Organic Photochemical Reactions. XIV. The Photocycloaddition of Acetone to Cyclooctene and 1,3-Cyclooctadiene[1]

Kensuke Shima, Yoshiki Sakai, and Hiroshi Sakurai

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka

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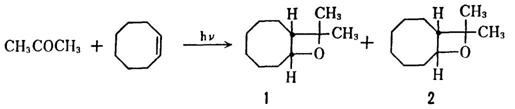
The photocycloaddition of acetone to cyclooctene (COE) or 1,3-cyclooctadiene (COD) yields isomeric *cis*- and *trans*-oxetanes in good yields. Kinetic studies of these reactions reveal that the photoaddition of acetone to COE proceeds *via* the attack of the triplet acetone on the ground state COE, while the addition to COD probably occurs by the attack of the excited singlet acetone on the ground state COD.

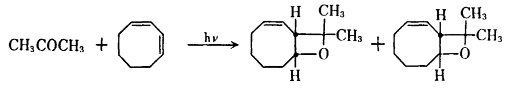
The photoaddition of carbonyl compounds to olefins to yield oxetanes (the Paterno-Büchi Reaction) has been the subject of much recent study. However, only a few papers on the photoreactions of ketones with eight-membered cyclic olefins or dienes have been published. The photocycloadditions of benzophenone, several *p*-quinones, and thiobenzophenone to cyclooctene and/or cyclooctadienes to yield oxetanes or thietanes have been reported.[2-4] We found that the photoaddition of acetone to cyclooctene (COE) or 1,3-cyclooctadiene (COD) afforded oxetanes in fairly good yields, while it is well-known that the photoreactions of acetone with cyclopentene or cyclohexene give mainly the products derived from hydrogen abstraction from these olefins by the acetone triplet, while oxetanes are minor products.[5] We also wish to report on the stereochemistry of oxetanes and on the kinetics of oxetane formation.

Results and Discussion

Photoaddition (Syntheses of Oxetanes). Acetone, when irradiated in the *n*-*π** region of the carbonyl group, readily adds to COE to give roughly equimolar mixtures of *cis*- and *trans*-oxetanes (**1** and **2**) in fairly good yields. Similarly, the irradiation of acetone and COD gives mainly *cis*- and *trans*-oxetanes (**3** and **4**, *ca.* 4 : 1).



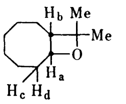
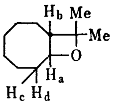
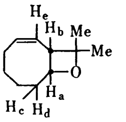
1　2



3　4

The products, **1**—**3**, were isolated by preparative VPC on a 3-m PEG-6000 column at 160°C. The structural identification of **1**—**4** is based on spectral analysis. The NMR spectra of **1**—**3** exhibit a low-field double triplet or septet at 5.45—5.65 *τ*. These absorptions are assigned to the ring hydrogen *α* to oxygen.[6] It is also well known that the coupling constant between H_a and H_b in *cis*-oxetanes are larger than that in *trans*-oxetanes.[7] The NMR data are shown in Table 1. These results support the stereochemical assignments for **1**, **2**, and **3**. **4** could not be separated by preparative VPC. Since the catalytic hydrogenation of **3** using an Adams catalyst gives **1**, and mixtures of **3** and **4** give those of **1** and **2**, **4** surely has a *trans*-configuration. The NMR data for **3** are similar to that of the thietane, **5**.[4,8] **1** and **2** give the same cracking patterns in the mass spectra.

Table 1. Summary of NMR data for oxetanes

	Chemical shift (*τ*)	Multiplicity	Proton assignment	Coupling constant (Hz)
	5.65	dt	H_a	$J_{ab}=J_{ac}=10$
	7.4—9.5	m	13H (Ring protons)	$J_{ad}=3.4$
	8.72	s	6H (Methyl)	
	5.45	sept	H_a	$J_{ab}=6$
	7.4—9.4	m	13H (Ring protons)	$J_{ac}=10$
	8.63	s	3H (Methyl)	$J_{ad}=3.5$
	8.81	s	3H (Methyl)	
	5.56	dt	H_a	$J_{ad}=J_{ac}=9$
	6.76	dd	H_b	$J_{ad}=3$
	4.48	m	2H (Vinyl)	$J_{be}=4$
	7.3—9.1	m	8H (Methylene)	
	8.61	s	6H (Methyl)	

Abbreviations used are as follows: m=multiplet; s=singlet; dt=doublet of triplets; dd=doublet of doublets; sept=septet.

The products from the photoreaction of acetone and

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[1] Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970. Part XIII, Y. Nagao, K. Shima, and H. Sakurai, *Tetrahedron Lett.*, **1970**, 2221.

[2] G. W. Griffin, unpublished results; D. R. Arnold, *Advan. Photochem.*, **6**, 373 (1968).

[3] a) D. Bryce-Smith and A. Gilvert, *Proc. Chem. Soc.*, **1964**, 87. b) D. Bryce-Smith, A. Gilvert, and M. G. Johnson, *J. Chem. Soc., C*, **1967**, 383. c) D. Bryce-Smith, A. Gilvert, and M. G. Johnson, *Tetrahedron Lett.*, **1968**, 2863.

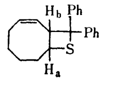
[4] a) K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, **32**, 3676 (1968). b) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, **1969**, 283.

[5] a) P. de Mayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961). b) J. B. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966). c) H.-D. Scharf and F. Korte, *Tetrahedron Lett.*, **1963**, 821; *Chem. Ber.*, **97**, 2425 (1964).

[6] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, **1964**, 1425.

[7] a) N. J. Turro and P. A. Wriede, *J. Org. Chem.*, **34**, 3562 (1969). b) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

[8] Stereochemistry of **5** has not been mentioned in Ref. 4, but **5** is considered to have *cis*-configuration. The authors with to thank Dr. K. Yamada, Chiba University, for obtaining the NMR chart of the thietane **5**.



5 $J_{ab}=10$ Hz

cyclopentene or cyclohexene are mainly unsaturated alcohols and dimers of olefins.[5] The photoreaction of acetone and COE, on the other hand, yields mainly oxetanes (**1** and **2**). These differences may be partly explained by the fact that the cycloocten-2-yl radical is less resonance-stabilized than the cyclohexen-2-yl or cyclopenten-2-yl radical, since it is well known that the two double bonds in COD are not coplanar.[4a] Consequently, in COE the addition of the acetone triplet to the double bond is more likely than the hydrogen abstraction.

Kinetic Studies. Degassed benzene solutions containing acetone (0.1—0.2 M) and varying amounts of COE or COD were irradiated using a 350-W high-pressure mercury lamp through quartz glass and a 10-mm filter solution of chromium potassium sulfate, which served to eliminate the absorption of the benzene used as a solvent. The quantum yields were determined by the simultaneous irradiation of actinometer solutions.[9] The quantum yield for oxetane formation in benzene was independent of the percentage of reaction up to 10%.

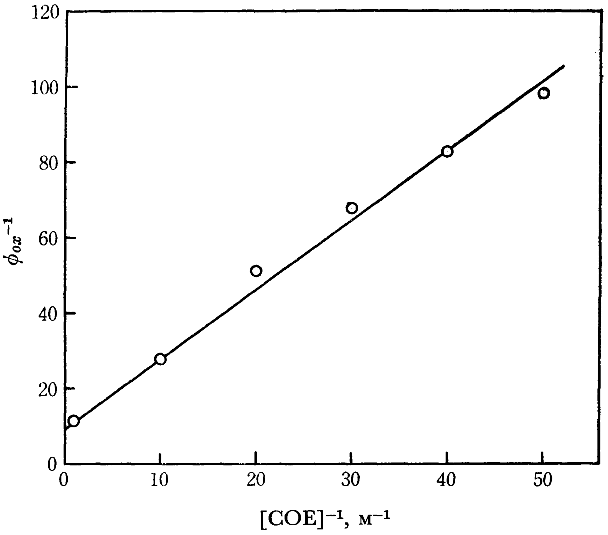


Fig. 1. Dependence of the reciprocal of the quantum yield for oxetane formation on the reciprocal of COE concentration. Acetone (0.2 M) in benzene, Slope=1.83 M, Intercept=9.5.

Kinetics for the Acetone-COE System. Figure 1 shows the effect of the COE concentration on the quantum yields for oxetane formation.[11] Recently, Turro and Wriede have shown from kinetic analysis and quantum yield studies,[12] that the photocycloaddition of acetone to *trans*- or *cis*-1-methoxy-1-butene involves both the acetone singlet and the acetone triplet. In our experiment, however, the Stern-Volmer plot is linear, indicating that there are no significant contributions from either state of acetone under these reaction conditions. Since it is known that the acetone singlet is not measurably affected by low concentrations of piperylene, while the acetone triplet is quenched by piperylene at a rate close to that for diffusion-controlled quenching,[12] we examined the effect of piperylene on oxetane formation. The results are shown in Fig. 2. It is apparent that oxetane formation proceeds *via* the acetone triplet on the basis of the Stern-Volmer plots.

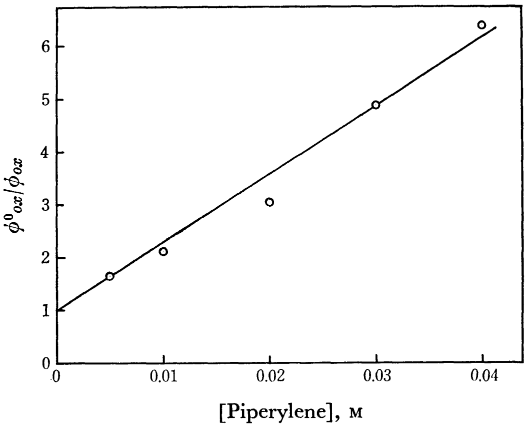


Fig. 2. Stern-Volmer plot of the quenching of oxetane formation by piperylene.
Acetone (0.2 M), COE (0.1 M) in benzene, Slope=132 M.

These observations are consistent with the following mechanism (Scheme 1):

$$A_0 \xrightarrow{h\nu} A_1 \qquad (1)$$

$$A_1 \xrightarrow{kf} A_0 + h\nu_f \qquad (2)^{13)}$$

$$A_1 \xrightarrow{k_{isc}} A_3 \qquad (3)$$

$$A_3 \xrightarrow{k_t} A_0 \qquad (4)$$

$$A_3 + \mathrm{Ol} \xrightarrow{k^3_c} [A_3\text{-}\mathrm{Ol}] \qquad (5)^{15)}$$

$$[A_3\text{-}\mathrm{Ol}] \xrightarrow{k^3_{ox}} \text{Oxetane} \qquad (6)$$

$$[A_3\text{-}\mathrm{Ol}] \xrightarrow{k^3_d} A_0 + \mathrm{Ol} \qquad (7)$$

$$A_3 + Q \xrightarrow{k_q} A_0 + Q_3 \qquad (8)$$

Scheme 1

In this scheme, Ol represents COE, [A_3-Ol], a triplet 1,4-biradical intermediate, and Q, a triplet quen-

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[9] Acetone-2-methyl-2-butene system was employed as an actinometer. The limiting quantum yield for this system (0.50) was determined using ferrioxalate actinometry.[10]

[10] H. Sakurai, K. Shima, and S. Toki, *Nippon Kagaku Zasshi*, **89**, 537 (1968).

[11] In this paper, the quantum yields for oxetane formation are the sum of the quantum yields for oxetane **1** and **2** or oxetane **3** and **4**. We also have found that the ratio of **1** to **2** varies with the irradiation time, the concentration of cyclooctene, the amount of piperylene added, and the solvent used. These interesting problems are now under investigation and will be presented in near future.

[12] N. J. Turro and P. W. Wriede, *J. Amer. Chem. Soc.*, **92**, 20 (1970).

[13] Borkman and Kearns have shown that in the absence of singlet quenchers, all acetone singlets either intersystem cross or fluoresce and $k_{isc} \gg k_f$.[14] Therefore, unimolecular nonradiative decay process of the acetone singlet is negligible.

[14] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966); *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

[15] In other words, this is the quenching process of the acetone triplet by cyclooctene. We previously proposed the intermediacy of such 1,4-biradical intermediate in the photoaddition of benzophenone to furan.[16]

[16] S. Toki and H. Sakurai, This Bulletin, **40**, 2885 (1967).

cher (piperylene). Since it has been established that the quenching of the acetone singlet by COE can very probably be excluded, kinetic analysis of Scheme 1 using the steady state approximation leads to the following expression:

$$\frac{1}{\phi_{ox}} = \left(1+\frac{k_f}{k_{isc}}\right)\left(1+\frac{k^3{}_d}{k^3{}_{ox}}\right)\left(1+\frac{k_t}{k^3{}_c[\mathrm{Ol}]}\right) \tag{9}$$

In the presence of a triplet quencher,

$$\frac{\phi^0{}_{ox}}{\phi_{ox}} = 1 + \frac{k_q[\mathrm{Q}]}{k_t + k^3{}_c\,[\mathrm{Ol}]} = 1 + k_q[\mathrm{Q}]\tau_t \tag{10}$$

where ϕ_{ox} is the quantum yield for oxetane formation and where $\phi^0{}_{ox}$ is the quantum yield for oxetane formation in the absence of an added quencher.

From the slope and intercept in Fig. 1 and $k_{isc} \gg k_f$,[14] we obtain the limiting quantum yield, $\phi_{ox}=0.11$, $k^3{}_d/k^3{}_{ox}=8.5$, $k^3{}_c/k_t=5.19\ \mathrm{M}^{-1}$. We can now calculate the value of the rate constants, k_t and $k^3{}_c$, from Fig. 2, since k_q, the rate constant for the quenching of A_3 by piperylene in benzene, is known to be equal to the diffusion-control quenching constant, which we shall estimate to be $5\times10^9\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$.[17] Thus, $k_t=2.5\times10^7\ \mathrm{sec}^{-1}$ and $k^3{}_c=1.3\times10^8\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$. These values are in reasonable agreement with the values obtained from the photoaddition of the acetone triplet to 1-methoxy-1-butene by Turro *et al.*[12,18]

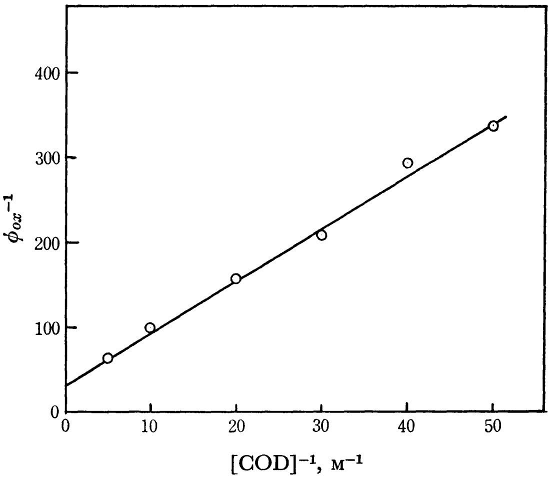

Fig. 3. Dependence of the reciprocal of the quantum yield for oxetane formation on the reciprocal of COD concentration. Acetone (0.2 M) in benzene, Slope=6.0 M, Intercept=32.

Kinetics for the Acetone-COD System. The quantum yields for oxetane formation at various COD concentrations are plotted as reciprocals in Fig. 3. In this acetone-COD system, the Stern-Volmer plot is also linear. Recently, we proposed that the photoaddition of propionaldehyde to conjugated dienes, such as 1,3-cyclohexadiene, 2,3-dimethyl-1,3-butadiene, isoprene, and piperylene, occurs from an excited singlet state of propionaldehyde.[19] The photoreaction of acetophenone with COD did not afford oxetanes at all, but gave the dimers of COD as the main products. These dimers are obtained from the attack of the triplet COD produced by acetophenone sensitization on the ground-state COD. These aromatic ketones have singlet state lifetimes of the order of 10^{-10} sec, too short for efficient bimolecular reactions to occur.[20] The oxetane formation from acetone and COD was little affected by the addition of 1,3-cyclohexadiene, which is very efficient triplet quencher.[21] These observations support the concept that oxetanes are produced from the interactions between an excited singlet state of acetone and ground state COD.

Scheme 2 accomodates our observations of the acetone-COD reaction:

$$\mathrm{A}_0 \xrightarrow{h\nu} \mathrm{A}_1 \tag{1}$$

$$\mathrm{A}_1 \xrightarrow{k_f} \mathrm{A}_0 + h\nu_f \tag{2}$$

$$\mathrm{A}_1 \xrightarrow{k_{isc}} \mathrm{A}_3 \tag{3}$$

$$\mathrm{A}_1 + \mathrm{D} \xrightarrow{k^1{}_c} [\mathrm{A}_1\text{-}\mathrm{D}] \tag{11$^{22)}$}$$

$$[\mathrm{A}_1\text{-}\mathrm{D}] \xrightarrow{k^1{}_{ox}} \text{Oxetane} \tag{12}$$

$$[\mathrm{A}_1\text{-}\mathrm{D}] \xrightarrow{k^1{}_d} \mathrm{A}_0 + \mathrm{D} \tag{13}$$

Scheme 2

D is COD, and $[\mathrm{A}_1\text{-}\mathrm{D}]$, a singlet complex. A Stern-Volmer analysis of the oxetane formation from acetone and COD as a function of the COD concentration, assuming Scheme 2, results in Eq. (14).

$$\frac{1}{\phi_{ox}} = \left(1+\frac{k^1{}_d}{k^1{}_{ox}}\right)\left(1+\frac{k_f + k_{isc}}{k^1{}_c[\mathrm{D}]}\right) \tag{14}$$

From the slope and intercept in Fig. 3, we obtain the limiting quantum yield, $\phi_{ox}=0.031$, $k^1{}_d/k^1{}_{ox}=31$, and $k^1{}_c/(k_f+k_{isc})=5.3\ \mathrm{M}^{-1}$. $(k_f+k_{isc})^{-1}$ is equal to τ_s, the measured acetone singlet lifetime in the absence of the singlet quencher,[14] while τ_s has been reported to be *ca.* 2 nsec.[23,25] Using this value of τ_s, the calculated

TABLE 2. LIMITING QUANTUM YIELDS AND RATE CONSTANTS FOR OXETANE FORMATION

Carbonyl compounds	Diene	ϕ_{ox}	$k^1{}_d/k^1{}_{ox}$	$k^1{}_c/(k_f+k_{isc})$ M^{-1}
Acetone	COD	0.031	31	5.3
Propionaldehyde	COD	0.2	4	2.2
Propionaldehyde	CHD	0.086	10.6	7.3

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17) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

18) They report the value of $\sim1.7\times10^8$ and $\sim7\times10^7\ \mathrm{M}^{-1}$ for rate constants for quenching of the acetone triplet by 1-methoxy-1-butene, and $\sim10^7\ \mathrm{sec}^{-1}$ for k_t.

19) T. Kubota, K. Shima, S. Toki, and H. Sakurai, *Chem. Commun.*, **1969**, 1462.

20) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

21) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

22) This is the quenching process of the acetone singlet by COD. The nature of the singlet complex is uncertain yet. We have considered that the inefficiency in this photocycloaddition is attributed to the formation of the intermediate complex, which combines to give oxetanes or dissociates to ground-state acetone and COD. This concept has been suggested by Turro *et al.*[23] and Singer *et al.*[24]

23) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970).

24) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969).

25) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

rate constant for the formation of the singlet complex ($k^1{}_c$) is 2.7×10^9 M^{-1} sec^{-1}. This rate constant is within an order of magnitude of the diffusion-controlled rate constant in benzene, and it is in good agreement with that of the quenching of the singlet acetone by 1,2-dicyanoethylene.[23,26]

Table 2 summarizes the results of oxetane formation from the acetone singlet, as well as the preliminary results obtained from the singlet addition of propionaldehyde to 1,3-cyclohexadiene (CHD) and COD.

Since the rate constants for intersystem crossing or fluorescence in propionaldehyde are still unknown, a detailed comparison of the results is impossible, but the large limiting quantum yield in the case of propionaldehyde is probably due to the more efficient oxetane formation from a singlet complex.[27]

Experimental

General. The nuclear magnetic resonance spectra were taken on a Hitachi Perkin-Elmer R-20 High Resolution NMR Spectrometer, using tetramethylsilane as the internal standard. The gas-chromatographic analyses were run on a Shimadzu Gas Chromatograph, GC-3AF. The acetone (Wako Pure Chem. Co.) was purified by the ordinary method.[28] The COE and COD were purified by fractional distillation using a spinning-band column, and were redistilled prior to use. The benzene was purified by three successive crystallizations, with a rejection of about one-fourth of the benzene at each freezing, and by distillation with a spinning-band column.

Photoaddition of Acetone to Cyclooctene. Pyrex, doughnut-type vessels containing acetone (29 g) and COE (55 g) were placed outside a quartz immersion well and irradiated for 50 hr with a 350-W high-pressure mercury lamp at room temperature. The unreacted materials were then distilled off, and the portion boiling at 70—85°C/4 mmHg (10.8 g) was collected. Residues, 16.6 g. The adducts were isolated by preparative VPC on a 3-m PEG-6000 column (10 mm i. d.) at 160°C. Bp 73—74°C/4 mmHg; n_D^{27} 1.4644.

Found: C, 78.55; H, 11.91%; mol wt, 171. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%; mol wt, 168.

Adduct **1** had a retention time of 11.2 min at 160° and was collected as a colorless oil by preparative VPC: IR spectra 970 and 945 cm^{-1}: NMR ($CDCl_3$) τ 5.65 (H_a, dt, $J_{ab}=J_{ac}=10$ Hz; $J_{ad}=3.4$ Hz), 8.72 ($2CH_3$, 6H, s), 7.4—9.5 (13H, m); $m/e=168$ (parent), 110 ($M-CH_3COCH_3$).

Adduct **2**: retention time, 12.5 min. (160°C); IR spectra 960 cm^{-1}; m/e, 168 (parent), 110 ($M-CH_3COCH_3$); NMR ($CDCl_3$), τ 5.45 (H_a, sept, $J_{ab}=6$ Hz; $J_{ac}=10$ Hz); $J_{ad}=3.5$ Hz), 8.63 and 8.81 (CH_3, s), 7.4—9.4 (13H, m).

Photoaddition of Acetone to 1,3-Cyclooctadiene. A mixture of acetone (34 g) and COD (53 g) was irradiated through Pyrex for 50 hr. After the removal of the unreacted materials, the fraction boiling at 100—110°C/18 mmHg was collected; yield, 19.0 g. Residue, 9.5 g. The 1 : 1 adducts were isolated by preparative VPC; bp 102—103°C/17 mmHg, n_D^{25} 1.4769.

Found: C, 79.63; H, 10.96%; mol wt, 169. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%; mol wt, 166.

Quantum Yields. Benzene solutions (4 m*l*) containing 0.1—0.2 M acetone and 0.02—1.0 M COE or COD were degassed and sealed in 10-mm o. d. quartz tubes which had been attached to Pyrex tubes *via* graded seals. The sample tubes were then irradiated on a merry-go-round apparatus at room temperature, using a 350-W high-pressure mercury lamp and a filter solution with a path length of about 1 cm containing 150 g chromium potassium sulfate made up to 1 *l* with distilled water. This filter system completely eliminated the absorption of the benzene used as the solvent. Photolyses were carried out to 10% or less conversion (irradiation time, less than 6 hr); the conversion was linear to the irradiation time in these regions. Actinometers (acetone-2-methyl-2-butene system) were photolyzed simultaneously, and the quantum yields were computed relative to the actinometers. The solutions were analyzed on a Shimadzu Gas Chromatograph, GC-3AF, with a 3-m column packed with PEG-6000 (25%) on Shimalite at 160°C, using acetophenone (in the case of COE) or propiophenone(COD) as the internal standard.

Quenching Studies. The samples were prepared, degassed, and analyzed in the same way as in the quantum-yield determination, except that varying amounts of quenchers were added to the solution.

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26) Turro *et al.* report the following values.
$k^1{}_c/(k_f+k_{isc})=5.1$ M^{-1}, $k^1{}_c=2.5-5.0\times 10^9$ M^{-1} sec^{-1}.

27) Quantum yields for oxetane formation from the propionaldehyde triplet and olefins are also as about 10 times as larger than those from the acetone triplet and olefins.[10] We have proposed that these differences are due to the more efficient oxetane formation from a triplet 1,4-biradical intermediate in the case of propionaldehyde.[10]

28) A. Bramley, *J. Chem. Soc.*, **59**, 10 (1916).