a Varian A-60A. Linearity of detector response was confirmed by integration of authentic toluene and α-deuteriotoluene. The results shown in Table I are generally the average of two or more determinations, and should be accurate to within 5%. The standard deviation of the individual integrals was generally 2–3%. About ten integrations were performed in each determination.

Quenching Studies. The myrcene was purified by high-pressure liquid chromatography, eluting with pentane from a μPorasil (Waters Associates) column. Photolysis of a solution of phenylacetic acid in 2-propanol containing 0.02 M myrcene to 15% conversion showed $\Phi/\Phi_0 = 0.90$. UV of the photolysate showed that a strongly absorbing impurity was beginning to absorb some of the light at this stage. A second photolysis to 20% conversion confirmed this, indicating a value of $\Phi/\Phi_0 = 0.53$.

In a control experiment we established that a good triplet sensitizer (xanthone) caused complete conversion of the myrcene to the triplet products with an equivalent amount of photolysis time.

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Mechanism of Intramolecular Photoreactions of Two Rigid Cyclopentenones[1]

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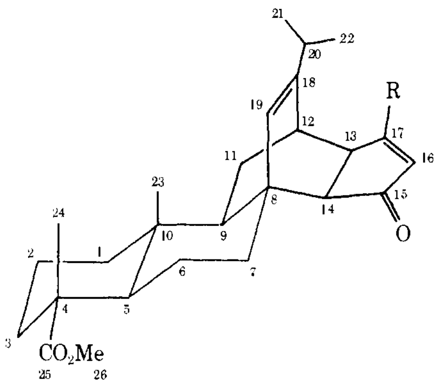
Abstract. The mechanism for the formation of **2b** and **3** upon irradiation of **1b** in benzene has been investigated by spectroscopic and by quenching and sensitization methods. A long-lived structureless emission at 77 K suggests a lowest π–π^* enone triplet in **1b**. The triplet state, reached with unit efficiency in **1b**, is very short-lived at 30 °C in solution, $\simeq 17$ ns, probably owing to very rapid addition or excitation transfer to the neighboring double bond. Formation of **3** is more strongly quenched than formation of **2b**, suggesting that the triplet state of the isolated double bond can be intercepted by quenchers in competition with intramolecular hydrogen abstraction. Alternatively, more than one triplet state of the enone moiety may be involved, each having different probabilities of cycloaddition and energy transfer. The latter possibility is supported by observations starting with **3**, which also has a lowest π–π^* triplet state (77 K, phosphorescence), and which in solution at room temperature undergoes competitive hydrogen abstraction at the α and β positions of the enone moiety to give **4** and **5**. The triplet states of **3** are also reached with unit efficiency. Differential quenching of **4** and **5** is observed indicating the participation of more than one enone triplet state of **3** in the photoreactions. 9,10-Dibromoanthracene quenches the reactions of **1b** or **3** about two orders of magnitude more efficiently than 1,3-dienes, suggesting that triplet excitation transfer to the 1,3-dienes is significantly slower than diffusion controlled.

Irradiation of **1a** gives the expected 2 + 2 cycloaddition product **2a**, while irradiation of **1b** gives mainly a new isomer **3**.[1-5] Conversion of **1b** to **2b** occurs as a minor photoreaction and is reversible.[6] Irradiation of **3** yields **4** and **5**. The structure of **5**, a previously unreported minor product, is discussed in the Appendix.[9] The transformations **2b** → **3** → **4** are intramolecular, since no deuterium incorporation results when the irradiations are carried out in CH_3OD and CD_3OD.

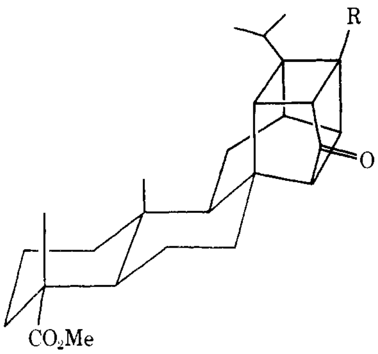
The remote intramolecular hydrogen abstraction reaction in **1b** and the hydrogen abstractions by the α and β positions of the enone moiety in **3** were at the time unprecedented photochemical reactions,[10,11] and warranted the more thorough mechanistic investigation which is described in this paper.

Results

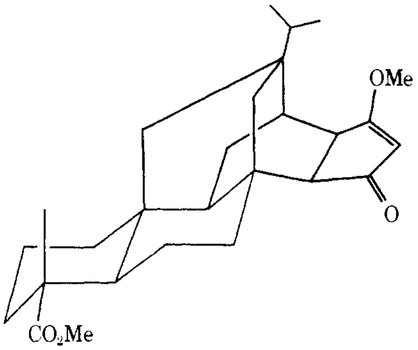
Photochemical Observations. Conversions of **1b** to **2b** and **3** and of **3** to **4** and **5** were determined in the presence of 1,3-cyclohexadiene, C, *cis*-1,3-pentadiene, c-P, and 9,10-dibromoanthracene, DBA. The benzophenone-sensitized isomerization of *cis*-1,3-pentadiene was employed for actinometry.[12] Conversions were corrected for back reaction and the number of einsteins absorbed was calculated using $\phi_{c\to t} = 0.55_5$.[12,13] In samples for which light absorption was incomplete concentrations of **1b** or **3** and benzophenone were chosen so that all solutions absorbed nearly equal fractions of 313-nm incident light. Observations starting with **1b** and **3** are shown in Tables I and II, respectively. In correcting cis–trans conversions for back reaction photostationary states for **1b** and **3** as sensitizers were assumed to correspond to 55.5% trans, the value obtained for high-energy donors. These corrections were generally very small and no significant errors in $\phi_{c\to t}$ would result if this assumption were not valid.[14] Quantum yields of cis–trans isomerization and dimerization of the 1,3-diene quenchers were also determined in some of these experiments and are included



1a, R = H
b, R = OMe[27]



2a, R = H
b, R = OMe



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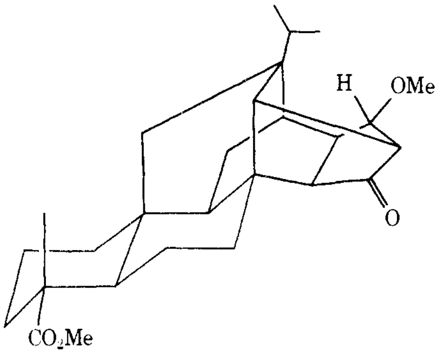

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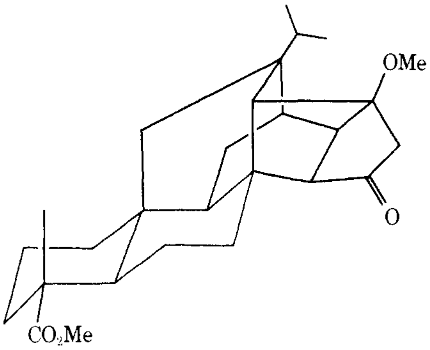

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in Tables I and II. In the case of DBA, observed conversions were corrected for incomplete light absorption by **1a** and **3** before converting them to quantum yields. Additional results for the **1b**- and **3**-sensitized dimerization of C are presented in Table III. The quantum yields of **3**-sensitized cis–trans isomerization of c-P in benzene was determined at [c-P] = 0.300 M. The concentration of **3** was 0.027 M and benzophenone, 0.050 M, with c-P, 0.300 M was used for actinometry.

Table I. Effect of Quenchers on **1b** Quantum Yields, Benzene, 313 nm

Quencher	$[Q]_0 \times 10^2$, M	ϕ_{2b}	ϕ_3	
C[a]	0	0.062	0.094	
	3.12	0.042	0.074	
	6.25	0.029	0.068	
	12.5	0.028	0.042	
	25.0	0.015	0.021	
	50.0	0.0062	0.0061	
				$\phi_{c \to t}$
c-P[b]	0	0.056_2	0.074_1	
	5.0	0.040_0	0.048_4	0.24_8
	10.0	0.028_8	0.032_1	0.33_8
	15.0	0.020_9	0.023_9	0.38_2
	20.0	0.017_9	0.018_5	0.42_4
	30.0[c]	0.004_9	0.012_2	0.44_2
				f_{1b}
DBA[d]	0	0.038_4	0.12_8	1.00
	0.25_0	0.029_4	0.059_9	0.71
	0.25_0	0.025_6	0.055_6	0.71
	0.50	0.020_2	0.035_8	0.55
	1.00	0.014_2	0.018_9	0.38
	2.00	0.0052_6	0.0074_4	0.23

[a] In the absence of C $[\mathbf{1b}]_0 = 6.7_8 \times 10^{-3}$ M; in other samples $[\mathbf{1b}]_0$ = 0.042 M. [b] Unless otherwise indicated $[\mathbf{1b}]_0 = 6.8_1 \times 10^{-3}$ M; last column lists *cis–trans*-1,3-pentadiene quantum yields. [c] $[\mathbf{1b}]_0$ = 0.036 M. [d] $[\mathbf{1b}]_0$ = 0.036 M; last column gives fraction of incident light absorbed by **1b**.

Net corrected conversions were 11.3 and 11.2% t-P for **3** and benzophenone, respectively, giving $\phi_{c \to t} = 0.56$ for **3**. No **4** and **5** formation could be detected under these conditions.

Conversions of **3** to **5** were in some instances too small for accurate measurement, especially in the presence of quenchers. Quantum yields in the absence of quencher are listed in Table IV. An experiment was also carried out in acetonitrile employing lower [**3**] (3.0×10^{-4}, 6.0×10^{-4}, 9.0×10^{-4}, and 12×10^{-4} M) and using the 254-nm line from a low-pressure mercury lamp as the excitation source. Quantum yields were not determined, but the relative yields of **4** and **5** were found to be concentration independent with $\phi_4/\phi_5 = 3.27 \pm 0.10$.

The effect of oxygen on the photoreactions of **1b** and **3** was evaluated qualitatively in cyclohexane (Pyrex filter). Degassed **1b**, 3.0×10^{-3} M, gave 23.1 ± 0.9% **2b** and 30.2 ± 0.2% **3**, while parallel irradiation of an identical air-saturated sample gave 23.9 ± 0.9% **2b** and 18.3 ± 0.5% **3**. Irradiation of **3**, 8.7

Table II. Effect of Quenchers on **3** Quantum Yields, Benzene, 313 nm

Quencher	$[Q]_0 \times 10^2$, M	$\phi_4 \times 10^2$	$\phi_5 \times 10^2$	
				ϕ_D
C[a]	0	0.89 (0.90)		
	0.52_5	0.62 (0.54)		0.068 (0.061)
	0.78_8	0.58 (0.49)		0.090 (0.084)
	1.05	0.44 (0.41)		0.123 (0.122)
	1.58	0.41 (0.34)		(0.169)
				f_3
DBA[b]	0	0.84	0.20	1.00
	0.025	0.33	0.047	0.96
	0.050	0.25	0.030	0.92
	0.075	0.17	0.019	0.89
	0.100	0.16	0.016	0.86

[a] $[\mathbf{3}]_0$ = 0.027 M; values in parentheses are for a shorter irradiation period; last column gives C dimerization quantum yields. [b] $[\mathbf{3}]_0$ = 0.027 M; last column gives fraction of incident light absorbed by **3**.

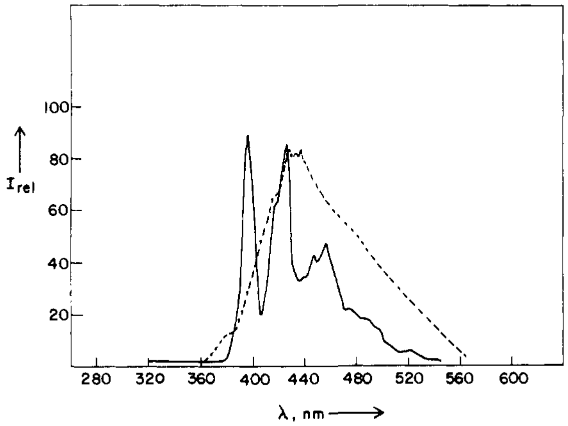


Figure 1. Phosphorescence spectra of **1a** at 77 K in methylcyclohexane without (—) and with (- - -) silica gel.

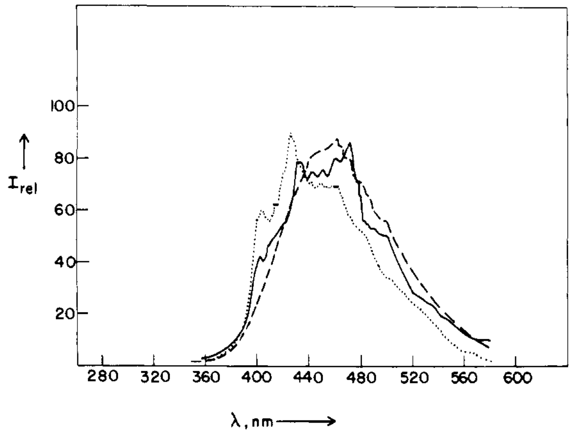


Figure 2. Phosphorescence spectra of **1b** at 77 K in methylcyclohexane without (—) and with (- - -) silica gel, and in EPA (· · ·).

Table III. **1b**- and **3**-Sensitized Photodimerization of C, Benzene, 313 nm

	$[C]_0 \times 10^2$, M	ϕ_D[a]
[**1b**] × 10², M		
3.6	$50._0$	0.95
2.7	1.0_5	0.50
	2.1_0	0.11_1 (0.11_1)
	4.2_0	0.24_5 (0.25_4)
	5.2_5	0.28_4
0.68[b]	$52._5$	0.97
[**3**] × 10², M		
2.7	$50._0$	0.95
0.50	0.52_5	0.055_3
	0.78_8	0.082
	1.0_5	0.11_2
	1.5_8	0.15_2

[a] Values in parentheses are for duplicate samples. [b] Parallel irradiation of benzophenone, 0.0077_9 M, C, 0.525 M gave $\phi_D = 0.94$ for benzophenone sensitization.

Table IV. Formation of **4** and **5** from **3**, 313 nm[a]

$[\mathbf{3}]_0 \times 10^2$, M	$\phi_4 \times 10^2$	$\phi_5 \times 10^2$	ϕ_4/ϕ_5
3.3_0	1.0_3	0.29	3.5
2.7_0	0.89 (0.90)	0.23	3.9
2.7_0	0.84	0.20	4.1
0.50	0.86 (0.94)	0.25 (0.30)	4.0 (3.2)
0.50[b]	0.75 (0.76)	0.16	4.6

[a] In benzene, unless otherwise indicated; values in parentheses are for independent determinations. [b] In cyclohexane.

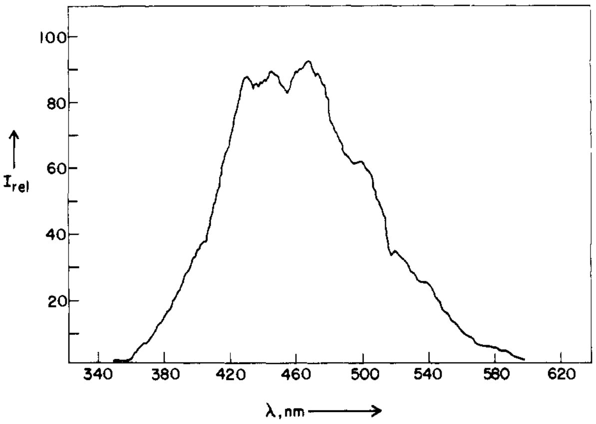


Figure 3. Phosphorescence spectrum of **3** at 77 K in methylcyclohexane.

Table V. Ultraviolet Spectra of **1a, 1b**, and **3**

	n–π*				π–π*			
	Cyclohexane		95% Ethanol		Cyclohexane		95% Ethanol	
Compd	λ, nm	ε	λ, nm	ε	λ, nm	ε	λ, nm	ε
1a	310	100	294	103	235	7340	242	11 200
1b	320	60	295	112	230.5	9618	237.5	11 200
	293	111						
3	318	163	290	170	237	9820	247.0	12 500

× 10^{-3} M, gave 38.6 and 7.0% **4** in degassed and air-saturated solutions, respectively.

A qualitative experiment was also carried out using xanthone as a sensitizer for the conversion of **1b** to **2b** and **3**. A degassed cyclohexane solution containing xanthone and **1b**, each 5.0 × 10^{-3} M, was irradiated (uranium glass filter) simultaneously with a solution containing only **1b**, 5.0 × 10^{-3} M. After prolonged irradiation **1b** remained unchanged in the control solution, while in the solution containing xanthone it was partially converted to **2b**, 23% and **3**, 27%.

Spectroscopic Observations. Table V lists UV maxima of **1a**, **1b**, and **3** in cyclohexane and 95% ethanol. Emission spectra were recorded for methylcyclohexane glassy solutions at 77 K in the presence and absence of silica gel, Figures 1–3. Emission spectra of **1a** and **1b** were also measured by Dr. A. Lamola[17] in an ethanol glass at 77 K. Except for a slight blue shift (2 kcal/mol for **1b**) the spectra in ethanol were very similar to those in methylcyclohexane. The decay of **1a** was too fast to record under the experimental conditions ($\tau \leq 0.01$ s, ethanol); in contrast, the decay of **1b** in ethanol was long-lived, but could not be fitted by a single exponential. It exhibited a minor component, $\tau = 0.3_4$ s and a major longer lived component, $\tau = 1.4$ s.[17]

Discussion

A considerable body of work exists indicating triplet multiplicity for the chemically active electronically excited state in cyclopentenone photochemistry.[18,19] Much of the current interest centers on establishing the electronic character, n–π* or π–π*, of the triplet state(s) responsible for the various photochemical reactions which are encountered.

Comparison of the long wavelength ε values of **1a** and **1b** with that of **3**, Table V, suggests that charge transfer between the enone and alkene moieties in the former compounds is not responsible for the relatively high ϵ values. The phosphorescence spectra of **1a**, **1b**, and **3** have previously been discussed.[4,20] The relatively featureless and long-lived phosphorescence spectra of **1b** and **3**, Figures 2 and 3, respectively, characterize their lowest emitting triplets as π–π^*. By contrast, the highly structured emission spectrum of **1a**, Figure 1, whose excitation produces only **2a** and no substances of type **3** and **4** shows the characteristics of a typical emission from an n–π^* triplet. The vibrational spacing between the 0–0 band (72 kcal/mol) and the 0–1 band is 1720 cm^{-1}, in good correspondence with the carbonyl stretching frequency, and the lifetime of the excited species is shorter than 10^{-2} s. The reversal of the triplet levels in **1a** as compared with those of **1b** and **3** has been attributed to the electron-donating influence of methoxy substitution in lowering the π–π^* triplet energy while raising the n–π^* triplet energy.[4,20] Similar substituent effects have also been observed in acetophenones,[21-23] butyrophenones,[23-24] and cyclohexenones.[25-27]

In molecules with lowest n–π^* but with close-lying π–π^* triplets introduction of a polar environment such as silica gel has been shown to raise the n–π^* triplet energy so significantly as to invert the relative energies of the n–π^* and π–π^* triplets.[20,28] The observation that the presence of silica gel does not appreciably alter the emission characteristics of **1b** but causes the emission spectrum of **1a** to become very similar to the emission spectra of **1b** and **3** supports the above spectral assignments. Evident in the phosphorescence excitation spectra of **1a** in the presence and absence of silica gel is a large blue shift of the singlet n–π^* transition in the polar environment. The n–π^* absorption band of **1a**, which is clearly distinct in the excitation spectrum in the absence of silica gel, is completely buried under the π–π^* band in the presence of silica gel.[29]

The quantum yields for **1b**- and **3**-sensitized dimerization[30] of C and isomerization[12,13] of c-P at high diene concentrations, Tables I and III, establish that, as with previously studied cyclopentenones,[18,19] the reactive states of **1b** and **3** are triplet states, which are formed with unit efficiency, and whose interaction with 1,3-dienes gives 1,3-diene triplets.

The Photochemistry of 1b. In attempting a quantitative interpretation of the concentration dependence of the various quantum yields it is tempting to begin by attributing the difference in photochemical behavior between **1a** and **1b** to the different electronic character of the lowest triplet state of each, which is evident in the low-temperature phosphorescence spectra. Intramolecular cycloaddition giving **2a** and **2b** would accordingly be associated with the n–π^* triplet state, while intramolecular excitation transfer to the double bond leading ultimately to **3** would be associated with the π–π^* triplet state. Since the spectroscopic triplet energies of **1a** and **1b** are 72 and 71 kcal/mol, respectively, in methylcyclohexane and any relaxation due to geometric distortions which might be achievable at room temperature and not at 77 K would be expected to reduce the energy of the π–π^* state and not that of the n–π^* state,[31] it seems necessary to conclude that the above hypothesis cannot be supported on energetic grounds. That is to say, it does not seem probable that excitation transfer to the double bond would be more efficient from the π–π^* than from the n–π^* enone triplet. Instead it would appear that the difference in behavior between **1a** and **1b** should be associated with a higher relative ease with which the n–π^* state gives cycloadduct. The above considerations suggest that interaction of the 1,3-dienes with **1b** triplets may be devilishly complicated. Intersystem crossing from the n–π^* singlet of **1b** could give rise to a lowest π–π^* triplet state, which may be present in equilibrium with a close-lying n–π^* triplet state. Each of these states could form an intramolecular triplet exciplex with the double bond, which could then undergo partition between cycloaddition and excitation transfer. The 1,3-dienes would thus have the opportunity to accept triplet excitation from two enone triplets, two triplet exciplexes, and an alkene triplet, each of which may possess a different triplet lifetime with some or all of these lifetimes being coupled through reversibility.

The quantum yields in Table I reveal trends of increased **2b**/**3** ratios with increasing quencher concentration. This conclusion seems firm especially for c-P and DBA, although the ratio **2b**/**3** in separate experiments shows some variation in the absence of quenchers. Differential quenching of **2b** and **3** formation rules out mechanisms involving a single triplet of **1b** in the pathway to **2b** and **3** and mechanisms involving two or more fully equilibrated triplet-state precursors of **2b** and **3**. The simplest mechanisms which meet the minimum requirement of two nonequilibrated triplet states, each involved in product formation and quenching interactions, are those in which two triplets form either consecutively, e.g., $^1\mathbf{1b}^* \rightarrow {}^3\mathbf{1b}^* \rightarrow {}^3\mathbf{1b}^{*\prime}$ or concurrently, e.g., $^1\mathbf{1b}^* \rightarrow {}^3\mathbf{1b}^*$, $^1\mathbf{1b}^* \rightarrow {}^3\mathbf{1b}^{*\prime}$. If, as indicated by the phosphorescence spectra, triplet excitation initially resides in the enone moiety, the remoteness of this moiety from the reaction site leading to **3** suggests a preference for the consecutive triplet mechanism, eq 1–12, for **1b**, where $^3\mathbf{1b}^*$ and $^3\mathbf{1b}^{*\prime}$ designate triplet excitation of the enone and alkene moieties, respectively, and Q represents any quencher.

$$\mathbf{1b} \xrightarrow{h\nu} {}^1\mathbf{1b}^* \xrightarrow{k_1} \mathbf{1b} \tag{1}$$

$$^1\mathbf{1b}^* \xrightarrow{k_2} {}^3\mathbf{1b}^* \tag{2}$$

$$^3\mathbf{1b}^* \xrightarrow{k_3} \mathbf{1b} \tag{3}$$

$$^3\mathbf{1b}^* \xrightarrow{k_4} {}^3\mathbf{1b}^{*\prime} \tag{4}$$

$$^3\mathbf{1b}^* \xrightarrow{k_5} \mathbf{2b} \tag{5}$$

$$^3\mathbf{1b}^{*\prime} \xrightarrow{k_6} \mathbf{1b} \tag{6}$$

$$^3\mathbf{1b}^{*\prime} \xrightarrow{k_7} \mathbf{3} \tag{7}$$

$$^3\mathbf{1b}^* + \text{Q} \xrightarrow{k_8{}^{\text{q}}} \mathbf{1b} + {}^3\text{Q}^* \tag{8}$$

$$^3\mathbf{1b}^{*\prime} + \text{Q} \xrightarrow{k_9{}^{\text{q}}} \mathbf{1b} + {}^3\text{Q}^* \tag{9}$$

$$^3\text{C}^* \xrightarrow{k_{10}} \text{C} \tag{10}$$

$$^3\text{C}^* + \text{C} \xrightarrow{k_{11}} \text{D} \tag{11}$$

$$^3\text{P}^* \longrightarrow \alpha\text{t-P} + (1 - \alpha)\text{c-P} \tag{12}$$

Application of the steady-state approximation to all excited species leads to quantum yield expressions

$$\phi_{\mathbf{2b}}{}^{-1} = \left(\frac{1}{\phi_{\text{is}}}\right)\left(\frac{1}{k_5\tau_{\text{e}}}\right)(1 + k_8\tau_{\text{e}}[\text{Q}]) \tag{13}$$

$$\phi_{\mathbf{3}}{}^{-1} = \left(\frac{1}{\phi_{\text{is}}}\right)\left(\frac{1}{k_4\tau_{\text{e}}}\right)\left(\frac{1}{k_7\tau_{\text{a}}}\right)(1 + k_8\tau_{\text{e}}[\text{Q}])(1 + k_9\tau_{\text{a}}[\text{Q}]) \tag{14}$$

$$\phi_{\text{D}} = \left(\frac{\phi_{\text{is}}f_{\text{D}}}{1 + k_8{}^{\text{c}}\tau_{\text{e}}[\text{C}]}\right)\left(k_8{}^{\text{c}}\tau_{\text{e}}[\text{C}] + \frac{k_4\tau_{\text{e}}k_9{}^{\text{c}}\tau_{\text{a}}[\text{C}]}{1 + k_9{}^{\text{c}}\tau_{\text{a}}[\text{C}]}\right) \tag{15}$$

$$\phi_{\text{c-t}} = \left(\frac{\phi_{\text{is}}\alpha}{1 + k_8{}^{\text{P}}\tau_{\text{e}}[\text{c-P}]}\right)\left(k_8{}^{\text{P}}\tau_{\text{e}}[\text{c-P}] + \frac{k_4\tau_{\text{e}}k_9{}^{\text{P}}\tau_{\text{a}}[\text{c-P}]}{1 + k_9{}^{\text{P}}\tau_{\text{a}}[\text{c-P}]}\right) \tag{16}$$

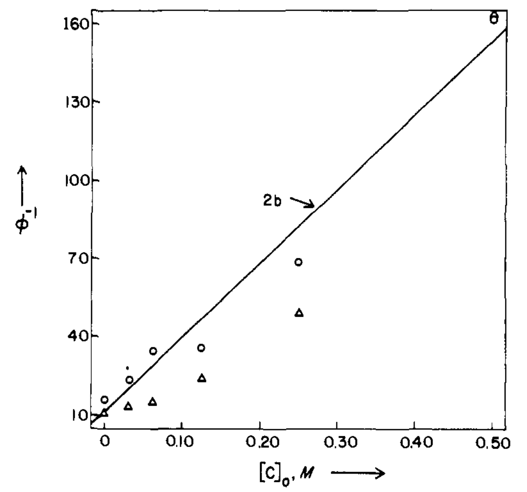


Figure 4. Quenching of **2b** and **3** formation by C.

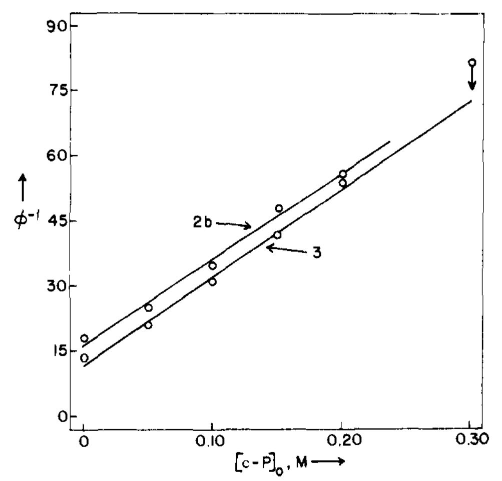


Figure 6. Quenching of **2b** and **3** formation by c-P.

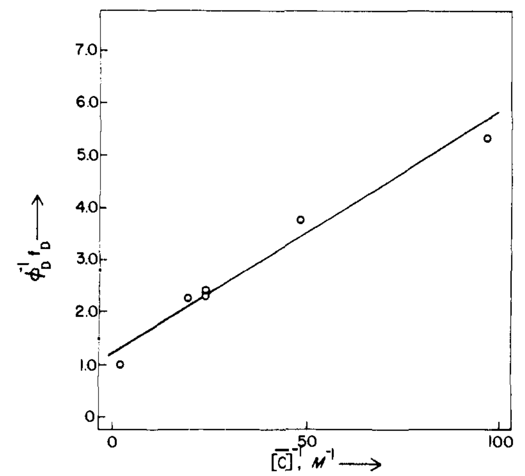


Figure 5. **1b**-sensitized photodimerization of C.

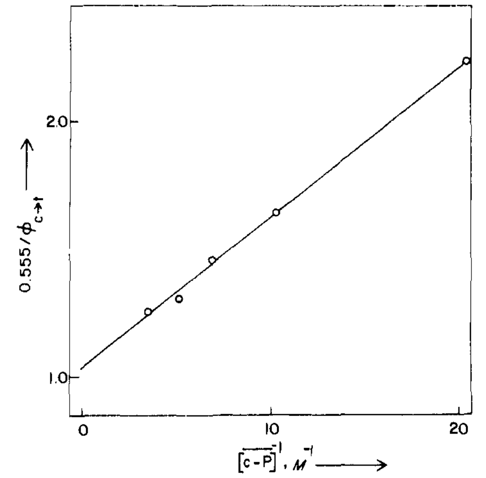


Figure 7. **1b**-sensitized cis-trans photoisomerization of c-P.

where $\phi_{is} = k_2/(k_1 + k_2)$, $\tau_e = (k_3 + k_4 + k_5)^{-1}$ and $\tau_a = (k_6 + k_7)^{-1}$, and $f_D = k_{11}[C]/(k_{10} + k_{11}[C])$ and $\alpha = 0.55_5$[12] are the fractions of diene triplets which give dimer, D, and t-P, respectively. Since $k_{10}/k_{11} = 0.029$ M has been determined previously,[32] f_D values can be calculated for each average concentration of C, $[\bar{C}]$. The rather complex expressions 14–16 reduce to more familiar forms when quenching of a single triplet is assumed. For example, for $k_9 = 0$ the quadratic [Q] dependence predicted in eq 14 is replaced by the usual linear [Q] dependence, and eq 15 is replaced by the equation

$$\phi_D^{-1} f_D = \left(\frac{1}{\phi_{is}}\right)\left(1 + \frac{1}{k_8{}^{c}\tau_e[\bar{C}]}\right) \qquad (17)$$

The fit of the **2b** quantum yields in the presence of C to eq 13 is adequate, Figure 4, and gives $k_8{}^{c}\tau_e = 27\ M^{-1}$. The **3** data plotted in the same way in Figure 4 show pronounced curvature as expected from eq 14. The somewhat erratic variation of **2b**/**3** ratios with [C] precludes a detailed application of eq 14 to these data. The [C] dependence of the dimerization quantum yields is satisfactorily accounted for by the single triplet expression 17, Figure 5, suggesting that $k_9{}^{c}$ is small. The intercept to slope ratio of the least-squares line in Figure 5 gives $k_8{}^{c}\tau_e = 25\ M^{-1}$, in close correspondence with the value obtained from the **2b** quenching data.

The plot of the **2b** quantum yields in the presence of c-P according to eq 13, Figure 6, gives $k_8{}^{P}\tau_e = 12.0\ M^{-1}$. The corresponding plot of the **3** quantum yields, also shown in Figure 6, gives a larger apparent value of $k_8{}^{P}\tau_e = 17.4\ M^{-1}$. A large apparent $k_8{}^{P}\tau_e = 17.5\ M^{-1}$ value is also obtained when a single triplet expression, analogous to eq 17, is applied to the cis–trans isomerization quantum yields, Figure 7. Since in this instance the conclusion that **2b** and **3** are differentially quenched seems inescapable, the more rigorous eq 14 can be applied to the data. Dividing eq 13 by eq 14 gives

$$\phi_{2b}/\phi_3 = \left(\frac{k_5}{k_4}\right)\left(\frac{1}{k_7\tau_a}\right)(1 + k_9\tau_a[Q]) \qquad (18)$$

A plot of **2b**/**3** ratios vs. [c-P] results in a satisfactory straight line whose slope to intercept ratio gives $k_9{}^{P}\tau_a = 1.2\ M^{-1}$. Accordingly, substitution of $\phi_{is} = 1.0$, $k_8{}^{P}\tau_e = 12\ M^{-1}$, and $k_9{}^{P}\tau_a = 1.2\ M^{-1}$ into eq 16 would allow calculation of $\phi_{c\to t}$ values for each c-P concentration if $k_4\tau_e$ were known. Interestingly, the best agreement between calculated and observed isomerization quantum yields is obtained when $k_4\tau_e$ is assumed to be nearly unity, suggesting that formation of a distinct triplet leading to **3** is the major fate of **1b** enone triplets.

Assuming that singlet excitation transfer from **1b** to DBA ($E_{T_1} = 40.2$, $E_{S_1} = 70.4$ kcal/mol)[33] is unimportant, for the DBA concentration range employed allows application of eq 13 to the quenching of **2b** formation. The ϕ_{2b} values for all but the highest DBA concentration give a linear plot, Figure 8. The ϕ_3 values are also plotted in Figure 8 for comparison. The slope to intercept ratios of the two lines are 174 and 709 M^{-1} for **2b** and **3**, respectively, demonstrating very pronounced differential quenching of **2b** and **3** formation by DBA. Since both products have been shown to originate in the triplet manifold the conclusion that the quenching efficiency for the two products is

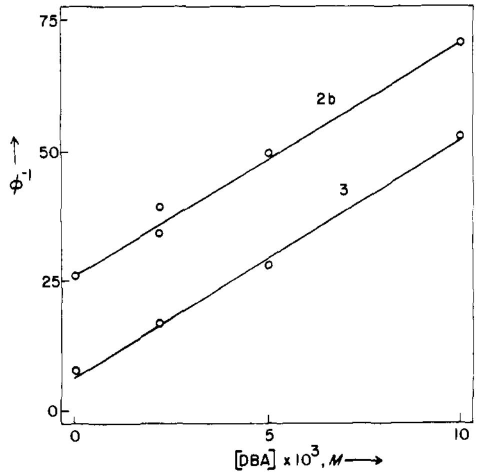


Figure 8. Quenching of **2b** and **3** formation by DBA.

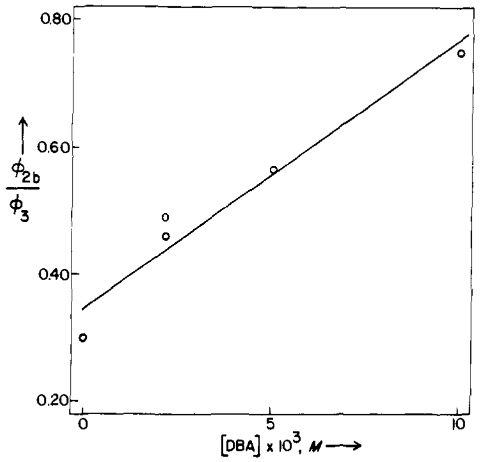


Figure 9. Differential quenching of **2b** and **3** formation by DBA.

different would not be affected if these numbers were to include some contribution from singlet excitation transfer. This can be demonstrated by considering eq 18, which is independent of any events occuring prior to intersystem crossing from ^{1}**1b***. The plot of the data applying eq 18 is shown in Figure 9 and gives $k_9{}^a\tau_a = 124\ M^{-1}$. Accordingly, the **2b** data in Figure 8 can be assumed to give a limiting value for $k_8{}^a\tau_e$ of $\leq 174\ M^{-1}$. Consideration of the significance of the above Stern-Volmer constants will follow the analysis of the quantum yields obtained starting with **3**. Best estimates of other relevant quantities obtained by averaging the experimental results, e.g., the intercepts in Figures 4, 6, and 8, are $k_5\tau_e = 0.05 \pm 0.01$, $k_4\tau_e \simeq 0.95$ (i.e., $k_3 \ll k_4 + k_5$), and $k_7\,\tau_a = 0.10 \pm 0.02$. It should be noted that in the experiment in which xanthone, $E_T = 74.2$ kcal/mol,[34] was employed as a photosensitizer a rather high ratio of **2b**/**3** = 0.85 was obtained. The relatively small amount of **3** observed suggests that no ^{3}**1b***′ forms directly in the excitation transfer events.

The Photochemistry of 3. Since the enone triplets of **3** do not have a nearby isolated double bond with which to interact, the photochemistry of **3** should in principle be less complex than that of **1b**. As indicated above the phosphorescence measurements suggest that the lowest triplet state of **3** is π–π*. If this is the reactive state at room temperature it would appear that it abstracts hydrogen intramolecularly at the α and β positions to give **5** and **4**, respectively. Abstraction of hydrogen by the β position of enone triplets has been observed in other enones with lowest π–π* spectroscopic triplets and has been associated with these states,[35] cf. also ref 11a. There is also one example of hydrogen abstraction at the α position of a cyclohexenone whose substitution pattern suggests a π–π* lowest triplet state.[11b] The possibility that hydrogen abstraction at the α position occurs from a higher energy n–π* triplet does not seem attractive, since upon increasing solvent polarity the ratio of **4**/**5** decreases modestly instead of increasing (4.5 in cyclohexane, 3.70 ± 0.4 in benzene, and 3.3 ± 0.1 in acetonitrile).[36] It should be noted that since the **4**/**5** ratio is essentially unaffected by a 100-fold variation in the concentration of **3**, dimeric structures for the product to which structure **5** was assigned are ruled out (see also Appendix).

As for **1b** the DBA quenching observations are most revealing concerning the possible involvement of more than one triplet state of **3** in the formation of **4** and **5**. The **4**/**5** ratio increases by more than a factor of 2 as the DBA concentration is increased. Since both photoreactions involve the same chromophore there is no a priori reason in this case for preferring consecutive over concurrent formation of different nonequilibrated triplet states. It is instructive therefore to consider a simple concurrent mechanism, eq 19–27

$$\mathbf{3} \xrightarrow{h\nu} {}^1\mathbf{3}^* \xrightarrow{k_{19}} \mathbf{3} \tag{19}$$

$$^1\mathbf{3}^* \xrightarrow{k_{20}} {}^3\mathbf{3}^* \tag{20}$$

$$^1\mathbf{3}^* \xrightarrow{k_{21}} {}^3\mathbf{3}^{*\prime} \tag{21}$$

$$^3\mathbf{3}^* \xrightarrow{k_{22}} \mathbf{4} \tag{22}$$

$$^3\mathbf{3}^* \xrightarrow{k_{23}} \mathbf{3} \tag{23}$$

$$^3\mathbf{3}^{*\prime} \xrightarrow{k_{24}} \mathbf{5} \tag{24}$$

$$^3\mathbf{3}^{*\prime} \xrightarrow{k_{25}} \mathbf{3} \tag{25}$$

$$^3\mathbf{3}^* + \mathrm{Q} \xrightarrow{k_{26}{}^q} \mathbf{3} + {}^3\mathrm{Q}^* \tag{26}$$

$$^3\mathbf{3}^{*\prime} + \mathrm{Q} \xrightarrow{k_{27}{}^q} \mathbf{3} + {}^3\mathrm{Q}^* \tag{27}$$

in accounting for the photochemistry of **3**. The corresponding quantum yield expressions are given in eq 28–30, where $\phi_{is}' = k_{20}/(k_{19} + k_{20} + k_{21})$, $\phi_{is}'' = k_{21}/(k_{19} + k_{20} + k_{21})$, $\tau_e' = (k_{22} + k_{23})^{-1}$, and $\tau_e'' = (k_{24} + k_{25})^{-1}$.

$$\phi_4{}^{-1} = \left(\frac{1}{\phi_{is}'}\right)\left(\frac{1}{k_{22}\tau_e'}\right)(1 + k_{26}{}^q\tau_e'[\mathrm{Q}]) \tag{28}$$

$$\phi_5{}^{-1} = \left(\frac{1}{\phi_{is}''}\right)\left(\frac{1}{k_{24}\tau_e''}\right)(1 + k_{27}{}^q\tau_e''[\mathrm{Q}]) \tag{29}$$

$$\phi_D f_D{}^{-1} = \phi_{is}'\left(\frac{k_{26}{}^c\tau_e'[\mathrm{C}]}{1 + k_{26}{}^c\tau_e'[\mathrm{C}]}\right) + \phi_{is}''\left(\frac{k_{27}{}^c\tau_e''[\mathrm{C}]}{1 + k_{27}{}^c\tau_e''[\mathrm{C}]}\right) \tag{30}$$

As pointed out above the **3**-sensitized dimerization and isomerization quantum yields observed for high 1,3-diene concentrations ($\phi_D = 0.95$ and $\phi_{c\rightarrow t} = 0.56$ for $[\mathrm{C}]_0 = 0.500$ M and $[\text{c-P}]_0 = 0.300$ M, respectively) establish the intersystem crossing efficiency for **3** as unity. Examination of eq 30 shows that at the high concentration limit this result corresponds to $\phi_{is}' + \phi_{is}'' = 1.0$, i.e., $k_{19} \ll k_{20} + k_{21}$. The quenching plot of $\phi_4{}^{-1}$ vs. [C] is linear, Figure 10, and gives $k_{26}{}^c\tau_e' = 99\ M^{-1}$ and $\phi_{is}'k_{22}\tau_e' = 8.7 \times 10^{-3}$. The latter value is in good agreement with $\phi_{is}'k_{22}\tau_e' = (9.1 \pm 0.5) \times 10^{-3}$ obtained by averaging the benzene quantum yields in Table IV. The ϕ_5 values in Table IV give $\phi_{is}''k_{24}\tau_e'' = (2.5 \pm 0.3) \times 10^{-3}$. Unfortunately the conversions to **5** in the presence of C

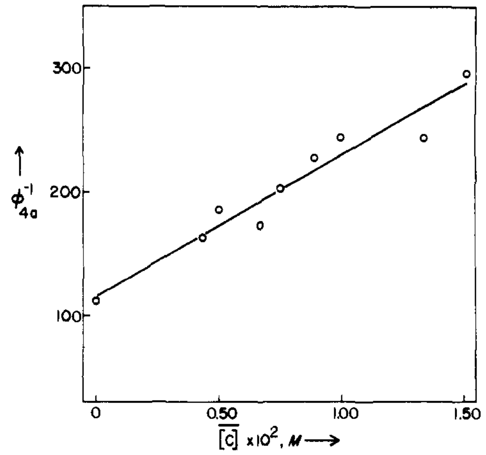


Figure 10. Quenching of **4** formation by C.

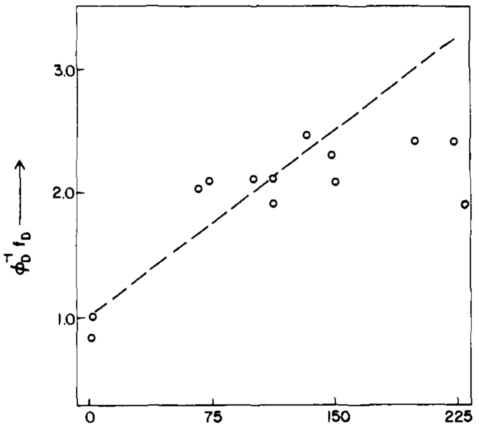


Figure 11. **3**-sensitized photodimerization of C.

were too small to be accurately measured. That $k_{27}{}^{c}\tau_e{}''$ is larger than 99 M^{-1} is suggested by the C dimerization quantum yields, which are not accounted for by the usual sensitization expression (see eq 17 for form) corresponding to a single triplet mechanism, Figure 11. The dashed line in Figure 11 corresponds to an intercept to slope ratio of 99 M^{-1} and shows the behavior expected if the formation of **4** and **5** were quenched with equal efficiency by C. The fact that ϕ_D values at low [C] are higher than predicted by this line would be consistent with eq 30 if $k_{27}{}^{c}\tau_e{}'' > k_{26}{}^{c}\tau_e{}'$. The scattered nature of the dimerization plot and the fact that $k_{27}{}^{c}\tau_e{}''$ was not independently determined preclude a more detailed application of eq 30 at this time.

Application of eq 28 and 29 to the DBA data gives satisfactory adherence to linearity, Figure 12. Since the DBA concentration range employed with **3** is smaller by a factor of 10 than that employed with **1b,** the assumption that singlet excitation transfer does not contribute to the quenching observations is probably better in this case. Accordingly, the slope/intercept ratios in Figure 12 give $k_{26}{}^{a}\tau_e{}' = 3.67 \times 10^3$ M^{-1} and $k_{27}{}^{a}\tau_e{}'' = 1.07 \times 10^4$ M^{-1}. The linearity of the ϕ_5 plot is consistent with a concurrent triplet mechanism, eq 29, and not with a consecutive triplet mechanism which would have predicted a quadratic concentration dependence, e.g., eq 14. This is further demonstrated by a nonlinear dependence of ϕ_4/ϕ_5 on [DBA]. Nonetheless, since differential quenching is almost as pronounced in **3** as in **1b,** despite the absence of a second photoreactive chromophore in the former system, it seems wise to include the possibility of the phenomenon having a common origin in different triplets of the enone moiety in the two molecules.

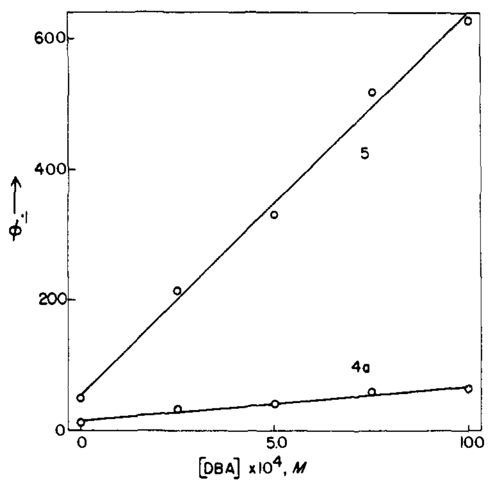


Figure 12. Quenching of **4** and **5** formation by DBA.

Conclusions

Before considering the above results in greater detail it is important to emphasize that the mechanisms for the above reactions are open to much speculation. Even if only two triplets were involved in each case their interconversion need not be fully irreversible.[40,41] Furthermore, the diradical intermediates which will result upon hydrogen abstraction are likely to contribute to the inefficiency in product formation and could also alter the meaning of the quantum yields in the absence of quenchers.[19c]

The quenching constants defined in this work are summarized in Table VI. Within the constraints indicated above, analysis of these constants can be based on the assumption that all triplet excitation transfer processes to DBA are diffusion controlled, i.e., $k_8{}^{a} = k_9{}^{a} = k_{26}{}^{a} = k_{27}{}^{a} = 1.0 \times 10^{10}$ M^{-1} s^{-1}.[42] This gives effective triplet lifetimes of 17.4, 12.4, 367, and 1070 ns for τ_e, τ_a, $\tau_e{}'$, and $\tau_e{}''$, respectively. Although the τ_e, $\tau_e{}'$, and $\tau_e{}''$ values must be regarded as upper limits, the fact that $k_9{}^{a}\tau_a$, which is independent of singlet quenching complications, is larger than the diene quenching constants suggests that these upper limits are probably close to the correct values. This conclusion is supported by the qualitative oxygen quenching observation for **3,** which, assuming $[O_2] = 1.5 \times 10^{-3}$ M for an air-saturated cyclohexane solution at ~25 °C, gives $k_{26}{}^{ox}\tau_e{}' \simeq 3 \times 10^3$ M^{-1}, where $k_{26}{}^{ox}$ is the rate constant for oxygen quenching in eq 26. This value, being close to the upper limit for $k_{26}{}^{a}\tau_e{}'$ is, if anything, higher than expected because due to spin-statistical factors $k_q{}^{ox}$ is usually $\leq 3 \times 10^9$ M^{-1} s^{-1}.[44] In any case, the results in Table VI suggest that excitation transfer to the 1,3-dienes is one to two orders of magnitude slower than diffusion controlled despite the expected exoergicity of each process. Such behavior has been noted previously with cyclic enones, and may indicate reversible formation of a triplet exciplex.[18,45] The shorter triplet lifetimes inferred for the triplet states of **1b** can probably be associated with a fast intramolecular interaction between the enone triplet(s) and the isolated double bond.

A recent pulse radiolysis study of norbornene triplets in benzene[46] could be relevant to the interpretation of the $k_{16}{}^{P}\tau_a$ and $k_{16}{}^{a}\tau_a$ values, if ^{3}**1b***′ does indeed represent the triplet state of the isolated double bond in **1b.** The results with norbornene suggest that its relaxed triplet state has $E_T = 57.2 \pm 1.5$ kcal/mol and a lifetime of 250 ns in benzene. The rate constant for triplet excitation transfer from norbornene to anthracene was found to be 6.8×10^9 M^{-1} s^{-1}, very close to the value assumed above for excitation transfer from ^{3}**1b***′ to DBA. The energy and lifetime of the relaxed norbornene triplet state were associated with the degree of twisting which can be achieved about the excited double bond in this relatively rigid molecule.

If this is correct, the assignment of a shorter triplet lifetime to the alkene moiety in **1b** suggests a higher degree of torsional relaxation and therefore a somewhat lower triplet excitation energy. This may account for the implied inefficiency of excitation transfer to c-P, $E_T = 57.3$ kcal/mol, $k_9{}^a/k_9{}^P \simeq 100$. A large energy separation between the enone and alkene triplets in **1b** is also consistent with the proposed irreversibility in intramolecular triplet excitation transfer from ^{3}**1b*** to ^{3}**1b***′.[47] We are less comfortable with the proposed noninterconversion between ^{3}**3*** and ^{3}**3***′, since these triplets are centered on the same chromophore. The longer lifetime associated with ^{3}**3***′ may suggest π–π^* character for this state. If so, the modest solvent effect on the **4**/**5** ratio is consistent with the involvement of a higher energy n–π^* state of **3**, i.e., ^{3}**3***, in the pathway to **4**. In view of the rigidity of the structure of **3** the alternative possibility[41] that different conformations represent energy minima on the potential energy surface of the π–π^* triplet state each possessing different probabilities of **4** and **5** formation, does not seem viable.

Finally, it should be noted that except for the formation of **2b** the reactions observed in **1b** and **3** and the related systems cited have in common the abstraction of a hydrogen atom by a relatively rigid double bond in a cyclic system and thus can be regarded as intramolecular counterparts of intermolecular hydrogen abstraction by cyclopentene triplets.[48]

Experimental Section

Procedures. Preparative irradiations were carried out in the quartz immersion well of a standard photochemical reactor using a 450-W Hanovia 679A-36 "high-pressure" mercury lamp. One set of experiments was carried out using a Nester–Faust low-pressure mercury lamp. The 2537-Å line from this lamp was isolated using chlorine gas as filter. Quantitative studies were carried out using a merry-go-round apparatus[53] with a solution filter isolating the 3130-Å line.[54] The apparatus and samples were immersed in a water bath thermostated at 30 °C. GLC analyses were done on a F & M 5750 research chromatograph using a flame detector. The best resolution of the photoproducts was obtained on a 9 ft × ⅛ in. stainless steel 5% W-98 80-100 S column maintained at 500 °F. Flame detector and injection port were maintained at 600 and 700 °F, respectively, carrier flow at 2.5 (meter reading), oxygen at 22 psig, and hydrogen at 10 psig. Quantitative analyses were carried out by cutting and weighing Xerox copies of the GLC traces. No internal standards were used in analyzing products from **1b** and **3**; it was assumed that areas under the GLC traces were proportional to the amount of each compound, since the products and starting materials are isomeric. *n*-Tetradecane, T, was used as internal standard for analysis of cyclohexadiene dimers, D. The molar response ratio of the GLC detector for T and D was measured, (response T)/(response D) = 1.13 ± 0.05. Benzophenone-sensitized cis–trans isomerization of *cis*-1,3-pentadiene was used for actinometry.[12,13] Solutions, usually 3-mL samples, were degassed by freeze–pump–thaw cycles at least three times at 1×10^{-5} Torr. Pentadiene conversions to the trans isomer following correction for back reaction were generally smaller than 16%. Conversions to **3** were less than 7, 8.5, and 22% in the presence of C, c-P, and DBA, respectively. Conversions to **4** were less than 0.5 and 2% in the presence of C and DBA, respectively. Conversions to D were less than 34 and 9% for the long and short irradiation period results in Table II and less than 4.5 and 30% for **1b** and **3** experiments in Table III, respectively, where $\%D = (2[D]/[C]_0)100\%$.

Ultraviolet spectra were recorded on a Cary 14 spectrometer. Molar decadic extinction coefficients at 313 nm in benzene for **1b**, **3**, benzophenone, and DBA are 58, 78, 50, and 341 M^{-1} cm^{-1}, respectively, and at 254 nm in acetonitrile for **3** 9260 M^{-1} cm^{-1}. Emission spectra were recorded for glassy solutions at 77 K using a Hitachi-Perkin-Elmer MPF-2A emission spectrometer. NMR spectra were determined on Varian HA-60 or Bruker HX-270 MHz instruments with Me_4Si as internal standard, IR spectra on a Perkin Elmer Model 257 spectrometer, high resolution mass spectra on an AEI MS-902 instrument.

Materials. Benzophenone, Fischer reagent grade was sublimed before use. *cis*-1,3-Pentadiene, J. T. Baker reagent grade, was bulb-to-bulb distilled under reduced pressure immediately before use, ≤0.55% trans by GLC. 1,3-Cyclohexadiene, Aldrich, was recrystallized from ethanol. Benzene, J. T. Baker, was passed through alumina and distilled. Cyclohexane, Mallinckrodt analytical reagent, was used without purification. Acetonitrile, Eastman spectrograde, was used without purification. Irradiation of **1b** in methanol (Pyrex filter) for 30 h while air was being bubbled through the solution gave **2b** (20%) and **3** (60%) which were separated by chromatography as described earlier.[2] Cyclohexadiene photodimers were prepared using benzophenone as sensitizer and isolated as previously described.[32]

Table VI. Quenching Constants for the Triplet States of **1b** and **3** in Benzene, 30 °C

Excited state	Quencher	Symbol	Value, M^{-1}
^{3}**1b***	C	$k_8{}^c\tau_e$	25
	c-P	$k_8{}^P\tau_e$	12
	DBA	$k_8{}^a\tau_e$	≤174[a]
^{3}**1b***′	c-P	$k_9{}^P\tau_a$	1.2
	DBA	$k_9{}^a\tau_a$	124
^{3}**3***	C	$k_{26}{}^c\tau_e'$	99
	DBA	$k_{26}{}^a\tau_e'$	$\leq 3.67 \times 10^3$ [a]
^{3}**3***′	DBA	$k_{27}{}^a\tau_e''$	$\leq 1.07 \times 10^4$ [a]

[a] This value is an upper limit due to the possibility of singlet quenching.

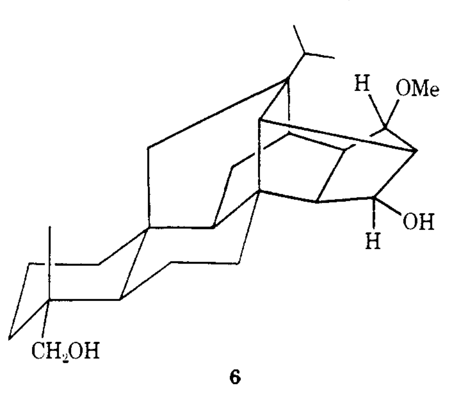
Preparation of 4. Irradiation of a 0.01 M solution of **3** in methanol without a filter, evaporation of solvent, and chromatography over alumina gave **4** in 65% yield, mp 170 °C; IR bands at 1775 (strained ketone) and 1750 cm^{-1} (ester), NMR signals at 4.18 (br, H-17), 3.63 (ester methoxyl), 3.13 (ether methoxyl), 1.26 (C-4 methyl), 0.87 and 0.84 (d, J = 7 Hz, isopropyl methyls).

Anal. Calcd for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98; O, 15.00. Found: C, 76.38; H, 9.05; O, 14.78.

A solution of 0.5 g of **4** in 20 ml of MeOH was hydrolyzed with 1 g of NaOH and evaporated. The residue was diluted with water, acidified, and extracted with ether. The washed and dried extract was evaporated; the residue was triturated with hexane, which resulted in crystallization and a quantitative yield of the acid, mp 235 °C. The NMR spectrum was similar to that of **4** except for the absence of the methoxyl singlet of the ester. The presence of an extra methoxyl singlet at 3.2 ppm and the analysis showed that the product was a methanol solvate.

Anal. Calcd for $C_{26}H_{36}O_4 \cdot CH_3OH$: C, 72.94; H, 9.07; O, 17.99. Found: C, 73.31; H, 9.03; O, 17.78.

The reduction of **4** to a hydroxy ketone with a limited amount of $LiAlH_4$ has been reported.[5] Reduction of 1 g of **4** in 30 mL of ether with excess $LiAlH_4$ (0.15 g) by refluxing overnight followed by the usual workup, trituration of the crude gum with hexane, and recrystallization from methanol gave a quantitative yield of **6**, which had mp 197–198 °C, IR absorption at 3400 cm^{-1}, and NMR signals at 4.8 (br, H-15), 4.0 (br, H-17), 3.25 (methoxyl), 3.25 (center of AB system, $-CH_2OH$), 0.82 (C-4 methyl), 0.85 and 0.82 (d, J = 7 Hz, isopropyl methyls).



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Anal. Calcd for $C_{26}H_{40}O_3$: C, 77.95; H, 10.06; O, 11.98. Found: C, 77.85; H, 9.96; O, 12.45.

Isolation of 5. Since trial experiments (GLC analysis) showed that an irradiation time of approximately 30 h produced optimum yields of **5**, degassed 5×10^{-3} M solutions of **1b** in benzene in Pyrex ampules

Table VII. ^{13}C NMR Spectra of **3**, **4**, and **5**[a]

Carbon No.	**3**	**4**	**5**
1	43.6 t	41.8 t	41.0 t
2	18.9 t	18.6 t	18.3 t
3	37.2 t	37.2 t	37.2 t
4	48.2	48.2	48.2
5	50.8 d[b]	48.1 d[b]	49.8 d[b]
6	30.0 t	31.0 t[c]	28.0 t
7	32.6 t	31.4 t[c]	32.4 t
8	39.4[c]	38.2[d]	44.9[c]
9	48.4 d[b]	47.3 d[b]	47.8 d[b]
10	37.5[c]	36.9[d]	35.2[c]
11	26.6 t	23.9 t	24.0 t
12	33.3 d	35.7 d	39.2 d
13	51.5 d	45.2 d[b]	53.6[d]
14	48.4 d[b]	47.6 d[b]	53.8[d]
15	205.7	210.7	211.8
16	107.4 d	47.7 d[b]	42.4 t
17	193.3	77.7 d	88.6
18	40.6[c]	42.3[d]	50.0[c]
19	35.3 t	44.7 d[e]	60.1 d
20	33.3 d	34.3 d	31.3 d
21	17.8 q[d]	17.8 q[f]	17.6 q[e]
22	16.4 q[d]	17.2 a[f]	18.6 a[e]
23	23.6 t	21.8 t	23.4 t
24	16.8 q[d]	16.6 a[f]	16.5 q[e]
25	178.5	178.5	178.7
26	52.2 q	51.7 q	51.7 q[f]
27	58.4 q	55.0 q	52.6 q[f]

[a] Run in $CDCl_3$ at 67.9 MHz on Bruker HX-270 instrument operating at 63 kG. The spectrum of **5** was obtained in a microcell. Unmarked signals are singlets. [b,c,d,e,f] Assignments may be interchanged.

tied to the outer jacket of the reactor were irradiated for 30 h, evaporated, and chromatographed over alumina. The benzene eluates were evaporated and triturated with hexane; this resulted in crystallization of most of the **4**. The mother liquor was evaporated and dissolved in pentane. On standing overnight, more **4** had crystallized and was filtered. The procedure was repeated until the material in the mother liquor was a mixture of 85% **5** and 15% **4**. This mixture was separated by preparative TLC using multiple elution with hexane-ethyl acetate (19:1). The yield of **5** which could not be induced to crystallize was 40 mg (7%) from several runs: IR bands at 1770 (strained cyclopentanone) and 1730 cm^{-1} (ester); NMR signals at 3.70 (ester methoxyl), 3.29 (ether methoxyl), 2.5 (H-19), 1.20 (C-4 methyl), and 0.75 ppm (d, J = 7 Hz, isopropyl methyls).

Anal. Calcd for $C_{27}H_{38}O_4$: mol wt, 426.2768. Found: mol wt (MS), 426.2766.

Appendix. Structure of 5

Combination of the crude product from several runs under conditions which produced optimum yields of **5** (see Experimental Section) followed by fractional crystallization and preparative TLC eventually resulted in isolation of a small amount of noncrystalline **5** isomeric with **1b**, **2b**, **3**, and **4** (high resolution mass spectrum) with a mass spectrometric fragmentation pattern completely different from that of **4** and somewhat similar, though not superimposable, on that of **3** and IR bands at 1770 (strained ketone or lactone) and 1730 cm^{-1} (ester). The 270-MHz ^1H NMR spectrum exhibited no signal downfield from the methoxyl resonance at 3.29 ppm; the upfield signals were similar to those of **4** except for the appearance of a sharp singlet at 2.50 ppm.

Two structural possibilities were therefore considered: (a) the unknown is one of the four possible photodimers of **3**; (b) the unknown is **5**, formed as the result of hydrogen abstraction from C-**1a** by the α-carbon of the enone system and ring closure between C-17 and C-19.[49]

The singlet at 2.50 ppm which must be due to a somewhat deshielded methine proton not coupled to any vicinal hydrogen atom could a priori be attributed either to H-16 of a head-to-tail dimer or to H-19 of formula **5**. However, the GLC retention time which was very close to that of **4**, the lack of identity between the mass spectra of **3** and the unknown, and the lack of dependence of the **4**/**5** ratio on the concentration of **3** strongly argued against a dimer structure. Comparison of the ^{13}C NMR spectrum of the unknown with the spectra of **3** and **4** (Table VII) also supported formula **5**.

Literature data,[51] application of chemical shift theory, and standard decoupling techniques were sufficient for assignments of frequencies to the carbons of **3** and **4** except for the ambiguities listed in the table. Pimaric and sandaracopimaric acid[51] served as models for ring A and B except for C-8 and C-9, the triplet at lowest field being assignable to C-1, just as in steroids, and that at highest field to C-2. Most of the other signals were assigned by using the usual chemical shift parameters, taking into account the values for α and β carbons, which exert a deshielding, and for γ carbons which exert a shielding effect. C-9 of **3** should be comparable to C-9 of steroids, the deshielding effect of the extra β carbon being nullified by the shielding effect of three extra γ carbons. Chemical shifts of the three doublets in the range 48–50 ppm of **3** and 47–48 ppm of **4** are too similar to permit distinction between C-5, C-9, or C-14; analogously, calculated chemical shifts for C-8, C-10, and C-18 are too similar to permit differentiation between the three singlets of **3** in the range 37–40 and the three singlets of **4** at 36.9, 38.2, and 42.8 ppm. The singlet at 48.2 ppm was assigned to C-4 by analogy with pimaric and sandaracopimaric acid.[51] C-23 would be expected to be more shielded than C-11 because of 1,3-interactions with the C-4 methyl group and axial C-11. The doublet at 51.5 ppm of **3** was assigned to allylic C-13, since it exhibits a significant upfield shift to 44.7 or 45.2 ppm in the spectrum of **4**. The assignment of the second doublet of **4** near 45 ppm to C-19 is based on the assumption that one of the doublets in the range 47.3–48.1 should be due to C-16, which is adjacent to a ketone.

The off-resonance decoupled spectrum of the minor photoproduct exhibited a number of singlets, doublets, triplets, and quartets appropriate for formula **5**. Most of the signals were similar to those of **4**; the differences can be explained on the basis of **5** as follows. The triplet at lowest field was assigned to C-16, since that carbon is adjacent to a ketone. The next higher triplet was assigned to C-1 as usual and the singlet at 48.2 to C-4. Shifts of three doublets at rather low field, 53.6, 53.8, and 60.1 ppm, which must be assigned to C-13, C-14, and C-19, differ significantly from corresponding shifts in the spectrum of **4**. The signal at 60.1 is provisionally assigned to C-19 because C-19 of **5** contains one more β and one less γ carbon than C-19 of **4**. This should produce a downfield shift of ca. 12 ppm to near 57 ppm, which is in reasonable agreement with 60 ppm if it is considered that C-19 is now part of a five-membered ring. One of the two remaining doublets, at 53.6 and 53.8 ppm, was assigned to C-13, which should be deshielded by about 7 ppm relative to C-13 of **4**;[52] the calculated shift of ~52 ppm is in good agreement with the observed value if the different nature of the ring system be taken into account. By exclusion the singlets at 44.9 and 50 ppm must be assigned to C-8 and C-18.

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(1) Supported in part by Grants from the National Science Foundation (GP-12582 and MPS 76-02439) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.
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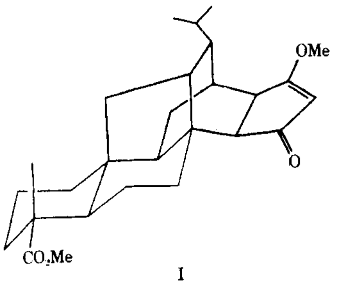
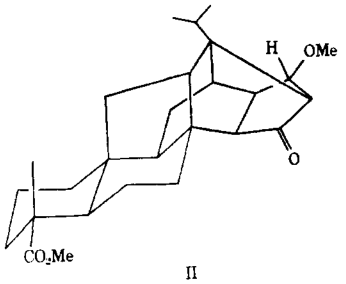


I



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