Organic Photochemical Reactions. XXVI. Photoaddition of Singlet and Triplet Methyl Pyruvate with 2,3-Dimethyl-2-butene[1]

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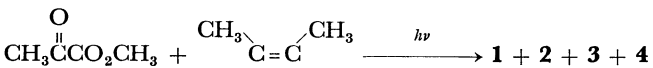
UV irradiation of methyl pyruvate in the presence of 2,3-dimethyl-2-butene leads to the formation of four primary photo-products in reasonable quantum yield: two unsaturated ethers (**1** and **2**) and two unsaturated alcohols (**3** and **4**). The effects of olefin concentration on the quantum yield of product formation, as well as quenching studies, suggest that **3** and **4** are formed from the excited singlet state of methyl pyruvate, while **1** and **2** are produced from the triplet state of methyl pyruvate. The role of exciplexes in this reaction is discussed. Quenching data of fluorescence of methyl pyruvate and the kinetic analysis of this reaction support these considerations.

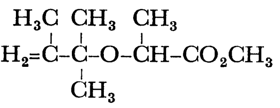
The photocycloaddition of carbonyl compounds with olefins to form oxetanes is a topic of recent preparative and mechanistic interest. An attack of the $^3(n\pi^*)$ carbonyl compound on a ground state olefin is not the only allowed mechanism for photoaddition reaction. Alkanals and alkanones can attack olefins or conjugated dienes by a mechanism involving the singlet excited state of the carbonyl compounds.[2] In some cases, photoaddition may occur by both singlet and triplet mechanisms concurrently, as in the addition of acetone to 1-methoxy-1-butene,[3] or the addition of fluorenone to a ketenimine.[4] Recently, it has been suggested that an exciplex which leads to oxetane formation is formed between excited carbonyl compounds and olefins.[2a,2f,5] Some years ago, we reported that biacetyl and methyl pyruvate add to 2,3-dimethyl-2-butene to afford allylic ethers.[6] In these photoadditions, no detectable amounts of oxetanes were isolated. These results were explained by the reactivity of the 1,4-biradical intermediates. In this paper we wish to report some results concerning the photoaddition of methyl pyruvate to 2,3-dimethyl-2-butene, and our studies concerning the mechanism of this addition.

Results and Discussion

Products Studies. A preparative UV photoreaction of methyl pyruvate in solution in the presence of 2,3-dimethyl-2-butene leads to the formation of four products, which can be detected by VPC analysis. These are separated by preparative VPC and assigned the structures **1**—**4**.

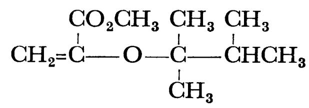


$$CH_3\overset{O}{\overset{\|}{C}}CO_2CH_3 + (CH_3)_2C{=}C(CH_3)_2 \xrightarrow[\text{in } CH_3CN]{h\nu} \mathbf{1}+\mathbf{2}+\mathbf{3}+\mathbf{4}$$



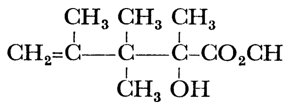
$CH_2{=}C(CH_3)-C(CH_3)_2-O-CH(CH_3)-CO_2CH_3$

1



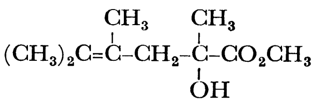
$CH_2{=}C(CO_2CH_3)-O-C(CH_3)_2-CH(CH_3)CH_3$

2



$CH_2{=}C(CH_3)-C(CH_3)_2-C(CH_3)(OH)-CO_2CH_3$

3

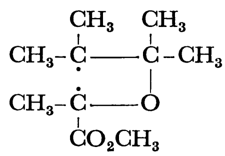


$(CH_3)_2C{=}C(CH_3)-CH_2-C(CH_3)(OH)-CO_2CH_3$

4

Compound **1** was assigned the allylic ether structure on the basis of its IR and NMR spectra (isopropenyl and $-OCH(CH_3)-$ groups). Compound **2** was identified as the isomeric vinyl ether by its IR and NMR spectra (isopropyl and $CH_2{=}C(CO_2CH_3){-}O{-}$ groups). The compound slowly decomposed on standing and thus the isolation of **2** had to be performed carefully. The structures of the unsaturated alcohols (**3** and **4**) were apparent from an examination and comparison of their IR and NMR spectra. **3** showed terminal methylene absorption in the IR and NMR spectra, and only one $CH_3\overset{|}{C}{=}$ signal in the NMR spectrum; **4** showed no vinyl proton, but signals for three $CH_3\overset{|}{C}{=}$ groups and an allylic methylene in the NMR spectrum.

1 and **2** are the products derived from the disproportionation of the 1,4-biradical intermediate (**5**), and **3** and **4** are the products expected from the hydrogen abstraction of excited methyl pyruvate from 2,3-dimethyl-2-butene.



$CH_3-\dot{C}(CH_3)-C(CH_3)_2-O-\dot{C}(CH_3)-CO_2CH_3$

5

Quantum Yields. In order to investigate the quantum yield for product formation as a function of the concentration of reactants, Pyrex tubes containing known concentrations of methyl pyruvate and 2,3-dimethyl-2-butene in acetonitrile were irradiated in a merry-go-round reactor. After irradiation, the photoproduct in each tube was subjected to VPC analysis. The quantum yields for product formation were obtained by tris(oxalato)ferrate(III) actinometry.

Figure 1 shows plots of the reciprocal of quantum yields for the formation of products against the reciprocal of concentration of 2,3-dimethyl-2-butene. This indicates that different precursors exist for the formation of unsaturated alcohols (**3** and **4**) and unsaturated ethers (**1** and **2**). The upward curvature for **1** and **2** seen in Fig. 1 at higher olefin concentration is due to the deactivation of the excited singlet state of methyl pyruvate by interaction with 2,3-dimethyl-2-butene.[7]

Quenching Studies. Quantitative studies were carried out using 2,3-dimethyl-1,3-butadiene as a triplet quencher in acetonitrile in the presence of methyl pyruvate and 2,3-dimethyl-2-butene. Plots of relative

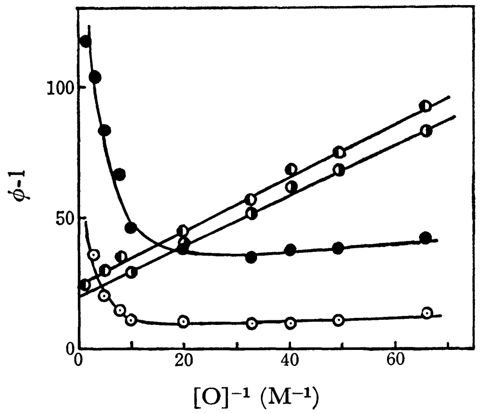


Fig. 1. Dependence of the reciprocal of the quantum yield for products formation on the reciprocal of 2,3-dimethyl-2-butene concentration.

●: Product **1**, ⊙: product **2**, ◐: product **3**, ◑: product **4**. [MP]=0.1 M in acetonitrile.

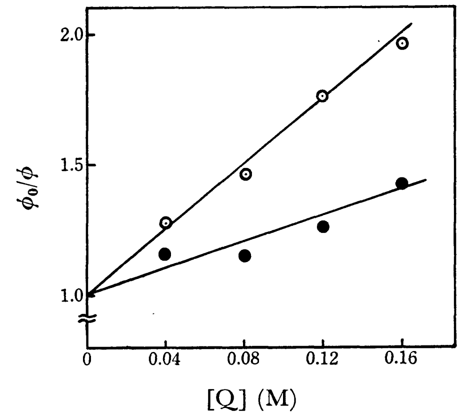


Fig. 2. Stern-Volmer plot of quenching of products **1**+**2** and **3**+**4** against 2,3-dimethyl-1,3-butadiene concentration.

⊙: **1**+**2**, ●: **3**+**4**. [MP]=0.1 M, [O]=0.2 M in acetonitrile.

quantum yields for **1**+**2** and **3**+**4** *vs.* quencher concentration in the presence of 0.2 M olefin concentration in acetonitrile are shown in Fig. 2. Apparently, **1**+**2** are more efficiently quenched than **3**+**4** are. It now seems established that, while conjugated dienes act as efficient quenchers of the triplet state of carbonyl compounds, dienes may also act as quenchers of the carbonyl singlet state.[2a)] From the above experiment, we propose that **3**+**4** are formed from the excited singlet state of methyl pyruvate, probably *via* an exciplex, and **1**+**2** are formed from the triplet state of methyl pyruvate. This is confirmed by the kinetic treatment discussed later.

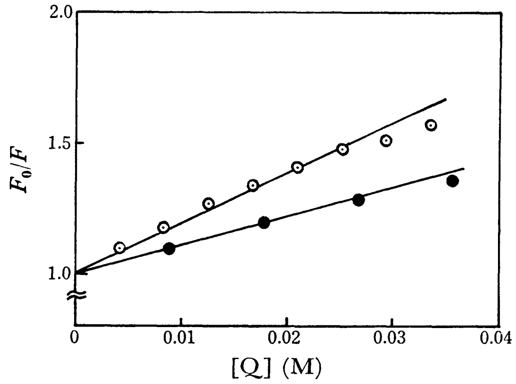


Fig. 3. Stern-Volmer plots for the fluorescence quenching of methyl pyruvate by 2,3-dimethyl-2-butene (⊙) and 2,3-dimethyl-1,3-butadiene (●) in acetonitrile.

[MP]=0.1 M.

Fluorescence Quenching. 2,3-Dimethyl-2-butene and 2,3-dimethyl-1,3-butadiene quench the fluorescence of methyl pyruvate, as the Stern-Volmer plots in Fig. 3 show. This quenching effect is not due to a ground-state charge-transfer formation between methyl pyruvate and quenchers. Absorption spectra taken of methyl pyruvate with higher concentrations of 2,3-dimethyl-2-butene or 2,3-dimethyl-1,3-butadiene than those used in the kinetic experiments are identical with the spectra of methyl pyruvate in the absence of quenchers. The fluorescence of methyl pyruvate was also quenched by other dienes and olefins (Table 1). In Fig. 4 the function log k_q is plotted against the ionization potentials of several dienes and olefins. The moderately good linear behavior indicates that a charge

TABLE 1. QUENCHING RATE CONSTANTS AND IONIZATION POTENTIALS OF UNSATURATED COMPOUNDS

Unsaturated compound	$k_q\tau_s$[a)] M^{-1}	$k_q \times 10^{-9}$ $M^{-1}s^{-1}$	IP[b)] eV
2,5-Dimethyl-2,4-hexadiene	94.8	11.56	7.84
1,3-Cyclohexadiene	32.1	3.91	8.30
2,3-Dimethyl-2-butene	19.0	2.32	8.42
1,3-Pentadiene	13.4	1.63	8.59, 8.65
2,3-Dimethyl-1,3-butadiene	10.4	1.27	8.72
2-Methyl-1,3-butadiene	10.8	1.32	8.85
2-Methyl-2-butene	11.0	1.34	8.85

a) [MP]=0.1M in CH_3CN, τ_s=8.2 ns. b) Vertical ionization potentials; see Refs. 2a and 8.

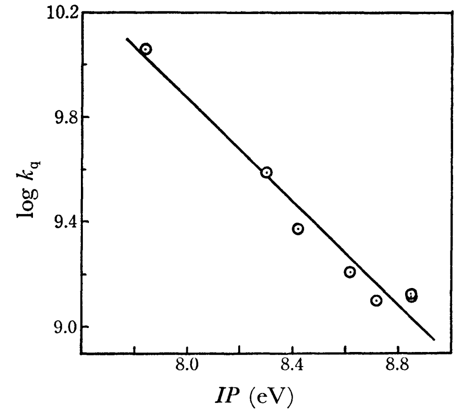


Fig. 4. Dependence of rates of methyl pyruvate fluorescence quenching by unsaturated compounds on their ionization potentials.

transfer interaction contributes to the stabilization of this quenching process. Similar correlations for fluorescence quenching of aromatic hydrocarbons,[8] alkanones,[2a] alkanals,[2e] azoalkanes,[9] and vinylene carbonates[10] by dienes or olefins have been attributed to exciplex formation.

Kinetic Analysis. The following mechanism is consistent with the above experiments:

	Rate Constant
$\mathrm{MP} \xrightarrow{h\nu} {}^1\mathrm{MP}$	
${}^1\mathrm{MP} \longrightarrow \mathrm{MP} + \Delta$ or $h\nu$	k_d^1
${}^1\mathrm{MP} \longrightarrow {}^3\mathrm{MP}$	k_{ST}
${}^1\mathrm{MP} + \mathrm{O} \longrightarrow {}^1(\mathrm{MP}\cdots\mathrm{O})$	k_c^1
${}^1(\mathrm{MP}\cdots\mathrm{O}) \longrightarrow \mathrm{MP} + \mathrm{O}$	k_a^1
${}^1(\mathrm{MP}\cdots\mathrm{O}) \longrightarrow \mathbf{3} + \mathbf{4}$	k_p^1
${}^1\mathrm{MP} + \mathrm{Q} \longrightarrow \mathrm{MP} + \mathrm{Q}$	k_q^1
${}^3\mathrm{MP} \longrightarrow \mathrm{MP}$	k_d^3
${}^3\mathrm{MP} + \mathrm{O} \longrightarrow {}^3(\mathrm{MP}\cdots\mathrm{O})$	k_c^3
${}^3(\mathrm{MP}\cdots\mathrm{O}) \longrightarrow \mathrm{MP} + \mathrm{O}$	k_a^3
${}^3(\mathrm{MP}\cdots\mathrm{O}) \longrightarrow \mathbf{1} + \mathbf{2}$	k_p^3
${}^3\mathrm{MP} + \mathrm{Q} \longrightarrow \mathrm{MP} + {}^3\mathrm{Q}$	k_q^3

MP: methyl pyruvate; O: 2,3-dimethyl-2-butene; Q: 2,3-dimethyl-1,3-butadiene; ${}^1(\mathrm{MP}\cdots\mathrm{O})$, ${}^3(\mathrm{MP}\cdots\mathrm{O})$: singlet and triplet exciplex, respectively.

Steady-state treatment of the species ${}^1\mathrm{MP}$, ${}^3\mathrm{MP}$, ${}^1(\mathrm{MP}\cdots\mathrm{O})$, and ${}^3(\mathrm{MP}\cdots\mathrm{O})$ leads to the expressions

$$\phi_{3+4} = \phi_A = \left(\frac{k_p^1}{k_a^1+k_p^1}\right)\left(\frac{k_c^1[\mathrm{O}]}{k_d^1+k_{ST}+k_c^1[\mathrm{O}]+k_q^1[\mathrm{Q}]}\right), \quad (1)$$

$$\phi_{1+2} = \phi_E = \left(\frac{k_{ST}}{k_d^1+k_{ST}+k_c^1[\mathrm{O}]+k_q^1[\mathrm{Q}]}\right)\left(\frac{k_p^3}{k_a^3+k_p^3}\right) \times \left(\frac{k_c^3[\mathrm{O}]}{k_d^3+k_c^3[\mathrm{O}]+k_q^3[\mathrm{Q}]}\right), \quad (2)$$

where ϕ_E and ϕ_A are the quantum yields for the formation of unsaturated ethers (**1**+**2**) and unsaturated alcohols (**3**+**4**), respectively.

First, consider the formation of **3**+**4**. In the absence of quenching by 2,3-dimethyl-1,3-butadiene, Eq. 1 becomes

$$\phi_A^{-1} = \left(1+\frac{k_a^1}{k_p^1}\right)\left(1+\frac{k_d^1+k_{ST}}{k_c^1[\mathrm{O}]}\right). \quad (3)$$

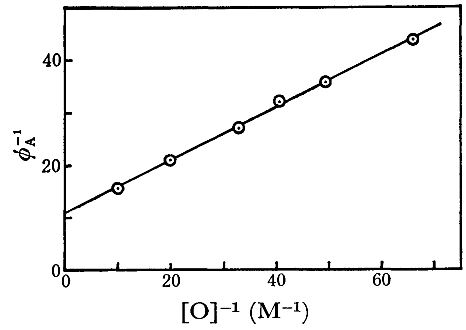


Fig. 5. Dependence of the reciprocal of the quantum yield for the formation of **3**+**4** on the reciprocal of 2,3-dimethyl-2-butene concentration. Slope=0.51 M, Intercept=10.7.

Figure 5 shows plots of the reciprocal of quantum yields for the formation of **3**+**4** against the reciprocal of concentration of 2,3-dimethyl-2-butene. A least-squares analysis of the points gave an intercept of 10.7 and a slope of 0.51 M. The intercept of Fig. 5 is now associated with $1+k_a^1/k_p^1$, and using this value in conjunction with the slope, we obtain the limiting quantum yield, $\phi_A^{\mathrm{lim}}=0.0937$, $k_a^1/k_p^1=9.67$, and $k_c^1/(k_d^1+k_{ST})=21.0$.

In the presence of the quencher, Q,

$$\frac{\phi_A^\circ}{\phi_A} = 1 + \frac{k_q^1[\mathrm{Q}]}{k_d^1+k_{ST}+k_c^1[\mathrm{O}]} = 1 + k_q^1\tau_s[\mathrm{Q}], \quad (4)$$

where ϕ_A is the quantum yield for the formation of **3**+**4** in the presence of Q, ϕ_A° is the quantum yield for the formation of **3**+**4** in the absence of Q, and τ_s is the lifetime of the excited singlet state in the absence of Q. 2,3-Dimethyl-1,3-butadiene quenches the formation of **3**+**4** in the presence of 0.2 M 2,3-dimethyl-2-butene in acetonitrile, as the Stern-Volmer plots in Fig. 2 show. From the slope in Fig. 2 we obtain the $k_q^1\tau_s$ value of 2.44; thus, $k_c^1/k_q^1=1.65$. A Stern-Volmer treatment of the fluorescence quenching in Fig. 3 yields a slope of 19.0 M^{-1} for 2,3-dimethyl-2-butene and 10.8 M^{-1} for 2,3-dimethyl-1,3-butadiene; thus, we get $k_c^1/k_q^1=1.82$. This is in good agreement with the value of k_c^1/k_q^1 (=1.65) obtained from the above calculation. These results indicate that the fluorescence quenching and the formation of **3**+**4** proceed *via* the excited singlet state of methyl pyruvate.

Next, consider the formation of **1**+**2**. In the absence of 2,3-dimethyl-1,3-butadiene, Eq. 2 leads to Eq. 5 by taking $k_{ST} \gg k_d^1$, since the triplet quantum yield for carbonyl compound is high:[11]

$$\phi_E^{-1} = \left(\frac{k_{ST}+k_c^1[\mathrm{O}]}{k_{ST}}\right)\left(1+\frac{k_a^3}{k_p^3}\right)\left(1+\frac{k_d^3}{k_c^3[\mathrm{O}]}\right). \quad (5)$$

Rearranging Eq. 5 gives

$$\left(\frac{k_{ST}}{k_{ST}+k_c^1[\mathrm{O}]}\right)\phi_E^{-1} = \left(1+\frac{k_a^3}{k_p^3}\right)\left(1+\frac{k_d^3}{k_c^3[\mathrm{O}]}\right). \quad (6)$$

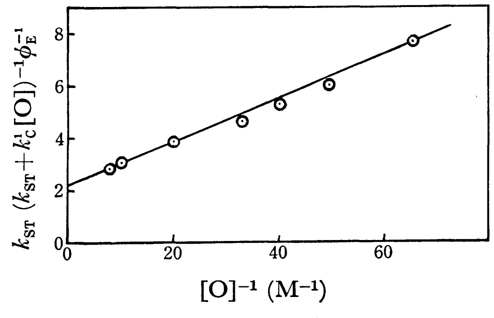


Fig. 6. Plot of $k_{ST}(k_{ST}+k_c^1[\mathrm{O}])^{-1}\phi_E^{-1}$ against [O]$^{-1}$. Slope=0.079 M, Intercept=2.22.

Figure 6 shows a plot of $k_{ST}(k_{ST}+k_c^1[\mathrm{O}])^{-1}\phi_E^{-1}$ against reciprocal olefin concentration. From the slope (=0.079 M) and intercept (=2.22) in Fig. 6, we obtain $k_a^3/k_p^3=1.22$, and $k_c^3/k_d^3=28.1$.

In the presence of Q,

$$\frac{\phi_E^\circ}{\phi_E} = \left(1+\frac{k_q^1[\mathrm{Q}]}{k_d^1+k_{ST}+k_c^1[\mathrm{O}]}\right)\left(1+\frac{k_q^3[\mathrm{Q}]}{k_d^3+k_c^3[\mathrm{O}]}\right). \quad (7)$$

Rearranging Eq. 7 gives

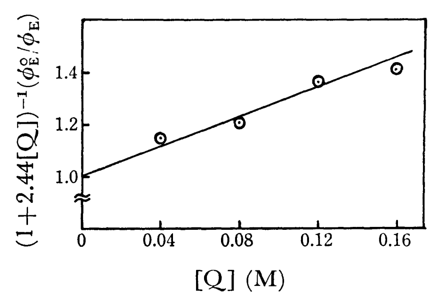


Fig. 7. Plot of $(1+2.44[Q])^{-1}$ (ϕ_E°/ϕ_E) against [Q]. Slope=2.78 M^{-1}.

TABLE 2. THE RATIO OF RATE CONSTANTS OF ELEMENTARY REACTIONS IN ACETONITRILE AND IN BENZENE[a)]

	CH_3CN	C_6H_6
k_c^1/k_{ST}	21.0	22.3
$k_c^1/{}_q^1$	1.65	1.64
k_a^1/k_p^1	9.67	14.5
k_c^3/k_d^3	28.1	37.4
k_c^3/k_q^3	1.53	1.50
k_a^3/k_p^3	1.22	1.05
$k_c^{1\,b)}$ $(M^{-1}\,s^{-1})$	2.5×10^9	2.7×10^9

a) [MP]=0.1 M. b) Fluorescence lifetime of methyl pyruvate: 8.2 ns (in benzene).

$$\left(1+\frac{k_q^1[Q]}{k_d^1+k_{ST}+k_c^1[O]}\right)^{-1}\left(\frac{\phi_E^\circ}{\phi_E}\right) = 1 + \frac{k_q^3[Q]}{k_d^3+k_c^3[O]}. \quad (8)$$

At 0.2 M olefin concentration, $k_q^1/(k_d^1+k_{ST}+k_c^1[O])=2.44$; the dependence of $(1+2.44[Q])^{-1}(\phi_E^\circ/\phi_E)$ on [Q] are shown in Fig. 7. From the slope ($=2.78\ M^{-1}$) in Fig. 7, we get $k_c^3/k_q^3=1.53$. The results are summarized in Table 2. Table 2 also includes the results in benzene solution. From the above experiments, we could calculate the ratio of the rate constants of elementary reactions; and if we take $\tau_S \simeq k_{ST}^{-1}=8.2$ ns, the rate constant of $2.5\times10^9\ M^{-1}\ s^{-1}$ for the singlet exciplex formation from methyl pyruvate and 2,3-dimethyl-2-butene in acetonitrile can be obtained. In this photoreaction, no predominant solvent effects were observed. In the case of biacetyl and 2,3-dimethyl-2-butene, the unsaturated ether formation and biacetyl phosphorescence quenching by 2,3-dimethyl-2-butene are 3—5 times larger in acetonitrile solution than in benzene solution.[12)]

Experimental

General. NMR spectra were recorded on a JEOL JNM-MH 100 machine, IR spectra on a JASCO IRA-1 spectrometer, mass spectra on a Hitachi Perkin-Elmer RMU-60 spectrometer, and fluorescence spectra on a Hitachi MPF-4 spectrofluorimeter. The fluorescence lifetime was measured using a Hitachi Time Resolved Photometer. VPC were performed on a Shimadzu GC-3BF or GC-6AM apparatus using a column of Carbowax 20M (20% on Celite 545, 3m) at 120 °C.

Methyl pyruvate was prepared by the reaction of pyruvic acid with methanol in the presence of catalytic amounts of *p*-toluenesulfonic acid.[13)] 2,3-Dimethyl-2-butene was prepared by the dehydration of 2,3-dimethyl-2-butanol,[14)] formed from the reaction of isopropylmagnesium bromide with acetone in ether. It was purified by efficient fractional distillation. 2,3-Dimethyl-1,3-butadiene was prepared by dehydration of pinacol with hydrobromic acid, followed by distillation.[15)] 1,3-Cyclohexadiene was prepared as described by Marvel and Hartzell.[16)] 2-Methyl-2-butene was prepared by the method of Whitmore *et al.*[17)] 2,5-Dimethyl-2,4-hexadiene, 1,3-pentadiene, and 2-methyl-1,3-butadiene were obtained commercially, and were purified by distillation before use. Acetonitrile was distilled three times from phosphorus pentaoxide and once from potassium carbonate.

Irradiation of Methyl Pyruvate with 2,3-Dimethyl-2-butene. A solution of methyl pyruvate (10.2 g) and 2,3-dimethyl-2-butene (8.4 g) in acetonitrile was irradiated for 120 h with a 300-W high pressure mercury lamp filtered through a hexane solution of naphthalene. After removal of the unreacted materials under vacuum, the remaining liquid was distilled under reduced pressure to give a liquid (5 g, bp 110—125 °C/30 mmHg) and leave a viscous liquid (1 g). VPC of the distillate showed four products (**1**—**4**) with the area ratios of 22: 15: 26: 37. These products were isolated by preparative VPC on a 3 m 20% Carbowax 20M column at 120 °C.

Methyl 2-(1,1,2-Trimethyl-2-propenyloxy)propionate (**1**): NMR (CCl_4) δ=1.23 (3H, s), 1.25 (3H, d, *J*=7 Hz), 1.29 (3H, s), 1.73 (3H, s), 3.62 (3H, s), 3.79 (1H, q, *J*=7 Hz), and 4.86 (2H, s); IR 3100, 2995, 2975, 1740, 1643, and 1120 cm^{-1}.

Methyl 2-(1,1,2-Trimethylpropoxy)acrylate (**2**): NMR (CCl_4) δ=0.97 (6H, d, *J*=7 Hz), 1.21 (6H, s), 1.92 (1H, sept, *J*=7 Hz), 3.66 (3H, s), 4.81 (1H, s), and 5.51 (1H, s); IR 2980, 2875, 1740, 1620, and 1140 cm^{-1}.

Methyl 2-Hydroxy-2,3,3,4-tetramethyl-4-pentenoate (**3**): NMR (CCl_4) δ=1.14 (3H, s), 1.16 (3H, s), 1.30 (3H, s), 1.75 (3H, s), 3.37 (1H, s), 3.67 (3H, s), and 4.77 (2H, m); IR 3540, 3085, 2980, 2960, 1720, and 1630 cm^{-1}.

Methyl 2-Hydroxy-2,4,5-trimethyl-4-hexenoate (**4**): NMR (CCl_4) δ=1.33 (3H, s), 1.63 (9H, s), 2.40 (1H, s), 2.45 (1H, s), 3.44 (1H, s), and 3.66 (3H, s); IR 3560, 2960, and 1730 cm^{-1}.

Quantum Yield Studies. Samples (4 ml) containing 0.1 M methyl pyruvate and varying concentrations of 2,3-dimethyl-2-butene in acetonitrile were placed in 10-mm o.d. Pyrex tubes. The samples were degassed using four freeze-pump-thaw cycles at $\approx 5\times10^{-4}$ mmHg and sealed. The tubes were photolyzed to <10% conversion on a merry-go-round apparatus using a HALOS PIH 300 mercury lamp and a potassium chromate filter solution to isolate the 313-nm irradiation. The entire apparatus was immersed in a water bath. After irradiation, an internal standard (naphthalene) was added to each tube, and product yields were measured by VPC analysis on machines with flame ionization detectors. The area ratios of the peak for pure samples of the products (**1**—**4**) and for naphthalene were plotted against the ratios of the amounts actually present. The calibration factors thus obtained were 1.84 for **1**, 4.79 for **2**, 2.74 for **3**, and 2.01 for **4**. Peak areas were measured by a planimeter. Light intensities were measured by tris(oxalato)ferrate(III) actinometry.[18)]

Quenching of Products by 2,3-Dimethyl-1,3-butadiene. Acetonitrile solutions containing 0.1 M methyl pyruvate, 0.2 M 2,3-dimethyl-2-butene, and various concentrations of 2,3-dimethyl-1,3-butadiene (0—0.16 M) were prepared. Four milliliters of each sample were degassed and irradiated at 313 nm. Photolyzed solutions were analyzed for product formation using a VPC column.

Fluorescence Quenching. Solutions of methyl pyruvate (0.1 M) with various concentrations of 2,3-dimethyl-2-butene or 2,3-dimethyl-1,3-butadiene were made up in acetonitrile. Solutions were placed in a quartz fluorescence cell and the fluorescence spectra were recorded. The excitation wavelength was 360 nm; the intensities of methyl pyruvate fluorescence at the maximum (410 nm) were measured in the absence (F_0) and presence (F) of various concentrations of quenchers. Stern-Volmer quenching plots were drawn of F_0/F against quencher molarity. No shifts in fluorescence maxima were observed upon increase in quencher concentration, and no new fluorescence bands were discernible in any of the measurements.

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