation $A^0/A^q = 1 + k_q{}^3\tau^0[q]$. A^0 and A^q are the absorbances of the enol transients in the absence and presence of quencher q, respectively, k_q is the second-order rate constant for quenching of ^{3}**1a** by piperylene, and $^3\tau^0$ is the lifetime of ^{3}**1a** in the absence of quencher. The amplitude ratio A^0/A^q of the *E* isomer increased linearly with piperylene concentration (6 points up to 1.5 M) with a slope of $k_q{}^3\tau^0 = 14 \pm 1$ M^{-1}.[37] Thus, the long-lived *E* isomer forms by the triplet pathway. Assuming a quenching rate constant of $k_q = 5 \times 10^9$ M^{-1} s^{-1}, the lifetime of ^{3}**1a** is estimated as $^3\tau^0 \approx 2.8$ ns. The Stern−Volmer plot for the *Z*-enol had about the same initial slope but reached a plateau at $A^0/A^q \approx 2$. Thus, formation of the *Z*-xylylenol is not fully quenched at high piperylene concentrations, because a large fraction (∼1/2) is generated by the singlet pathway.

Addition of sodium azide (NaN_3) also reduced the lifetimes of the photoenols *E* and *Z*. Plots of the rate constants versus the concentration of N_3^- (0−0.03 M, 5 points for *E*; 0−0.1 M, 4 points for *Z*) were linear with slopes of $(9.5 \pm 0.2) \times 10^5$ and $(1.62 \pm 0.04) \times 10^6$ M^{-1} s^{-1}, respectively. Upon addition of NaOH (5×10^{-4} M) the decay of the xylylenols was no longer biexponential. The decay of the two enols increased progressively upon addition of greater amounts of base ($(0.5-5) \times 10^{-3}$ M, 4 points). A Stern−Volmer plot yielded a quenching rate constant of $(2.0 \pm 0.1) \times 10^9$ M^{-1} s^{-1}. This corroborated our assignment of the enols, because sensitivity of photoenols to bases is to be expected.[23,26]

Two independent methods were used to estimate the absolute quantum yield for total enol formation ($E + Z$) from **1a** in methanol. First, the initial transient absorbance at 390 nm was compared with that at 525 nm of a matched solution of benzophenone in acetonitrile. The triplet state of benzophenone, $\lambda_{\mathrm{max}} = 525$ nm and $\epsilon = 7000$ M^{-1} cm^{-1}, is formed with unit quantum yield.[38] The extinction coefficient of the xylylenols is not known. Assuming $\epsilon \approx 3000$ M^{-1} cm^{-1}, which is the extinction coefficient of 2,2-dimethylisoindene,[39] we obtain $\phi_{Z+E} \approx 2$. Another estimate of $\phi_{Z+E} \approx 2$ was obtained by comparing the initial transient absorbances of **1a,d** in matched methanol solutions. Here, we assumed that the quantum yield for enol formation from **1d** is unity, because that of HCl release from **1d** is 0.76. Each of these estimates relies on an unproven assumption, and the result of both, $\phi_{Z+E} \approx 2$, is in fact unreasonably high. Nevertheless, the results do indicate that the total yield of enols from **1a** is on the order of unity.

Addition of 0.015 M of acetic acid did not affect the lifetime of the *Z*-xylylenol in methanol, but that of the *E* isomer increased about 30-fold. Further addition of acetic acid (up to 0.1 M) had no effect. This indicates that acid inhibits the decay of *E* back to starting material by rapid reprotonation (at oxygen) of any deprotonated *E* enol.

LFP of **1a** in benzene solution afforded analogous transients as in methanol. The lifetime of ^{3}**E** in air-saturated solution was 74 and 63 ns at 340 (decay) and 390 nm (growth), respectively. As expected, *Z* decayed more rapidly in benzene (420 ns at 390 nm), whereas *E* was much longer-lived in this solvent, with a lifetime of about 0.5 s. A Stern−Volmer plot of the amplitude ratio A^0/A^q of the *E* isomer versus piperylene concentration (6 points up to 1.5 M) gave a slope of $k_q{}^3\tau^0 = 2.18 \pm 0.06$ M^{-1}.[37] Assumption of a rate constant of $k_q = 5 \times 10^9$ M^{-1} s^{-1} yields $^3\tau^0 \approx 0.4$ ns for the lifetime of the ketone triplet.

The LFP results on **1c** in aerated methanol solution were similar to those obtained on **1a**. The photoenol triplet ^{3}**E** decayed with a lifetime of 71 ns at 340 nm. This corresponded to the initial growth at 390 nm (78 ns), which was followed by the decays of *Z* (6.8 μs) and *E* (2 ms). A plot of the amplitude ratio A^0/A^q for the *E*-photoenol versus quencher concentration (4 points up to 0.6 M) gave a value of $k_q{}^3\tau^0 = 7.4 \pm 0.4$ M^{-1}.[37]

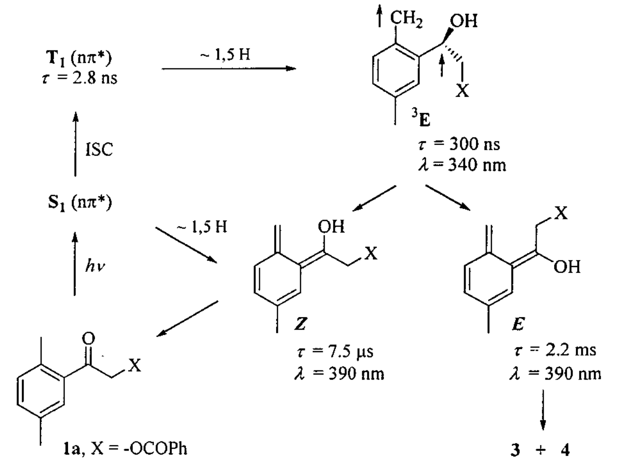
Discussion

Irradiation of DMP esters **1a**−**c** in methanol leads to efficient formation of the corresponding free acids **2a**−**c** along with **3** and **4** as coproducts. The transient intermediates observed by LFP of DMP ester **1a** in degassed methanol are shown in Scheme 2. The structural assignments are based on quenching studies with piperylene and previous work on the related transients observed by LFP of 2-methylacetophenone.[23]

A central issue of the present investigation is at which stage in the photokinetic scheme the elimination reaction actually takes place. Previous studies by Bergmark and Netto-Ferreira described the photochemistry of **1d**. Although Bergmark[31] did not exclude that product formation could take place directly from the triplet enol, ^{3}**E**, both he and Netto-Ferreira[32] favored the hypothesis of elimination occurring from the ground-state photoenols. They suggested *E*-xylylenol to be the most likely intermediate forming indanone **3**. Bergmark also proposed that the solvolysis reaction occurs via a $\mathrm{S_N1}$ displacement on either *Z* or *E*, whereas Netto-Ferreira concluded that the *Z* isomer reketonizes rapidly (≤20 ns) and does not play a role in the formation of the products.

That the elimination reaction takes place from either or both isomers of the xylylenols appears to be the most reasonable hypothesis. Elimination restores the aromaticity of the unstable photoenols. On the other hand, an adiabatic reaction from ^{3}**E** to form the products **3** or **4** in their excited triplet state would be energetically unfavorable because of the low triplet energy of ^{3}**E** (ca. 100 kJ mol^{-1}).[39,40]

SCHEME 2



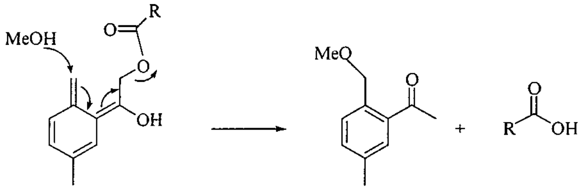
The results we obtained with the DMP esters **1a**−**c** studied here are surprisingly different from those reported for the DMP chloride **1d**. Quantum yields of DMP ester degradation were significantly lower in methanol than in nonpolar solvents, and the biexponential decay kinetics observed for the photoenol transients ($\lambda_{\mathrm{max}} = 390$ nm) clearly indicated formation of two xylylenol isomers. In contrast, Bergmark reported a quantum yield for the photoelimination of HCl from **1d** of 0.76 in methanol and of 0.11 in benzene solution. Netto-Ferreira and Scaiano observed formation of only one photoenol from **1d** in methanol, which they assigned to the *E* isomer.

In an effort to elucidate the origin of these qualitative differences, we reinvestigated **1d** and found that the reaction mechanism proposed earlier requires substantial revision.[36] Photorelease of HCl from **1d** in methanol to products **3** and **4** ($\phi = 0.76$) proceeds by efficient heterolytic elimination of chloride ion from the *Z*-xylylenol, which is the only photoenol formed in this solvent. The *E* isomer is not formed in methanol, because photoenolization from the singlet state is highly efficient, and the triplet pathway (reaction via ^{3}**E**) does not compete measurably. In benzene solution both the *E*- and *Z*-photoenols are formed, but only the *E* isomer gives product **3** by HCl elimination whereas the *Z* isomer decays predominantly by intramolecular reketonization to **1d** in this solvent.

The photoreaction of DMP esters **1a**−**c** parallels that of **1d** in benzene solution. Formation of **3** exclusively via the *E*-photoenol of **1a** in benzene is strongly supported by quenching experiments with piperylene. The *E*-photoenol forms only by the triplet pathway (Scheme 2). Quenching of the triplet ketone precursor with piperylene gives a linear Stern−Volmer relation for the amplitudes of the *E*-photoenol absorption determined by LFP, $A^0/A^q = 1 + k_q{}^3\tau^0[q]$. The slope $k_q{}^3\tau^0$ of 2.18 ± 0.06 M^{-1} is in satisfactory agreement with the value of $k_q{}^3\tau^0 = 1.8 \pm 0.1$ that is derived from the dependence of the quantum yield of photoelimination on piperylene concentration (Table 2).

The scenario changes in methanol solution. Carboxylate ions are much poorer leaving groups than the chloride ion, and the enols of the DMP esters do not dissociate as easily as that of **1d**. Quantum yields of DMP ester degradation in methanol are

SCHEME 3



substantially lower than those found in nonpolar solvents (Table 1). Therefore, a mechanism involving heterolytic cleavage is unlikely. If heterolysis took place, its rate should be similar for both isomers. In fact, both *Z* and *E* are formed and decay with very different lifetimes. On this basis, heterolysis of the shorter-lived *Z* isomer can be excluded. Contrary to **1d**, where the photoelimination of HCl proceeds from the *Z*-xylylenol in methanol solution,[36] the present results for esters **1a**−**c** indicate reaction predominantly via the *E*-xylylenol.

Flash photolysis data show that about half of the *Z* isomer is formed through the singlet pathway. We estimate the total quantum yield of enol formation ($E + Z$) to be close to unity. If reaction via *Z* would contribute to the overall quantum yield of photodegradation in methanol, we would expect a higher quantum yield in methanol than in benzene. This is the case for **1d** but opposite to what we find for **1a**−**c**. Quenching experiments with piperylene support this conclusion. Photodegradation is largely suppressed by addition of 2 M quencher concentrations. If *Z* were reactive and responsible for the formation of **3**, then we would observe a saturation of the quenching effect. The quantitative agreement between the $k_q{}^3\tau^0$ value of 14 ± 1 M^{-1} determined by LFP for the amount of *E* with that of 4.6 ± 0.3 M^{-1} determined from the reaction quantum yields (Table 2) is less than perfect. The discrepancy may be due to a small unquenchable contribution in the reaction quantum yields from reaction via *Z*-photoenol or, more likely, to experimental error in the determination of the latter. The data for the very slow conversion at high piperylene concentrations had to be determined near the detection limit for GC analysis.

We conclude that for the DMP esters **1a**−**c** the only productive photoenol is that of *E* configuration, and we withdraw an opposite proposal made in a preliminary communication.[19] The *Z*-photoenols revert to starting material by an intramolecular 1,5-hydrogen shift. Release rates for the acids **2a**−**c** are on the order of 10^3 s^{-1} in methanol. The lower quantum yield in methanol compared to benzene indicates that reketonization of the *E*-xylylenol by proton transfer through solvent competes efficiently with product formation. Competition by the reketonization reaction is also supported by the increased lifetime of *E* in the presence of small amounts of acetic acid that was observed by LFP.

The arguments given above indicate that heterolytic cleavage of the xylylenols from **1a**−**c** is inefficient. Formation of the solvolysis product **4** in methanol may then be attributed to a concerted mechanism, where nucleophilic attack of the solvent facilitates the elimination, as shown in Scheme 3. Such a mechanism is supported by the quenching effect of added azide on both xylylenols, which suggests that quantum yields >80% could be achieved by addition of 1 M azide ($k_q \approx 1 \times 10^6$ M^{-1} s^{-1}, $\tau^0 = 7.5$ μs).

Further experiments with better leaving groups such as phosphates will be required to explore whether the full potential of DMP as a photoremovable protecting group can be exploited to give quantum yields of elimination approaching unity.

Experimental Section

Materials and Methods. Benzene and methanol were purified by distillation through a vacuum-sealed column (70 cm) packed with glass detritus. 2,5-Dimethylphenacyl chloride (α-chloro-2′,5′-dimethylacetophenone) was prepared according to the standard procedure described elsewhere.[19,31] NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^{1}H and ^{13}C NMR data were measured in the solvent indicated with tetramethylsilane as an internal standard. Mass spectra were obtained using EI (30 eV). Gas chromatography was performed on a Shimadzu GC 17A gas chromatograph equipped with a DB1 column. Melting points were determined on a Kofler hot-stage Rapido 79-2106 and were not corrected.

General Method for Synthesis of 2,5-Dimethylphenacyl Esters. 2,5-Dimethylphenacyl chloride (32 mmol) in acetone (25 mL) was added to a stirred mixture of the corresponding acid (1.3−2 equiv) or its sodium salt (1.2 equiv), sodium iodide (1.2 equiv), and triethylamine (1.1 equiv) in 250 mL of acetone. The mixture was stirred and heated under reflux for ~8 h, and the product formation was monitored by TLC. The solids were removed, the solvent was distilled off, and the residue was extracted with benzene. The benzene layer was washed three times with 10% HCl (50 mL), 1 M aqueous sodium hydroxide (50 mL), and water. The organic layer was dried over $MgSO_4$, and the solvent was removed to obtain the crude products, which were purified by crystallization or by flash chromatography (petroleum ether−diethyl ether mixture, 4:1).

2,5-Dimethylphenacyl benzoate (1a): yield 4.5 g (95%); white solid; mp 90−91 °C (from diethyl ether); IR (KBr) 2944, 1720, 1700, 1597, 1450, 1372, 1283, 1229, 1122, 1019, 958 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3 H), 2.48 (s, 3 H), 5.40 (s, 2 H), 7.15−7.25 (m, 2 H), 7.43−7.48 (m, 3 H), 7.58 (t, $J = 7.6$ Hz, 1 H), 8.11−8.14 (m, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.8, 21.1, 67.9, 128.6, 128.9, 129.7, 130.1, 132.3, 133.1, 133.5, 134.7, 135.6, 136.1, 166.3, 196.0; MS (EI) *m/z* 268 (M$^+$), 147, 133, 105, 77. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.53; H, 6.11.

2,5-Dimethylphenacyl phenylacetate (1b): yield 3.9 g (84%); yellowish liquid; IR (KBr) 3030, 2927, 2867, 1744, 1702, 1497, 1453, 1239, 1145, 969 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3 H), 2.41 (s, 3 H), 3.74 (s, 2 H), 5.10 (s, 2 H), 7.07−7.31 (m, 8 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.4, 20.8, 40.7, 67.7, 127.1, 128.5, 129.4, 129.9, 131.9, 132.0, 132.2, 132.7, 133.6, 134.5, 135.3, 135.6, 170.9, 195.9; MS (EI) *m/z* 282 (M$^+$), 133, 105, 91, 77.

2,5-Dimethylphenacyl acetate (1c): yield 3.3 g (84%); yellow liquid; IR (KBr) 3023, 2930, 2870, 1750, 1702, 1422, 1372, 1229, 1176, 1080, 967 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (s, 3 H), 2.35 (s, 3 H), 2.45 (s, 3 H), 5.15 (s, 2 H), 7.13−7.26 (m, 2 H), 7.39 (s, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.6, 20.7, 21.0, 67.5, 128.7, 132.3, 133.0, 134.6, 135.5, 135.9, 170.5, 196.0; MS (EI) *m/z* 206 (M$^+$), 165, 133, 105, 91, 77.

6-Methyl-1-indanone (3): yellow solid; mp 48−51 °C (from petroleum ether); IR (KBr) 2959, 2921, 2855, 1708, 1491, 1282, 828, 805 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3 H), 2.65−2.69 (m, 2 H), 3.08 (dd, $J = 5.8$ Hz, 2 H), 7.35 (d, $J = 7.9$ Hz, 1 H), 7.40 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.5$ Hz, 1 H), 7.55 (broad s, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.1, 25.4, 36.6, 123.7, 126.4, 135.9, 137.2, 137.3, 152.5, 207.1; MS (EI) *m/z* 146 (M$^+$), 118, 115, 103, 91. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.39; H, 6.92.

2-(Methoxymethyl)-5-methylacetophenone (4): yellowish solid; mp 31−32 °C; IR (KBr) 2994, 2928, 2831, 1723, 1437, 1288, 1089, 996 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3 H), 2.57 (s, 3 H), 3.42 (s, 3 H), 4.70 (s, 2 H), 7.29 (d, $J_1 =$ 7.9 Hz, $J_2 =$ 8.2 Hz, 1 H), 7.50 (s, $J =$ 5.8 Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.0, 29.2, 58.6, 72.6, 128.0, 129.9, 132.5, 136.3, 136.6, 136.7, 201.6; MS (EI) *m*/*z* 178 (M^+), 163, 147, 117, 91. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.91; H, 7.96.

Quantum Yield Measurements. Solutions of the DMP ester ($\sim 5 \times 10^{-3}$ M) in benzene, methanol, or cyclohexane were irradiated simultaneously at >366 or > 300 nm with valerophenone solutions used as an actinometer in a "merry-go-round" apparatus immersed in a water bath. Samples in Pyrex tubes were degassed in three freeze−pump−thaw cycles before being sealed. The >366 and >300 nm bands from a medium-pressure 400 W Teslamp mercury lamp were isolated by filtration with Corning CS 0-52 and CS 7-37 filters or a CS 7-37 filter, respectively. The photoproduct yields were analyzed by GC calibrated with the authentic compounds. All quantum yields reported are calculated for the ester degradation.

Laser Flash Photolysis. Experiments were carried out by exciting the sample solutions with absorbances of $<0.5/\mathrm{cm}^{-1}$ at 308 nm with the 20 ns, ~100 mJ pulses of a XeCl excimer laser. A pulsed Xenon arc was used as the monitoring beam (4.5 cm path length, orthogonal to the excitation pulse). The detection system allowed monitoring of either the kinetics at a single wavelength using a transient digitizer or the whole transient spectrum, with an Optical Multichannel Array. Methanol stock solutions were prepared so that absorption at the irradiation wavelength was around 0.2. To avoid interference from the photoproducts, samples were discarded after each laser shot and replaced by fresh ones.

Acknowledgment. We gratefully acknowledge the Czech Ministry of Education, Youth, and Sport (CEZ: J07/98: 143100005) and the Swiss National Science Foundation (Grant No. 20-61746.00) for the support of this research. We thank J. Klánová for some gas chromatography measurements, and we are grateful to two anonymous reviewers who have contributed substantially by their constructive critical comments.

References and Notes

(1) Wuts, P. G. M.; Green, T. W. *Protective Groups in Organic Chemistry*; Wiley: New York, 1999.

(2) Marriott, G., Ed. *Methods in Enzymology*; Academic Press: New York, 1998; Vol. 291.

(3) Morrison, H. *Biological Applications of Photochemical Switches*; Wiley: New York, 1993.

(4) Sheenan, J.; Umezawa, J. *J. Org. Chem.* **1973**, *38*, 3771−3774.

(5) Epstein, W. W.; Garrossian, M. *J. Chem. Soc., Chem. Commun.* **1987**, (8), 532−533.

(6) Baldwin, J. E.; Mcconnaughie, A. W.; Moloney, M. G.; Pratt, A. J.; Shim, S. B. *Tetrahedron* **1990**, *46*, 6879−6884.

(7) Conrad, P. G.; Givens, R. S.; Hellrung, B.; Rajesh, C. S.; Ramseier, M.; Wirz, J. *J. Am. Chem. Soc.* **2000**, *122*, 9346−9347.

(8) Conrad, P. G.; Givens, R. S.; Weber, J. F. W.; Kandler, K. *Org. Lett.* **2000**, *2*, 1545−1547.

(9) Givens, R. S.; Athey, P. S.; Matuszewski, B.; Kueper, L. W.; Xue, J. Y.; Fister, T. *J. Am. Chem. Soc.* **1993**, *115*, 6001−6012.

(10) Givens, R. S.; Jung, A.; Park, C. H.; Weber, J.; Bartlett, W. *J. Am. Chem. Soc.* **1997**, *119*, 8369−8370.

(11) Givens, R. S.; Park, C. H. *Tetrahedron Lett.* **1996**, *37*, 6259−6262.

(12) Givens, R. S.; Weber, J. F. W.; Conrad, P. G.; Orosz, G.; Donahue, S. L.; Thayer, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 2687−2697.

(13) Park, C. H.; Givens, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 2453−2463.

(14) Banerjee, A.; Falvey, D. E. *J. Am. Chem. Soc.* **1998**, *120*, 2965−2966.

(15) Banerjee, A.; Falvey, D. E. *J. Org. Chem.* **1997**, *62*, 6245−6251.

(16) Banerjee, A.; Lee, K.; Falvey, D. E. *Tetrahedron* **1999**, *55*, 12699−12710.

(17) Banerjee, A.; Lee, K.; Yu, Q.; Fang, A. G.; Falvey, D. E. *Tetrahedron Lett.* **1998**, *39*, 4635−4638.

(18) Lee, K.; Falvey, D. E. *J. Am. Chem. Soc.* **2000**, *122*, 9361−9366.

(19) Klán, P.; Zabadal, M.; Heger, D. *Org. Lett.* **2000**, *2*, 1569−1571.

(20) Lutz, H.; Bréhéret, E.; Lindqvist, L. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 2096−2102.

(21) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405−422.

(22) Findlay, D. M.; Tchir, M. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1096−1100.

(23) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595−2607.

(24) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965−6970.

(25) Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227−366.

(26) Scaiano, J. C.; Wintgens, V.; Netto-Ferreira, J. C. *Tetrahedron Lett.* **1992**, *33*, 5905−5908.

(27) Wagner, P. J.; Subrahmanyam, D.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 709−710.

(28) Tseng, S.-S.; Ullman, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 541−544.

(29) Pellliccioli A. P.; Wirz J. Unpublished results.

(30) Bergmark, W. R. *J. Chem. Soc., Chem. Commun.* **1978**, 61−62.

(31) Bergmark, W. R.; Barnes, C.; Clark, J.; Paparian, S.; Marynowski, S. *J. Org. Chem.* **1985**, *50*, 5612−5615.

(32) Netto-Ferreira, J. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 5800−5803.

(33) Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489−7494.

(34) Wagner, P. J.; Thomas, M. J.; Harris, E.. *J. Am. Chem. Soc.* **1976**, *98*, 7675−7679.

(35) Zhu, Q. Q.; Schnabel, W.; Schupp, H. *J. Photochem.* **1987**, *39*, 317−332.

(36) Pellliccioli, A.-P.; Klán, P.; Zabadal, M.; Wirz, J. *J. Am. Chem. Soc.* **2001**, *123*, 7931−7932.

(37) To ensure homodispersity of experimental errors, $k_q{}^3\tau^0$ was determined by nonlinear fit to the inverse function $A^q/A^0 = \{1 + k_q{}^3\tau^0[q]\}^{-1}$.

(38) Bonneau, R.; Carmichael, I.; Hug, G. L. *Pure Appl. Chem.* **1991**, *63*, 289−299.

(39) Allan, M.; Asmis, K. R.; El houar, S.; Haselbach, E.; Capponi, M.; Urwyler, B.; Wirz, J. *Helv. Chim. Acta* **1994**, *77*, 1541−1548.

(40) Kumar, C. V.; Chattopadhyay, S. K., Das, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 5143−5144.