Unsaturated Lactone Photochemistry. Effect of Wavelength and Sensitizer Structure on Selective Population of Specific Excited States[1,2]

Edwin F. Ullman and Niklaus Baumann

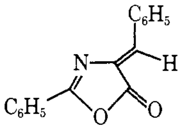
Contribution No. 16 from Synvar Research Institute, Palo Alto, California 94304.

Received February 26, 1970

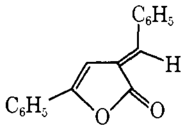
Abstract: The three lactones, 4-benzal-2-phenyl-5-oxazolone (I), α-benzal-γ-phenylbutenolide (II), and α-benzal-γ-butyrolactone (III), undergo two primary photochemical processes, hydrogen abstraction from solvent and geometrical isomerization. The efficiencies of the hydrogen abstraction processes are affected dramatically by wavelength, concentration, and choice of sensitizer. These reactions are shown to proceed through abnormally long-lived T_2 states of probable n,π^* symmetry. The geometrical isomerization reactions occur from T_1 states (probably π,π^*) and possibly also from π,π^* singlet states. Geometrical restrictions to crossing between states can account for the observed long lifetimes of the upper excited states. The ability of certain of the sensitizers to either selectively excite the lactones I and II to their T_1 (π,π^*) states or cause unselective excitation to both the T_1 and T_2 states correlates with orbital symmetry relationships between the sensitizers and the lactones.

The identity of the initial excited states populated upon absorption of light by organic molecules is controlled by the wavelengths of light absorbed. In solution, upper excited states produced by short wavelength light generally undergo rapid internal conversion or intersystem crossing to the lowest excited singlet (S_1) or triplet (T_1) states. Only reactions which occur within several molecular vibrations are usually considered to compete with this rapid process. Nevertheless within the past few years a number of photochemical reactions that proceed only with shorter wavelengths than required to ensure light absorption have been described.[3] Many of these reactions can be ascribed to rapid dissociative processes of upper excited states.[3,4] On the other hand several reactions of unsaturated carbonyl compounds have been reported which appear to proceed from upper excited states and yet probably occur by relatively slow primary processes.[1,3,5] The reason for the apparent long lifetimes of these upper excited states and the sequence of events leading to their formation remain poorly defined. The present investigation was undertaken to explore these questions.

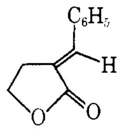
Qualitative Photochemistry of Lactones I–III. The photochemistry of the lactones I–III was found to be strongly wavelength dependent. The only isolable products on irradiation of the oxazolone I with 3650-Å light and the butyrolactone III with 3130-Å light were the corresponding geometrical isomers. The gross structures of the photoproducts, in which *syn* geometries were assigned, were deduced by their thermal reconversion to the more stable starting materials, the similarity of their optical spectra to the starting lactones, and the deshielding effect of the carbonyl groups on the vinyl hydrogen nmr signals in the photoisomer of III (see Experimental Section). Although the butenolide II was studied as a mixture of geometrical isomers which could be only partially separated by tlc, irradiation with 3650-Å light similarly caused geometrical isomerization. Ultraviolet spectroscopic monitoring of each of the reactions demonstrated good isosbestic points indicative of the presence of only two species. In each case a photostationary state was reached.



I



II



III

Irradiation of lactones I, II, and III with 2537-Å light likewise produced geometrical isomerization, but in addition the total absorption of the two geometrical isomers gradually diminished. Unlike the isomerization reaction, this second process was strongly inhibited by traces of oxygen. In carefully degassed solutions its rate was dependent on the hydrogen donor properties of the solvent, $CH_3CN <$ cyclohexane $<$ methanol $<$ isopropyl alcohol. This suggested that a radical reaction was initiated by the short-wavelength light, a conclusion which was supported by the appearance of numerous minor products and polymer. The cleanest reactions were obtained using isopropyl alcohol as solvent which was accordingly used throughout this study. With this solvent the oxazolone I yielded a major product IV (17% yield) and the butyrolactone III yielded a mixture of four γ-lactones (30%) plus pinacol. While no major product other than the *syn* isomer could be isolated from short-wavelength irradiation of the bu-

---

[1] A preliminary communication including portions of this work has been published: N. Baumann, M. Sung, and E. F. Ullman, *J. Amer. Chem. Soc.*, **90**, 4157 (1968); see also ref 2.

[2] E. F. Ullman and N. Baumann, *ibid.*, **90**, 4158 (1968).

[3] For a review see E. F. Ullman, *Accounts Chem. Res.*, **1**, 353 (1968).

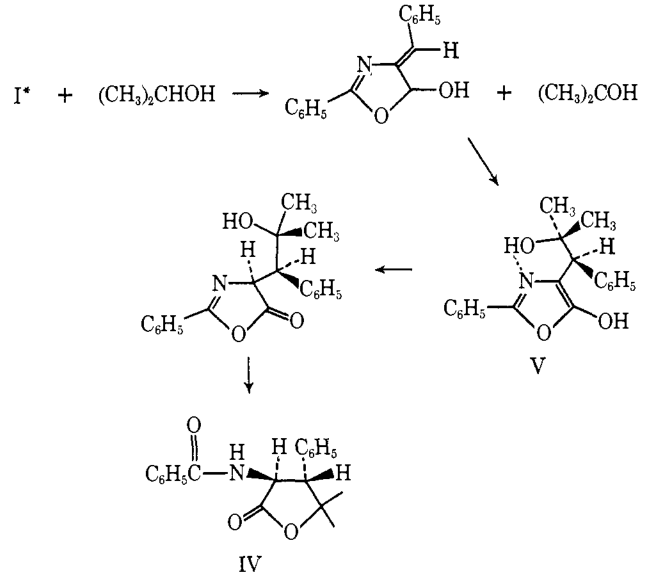
[4] (a) J. G. Pacifici and C. Diebert, *J. Amer. Chem. Soc.*, **91**, 4595 (1969); (b) W. H. Pirkle, S. G. Smith, and G. F. Koser, *ibid.*, **91**, 1580 (1969); (c) L. E. Friedrich and G. B. Schuster, *ibid.*, **91**, 7204 (1969); (d) W. Wehrli, C. Lehmann, P. Keller, J. J. Bonet, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 2218 (1966); (e) E. Baggiolini, E. G. Herzog, S. Iwasaki, R Schorta, and K. Schaffner, *ibid.*, **50**, 297 (1967); (f) H. Wehrli, C. Lehmann, T. Iiuzka, J. Schaffner, and O. Jeger, *ibid.*, **50**, 2403 (1967); (g) J. A. Saboz, T. Iizuka, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, **51**, 1362 (1968); (h) R. W. Hoffmann and K. R. Eicken, *Ber.*, **102**, 2987 (1969); (i) B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, **89**, 6911 (1967); (j) R. Simonaitis and J. N. Pitts, Jr., *ibid.*, **91**, 108 (1969).

[5] (a) W. Herz and M. G. Nair, *ibid.*, **89**, 5474 (1967); (b) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968); (c) G. Rämme, R. L. Strong, and H. H. Richtol, *ibid.*, **91**, 5711 (1969); (d) E. F. Ullman, E. Babad, and M. Sung, *ibid.*, **91**, 5792 (1969); (e) R. L. Cargill, A. C. Miller, D. M. Pond, P. deMayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, **1**, 301 (1969).

tenolide II, its photochemical behavior was found to closely parallel that of the oxazolone I.

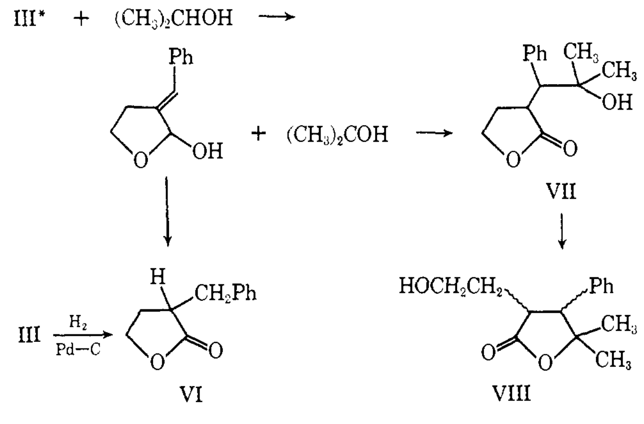
The structure of IV was unambiguously defined by its spectra and by the quantitative formation of benzoic acid upon alkaline hydrolysis (see Experimental Section). The *trans* stereochemistry is assigned on the basis of a 13-Hz coupling between the two ring protons in the nmr. This stereochemistry is consistent with the probable mechanism of formation of IV (Chart I). Hydrogen abstraction from solvent by excited I followed by radical recombination would be expected to yield the intermediate V. Protonation from the least hindered side of the hydrogen bonded conformation shown would yield the observed product.

Chart I



All but one of the four lactones derived from the butyrolactone III were oils which could be separated only with great difficulty. Although all were identified as saturated lactones from their infrared absorption at 1760 cm^{-1}, positive identification was possible only for VI and VIII. The latter compound was crystalline and was identified by its spectroscopic properties (see Experimental Section). The two incompletely separated unidentified lactones had similar mass spectra and hence are probably closely related to VIII, possibly a stereoisomer of VIII and/or stereoisomers of its probable precursor VII (Chart II). The remaining oily lactone VI was identified by comparison with an authentic sample prepared by hydrogenation of the starting lactone III.

Chart II



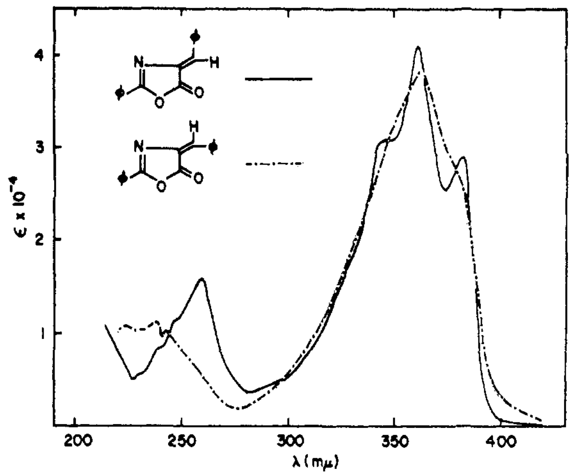


Figure 1. Ultraviolet spectra of the oxazolone I and its photoisomer in isopropyl alcohol.

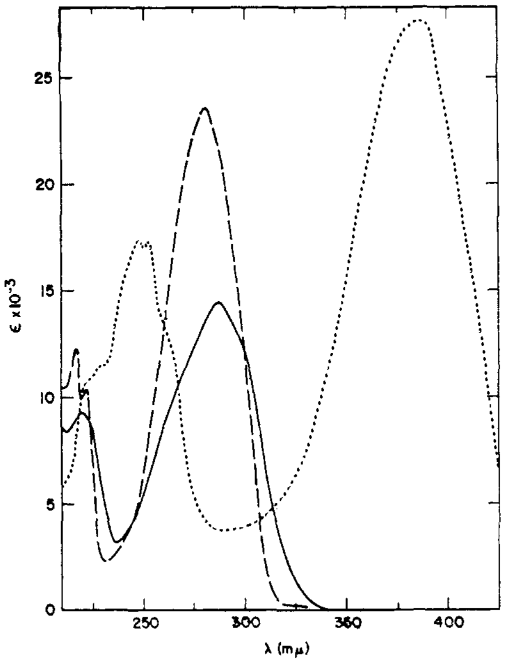


Figure 2. Ultraviolet spectra of the benzalbutenolide II, ..., the benzalbutyrolactone III, ------, and the photoisomer of III, ——.

Wavelength Dependence. The spectra of lactones I–III are given in Figures 1 and 2. The total quantum yields for the disappearance of both geometrical isomers were taken as the quantum yields for the hydrogen abstraction reactions. The reactions were carried out in degassed isopropyl alcohol and were followed by monitoring the absorption spectra at isosbestic points (λ: I, 378; II, 399; III, 300 mμ). The quantum yields for the hydrogen abstraction reactions as a function of wavelength are given in Table I. Quantum yields for geometrical isomerization were generally higher but were not studied quantitatively because the spectral changes were too small to provide reproducible data.

The dramatic effect of wavelength on the hydrogen abstraction reaction of III suggests that the reaction

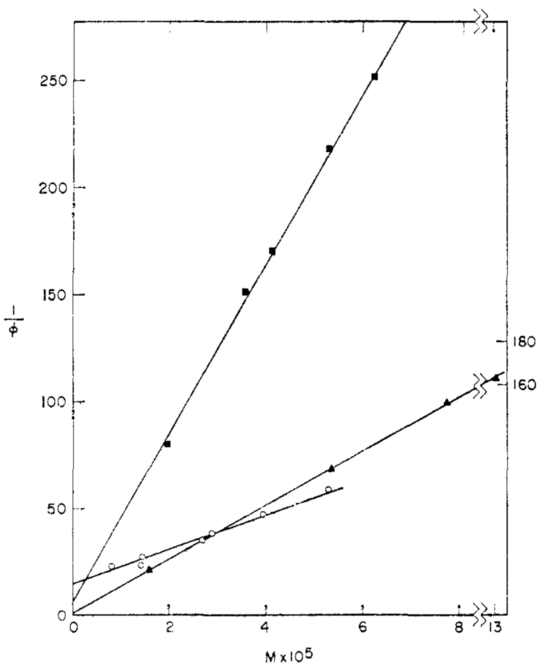


Figure 3. Concentration of lactones I (open circles), II (squares), and III (triangles) *vs.* reciprocal of the quantum yields of hydrogen abstraction in isopropyl alcohol.

only proceeds when an upper singlet state (S_2) becomes populated. As this reaction occurs entirely from the triplet manifold (*vide infra*) either intersystem crossing from S_2 must be unusually rapid or, more probably, internal conversion to S_1 is abnormally slow. Moreover, the failure of III to undergo the hydrogen abstraction reaction upon population of its S_1 state requires that intersystem crossing of S_1 to the reactive triplet state likewise is abnormally inefficient.

Table I. Quantum Yields of Hydrogen Abstraction by Lactones I–III as a Function of Wavelength

λ, Å	ϕ_{I}^a	ϕ_{II}^b	ϕ_{III}^c
2537	0.026	0.0031	0.015
3130	0.035	0.0074	$<1 \times 10^{-6}$
3650	0.00018	0.000067	
3800	0.062		
4050		0.0061	

[a] 2.88×10^{-5} *M*. [b] 8.15×10^{-5} *M*. [c] 6.7×10^{-5} *M*.

The effect of variation of wavelength on I and II was more complicated. Low but finite quantum yields for hydrogen abstraction were observed at 3650 Å whereas much higher efficiencies were observed at both shorter and longer wavelengths. Since these lactones likewise undergo the hydrogen abstraction reaction exclusively from triplet states (*vide infra*), the S_1 states of these lactones must be capable of intersystem crossing. However the unreactive S_2 states must undergo neither efficient internal conversion to S_1 nor intersystem crossing to the reactive triplets. The appearance of relatively efficient hydrogen abstraction reactions with still shorter wavelengths is not inconsistent with this picture since population of S_3 could result in direct intersystem crossing to the triplet manifold or internal conversion to S_1.

Concentration Quenching. The effect of concentration on the quantum yields of I–III is quite unusual (Table II). Unlike normal concentration quenching which is a result of singlet quenching at high concentrations, variation of concentration of I–III in the 10^{-5} *M* range causes pronounced effects on the quantum yields of hydrogen abstraction.[6] No comparable effect on the isomerization reactions was observed. The data fit the usual Stern–Volmer eq 1 (Figure 3) where ϕ is the

$$\frac{1}{\phi} = \frac{1}{\phi_0} + \frac{kq\tau}{\phi_0}[\text{Q}] \tag{1}$$

quantum yield, ϕ_0 is the quantum yield at infinite dilution, τ is the lifetime of the quenched excited state, [Q] is the concentration of the lactone, and k_q is the quenching rate constant which is taken here as the diffusion-controlled rate in isopropyl alcohol of 2.7×10^9 l./mol sec.[7a] The quantum yields at infinite dilution, ϕ_0, were obtained by extrapolation and are given in Table III along with the derived values for τ and for k_r and k_d, the rate constants for reaction and decay of the excited state intermediate.

Table II. Quantum Yields of Hydrogen Abstraction by Lactones I–III at 2537 Å as a Function of Concentration in Isopropyl Alcohol

[I] $\times 10^5$ *M*	$\phi_{\text{I}} \times 10^3$	[II] $\times 10^5$ *M*	$\phi_{\text{II}} \times 10^3$	[III] $\times 10^5$ *M*	$\phi_{\text{III}} \times 10^3$
5.30	17	8.15	3.05	13.0	6.13
3.96	21	6.23	3.96	7.75	10.0
2.88	26	5.30	4.59	5.36	14.6
2.68	29	4.11	5.86	1.57	46.7
1.44	37	3.59	6.57		
1.41	43	1.95	12.5		
0.807	44				

Table III. Reaction Parameters of Lactone Triplets Obtained from Concentration Quenching and Singlet–Triplet Absorption Spectra

Lactone	$\phi_0 \times 10^2$	$\tau \times 10^5$ sec	$k_d \times 10^{-3}$ sec^{-1}	$k_r \times 10^{-3}$ sec^{-1}	$E_{T_1}{}^a$ kcal/mol
I	7.2	2.3	40	3.1	43.0
II	16	23	3.6	0.69	41.3
III	44	20	2.8	2.2	57.0

[a] Determined from longest wavelength maxima of solutions of lactone in chloroform under an oxygen pressure of 2100 psi according to the method of D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

Although the long extrapolations introduce some uncertainty in these data two important conclusions may be drawn. First, the lifetimes of the intermediate excited states are only consistent with triplet intermediates. Second, the linearity of the plots requires that there is less than 5% (less for II and III) competing reaction pathways which involve excited state intermediates with lifetimes differing more than an order of magnitude from those observed. Although two simultaneously formed triplets having fortuitously similar lifetimes and reaction rates would not be detected, the linearity of all three plots makes this unlikely. Thus these reactions

---

(6) The only report known to us of concentration quenching at relatively low concentrations (10^{-3} *M*) is given by S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, 72, 3782 (1968).

(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966: (a) p 627; (b) p 728, *et seq.*

Table IV. Sensitization of the Hydrogen Abstraction Reaction of 4-Benzal-2-phenyl-5-oxazolone (I) in Isopropyl Alcohol[a]

		Direct sensitization				Double sensitization			
Sens E_T, kcal/mol[b]	Sensitizer	[Sens] $M \times 10^3$	[I] $M \times 10^5$	$\phi^c \times 10^2$	% quench by piperylene[d]	[Sens] $M \times 10^4$	[Triph] $M \times 10^3$	[I] $M \times 10^5$	$\phi \times 10^2$
84.0[e]	Benzene	24.6	3.81	11	97				
68.0[e,f]	Triphenylene	0.40	3.81	$<2 \times 10^{-3}$					
67.9[f]	Fluorene	3.86	4.23	1.6	88				
65.5[g]	Biphenyl	3.94	4.03	1.5	84				
61.8[e,g]	Phenanthrene	1.20	4.03	$<2 \times 10^{-3}$					
61.7[g]	*o*-Terphenyl	4.66	3.15	$<2 \times 10^{-3}$					
60.9[e]	Naphthalene	18.0	3.81	2.2	80	10	2.38	2.9	0.08
58.9[g]	1-Phenylnaphthalene	16.0	4.16	$<1 \times 10^{-3}$		2.67	0.98	2.67	$<1 \times 10^{-3}$
58.8[g]	2-Phenylnaphthalene	1.26	4.16	0.12	23	2.67	9.16	2.67	0.06
58.4[g]	*p*-Terphenyl	3.18[j]	2.40	3.5×10^{-3} [m]		2.67	26.7	2.67	0.21
56.6[e]	Chrysene	2.64[j]	4.16	$<1 \times 10^{-3}$		5.15	76.5	5.15	$<1 \times 10^{-3}$
52.7[h]	Fluoranthene	0.09[k]	4.16	0.058		1.91	160	2.67	$<1 \times 10^{-3}$
48.0[i]	Pyrene	4.12[l]	3.81	1.2×10^{-3}		5.15	76.5	5.15	$<1 \times 10^{-3}$

[a] 2537-A light used unless otherwise indicated. [b] 0–0 band in EPA except as noted. [c] Relative quantum yields. Absolute values may be in error. [d] 2.0×10^{-2} *M*. [e] D. S. McClure, *J. Chem. Phys.*, **19,** 670 (1951). [f] F. Dörr and H. Gropper, *Z. Elektrochem.*, **67,** 193 (1963); solvent ethanol. [g] A. P. Marchetti and D. R. Kearns, *J. Amer. Chem. Soc.*, **89,** 768 (1967). [h] C. Dijkgraaft and G. T .Hoijtink, *Tetrahedron, Suppl.*, **No. 2,** 179 (1963); solvent bromoform. [i] D. S. McClure, *J. Chem. Phys.*, **17,** 905 (1949). [j] Solvent was 10% isopropyl alcohol in tetrahydrofuran. [k] 3650-Å light used, 20% of which was absorbed by the fluoranthene. Light of this wavelength absorbed by I did not cause the hydrogen abstraction reaction to occur at a significant rate. [l] 3130-Å light used. [m] Low quantum yield related to low quantum yield of intersystem crossing of *p*-terphenyl (compare double sensitization result).

probably each proceed through only one triplet intermediate which might be formed from one geometrical isomer or be common to both.

A possible explanation for the unusual triplet concentration quenching rests on the assumption that the triplet is an upper excited state, T_2. The following pathways of decay of T_2 might then occur. The significant

$$T_2 \not\longrightarrow T_1 \tag{2}$$

$$T_2 \longrightarrow \text{hydrogen abstraction products} \tag{3}$$

$$T_2 \longrightarrow S_0 \tag{4}$$

$$S_0 + T_2 \longrightarrow T_1 + S_0 \tag{5}$$

$$T_1 \not\longrightarrow \text{hydrogen abstraction products} \tag{6}$$

steps are eq 2, which must be postulated to account for the long lifetime of the reactive triplet, and eq 5, which is a spin-allowed exothermic triplet-energy transfer between like molecules in different states. The occurrence of the previously unpostulated process in eq 5 is an *expected consequence of an unusually long-lived T_2 state.* The fate of T_1 formed by eq 5 would have no effect on the quenching behavior provided T_1 fails to undergo the hydrogen abstraction reaction (eq 6). The occurrence of the hydrogen abstraction reaction from only one of these two triplet states is most probably related to the observed wavelength dependence.[8]

Sensitization. The data presented to this point suggest that the hydrogen abstraction reactions of I and II are initiated by long wavelengths but proceed exclusively through reactive T_2 states (eq 7). Similarly, hydrogen abstraction by III appears to proceed through the T_2 state but it is initiated only with short wavelengths (eq 8). The foregoing data did not

$$S_1(\text{I or II}) \longrightarrow T_2(\text{I or II}) \longrightarrow \text{hydrogen abstraction} \tag{7}$$

$$S_2(\text{III}) \longrightarrow T_2(\text{III}) \longrightarrow \text{hydrogen abstraction} \tag{8}$$

provide evidence for triplet intermediates in the isomerization reactions. These reactions occur in I and II with shorter wavelengths (3650-Å) and must therefore proceed either directly from the S_2 states or indirectly by crossing of S_2 to the T_1 states (eq 9). Similarly, lactone III may isomerize *via* a T_1 state although in this case initial excitation to S_1 is required (eq 10). The

$$S_2(\text{I or II}) \longrightarrow [T_1(\text{I or II})]? \longrightarrow \text{isomerization} \tag{9}$$

$$S_1(\text{III}) \longrightarrow [T_1(\text{III})]? \longrightarrow \text{isomerization} \tag{10}$$

following sensitization studies were aimed at clarifying the possible roles of separate triplet intermediates in the two types of reactions.

The sensitizers employed were limited to hydrocarbons to avoid possible reactions of sensitizer with the solvent, and sufficient sensitizer was used in each experiment to absorb >99% of the light. The butyrolactone III was found to undergo both sensitized hydrogen abstraction and isomerization with every sensitizer studied, namely, fluorene, triphenylene, biphenyl, phenanthrene, and naphthalene. These results suggest that both reactions may proceed through triplet states but no additional information concerning the question of two possible triplet intermediates was obtained. On the other hand, the sensitization studies of the lactones I and II proved quite illuminating. All the sensitizers studied sensitized the isomerization reactions, whereas only certain sensitizers sensitized the hydrogen abstraction reactions (Table IV and V). Provided triplet energy was transferred in these experiments, these results suggest that each lactone has two triplet states with different reactivities. However, since the

---

[8] An alternative self-quenching scheme that avoids postulating a long-lived T_2 state incorporates eq i–iv. Although this scheme satis-

$$T_1 \longrightarrow \text{hydrogen abstraction products} \tag{i}$$

$$S_0 + T_1 \longrightarrow {}^3(\text{eximer}) \tag{ii}$$

$${}^3(\text{eximer}) \not\longrightarrow \text{hydrogen abstraction products} \tag{iii}$$

$${}^3(\text{eximer}) \longrightarrow S_0 + S_0 \tag{iv}$$

factorily rationalizes the concentration quenching data, it leaves the wavelength dependence of these lactones to be explained as a completely unrelated phenomenon. The concurrence of both of these unusual phenomena in all three lactones makes this explanation unlikely.

ability of the sensitizers to initiate hydrogen abstraction reactions did not appear to be related to the sensitizer triplet energies, additional information was sought concerning the nature of the energy transfer processes.

Table V. Sensitization of the Hydrogen Abstraction Reaction of α-Benzal-γ-phenylbutenolide (II) with 2537-Å Light[a]

Sens E_T, kcal/mol[b]	Sensitizer	[Sens] $M \times 10^3$	[I] $M \times 10^5$	$\phi^c \times 10^2$
68.0	Triphenylene	0.57	4.57	$<1 \times 10^{-3}$
67.9	Fluorene	4.62	4.57	1.5
65.5	Biphenyl	5.08	4.57	4.2
61.8	Phenanthrene	1.47	4.57	$<1 \times 10^{-3}$
61.7	*o*-Terphenyl	7.85	4.72	$<1 \times 10^{-3}$
60.9	Naphthalene	29.2	4.57	0.75
60.9	Naphthalene[d]	0.91	4.57	0.14
58.9	1-Phenylnaphthalene	19.3	4.72	$<1 \times 10^{-3}$
58.8	2-Phenylnaphthalene	1.87	4.72	$<1 \times 10^{-3}$
58.4	*p*-Terphenyl[e]	6.66	4.72	$<1 \times 10^{-3}$
56.6	Chrysene[e]	2.83	4.72	$<1 \times 10^{-3}$
52.7	Fluoranthene[f]	0.10	4.72	$<5 \times 10^{-3}$
48.0	Pyrene	6.43	4.57	$<1 \times 10^{-3}$

[a] Solvent was 1:1 isopropyl alcohol–ether. [b] 0–0 band in EPA except as noted. See Table IV. [c] Relative quantum yields. Absolute values may be in error. [d] Double sensitizer experiment in which triphenylene (2.18×10^{-3} *M*) absorbed 99% of the light. [e] Solvent diluted 50% with tetrahydrofuran. [f] 3650-Å light was used, 20% of which was absorbed by the fluoranthene.

Evidence that triplet energy transfer did in fact occur was initially suggested by the low acceptor concentrations ($2-4 \times 10^{-5}$ *M*) which would permit only very inefficient energy transfer at diffusion-controlled rates from the short-lived sensitizer singlets (~10^{-8} sec). In order to further decrease the possibility of singlet energy transfer, several double sensitizer experiments were conducted with the oxazolone I. Triphenylene, which failed when used alone to sensitize the hydrogen abstraction reaction (Table IV), was used in these experiments as the light-absorbing substance (>99% absorbed). Addition of a second sensitizer to the reaction mixtures was then found to cause sensitization of the hydrogen abstraction reaction with just those sensitizers and only those (with one exception) that were effective in the absence of triphenylene.[9] The initially excited triphenylene must therefore transfer its energy to the second sensitizer which in turn transfers its energy to the oxazolone I. The low concentrations of both the second sensitizer and I effectively rule out the possibility of two sequential transfers involving singlet energy. Only triplet energy transfer from the triphenylene to the second sensitizer and then to I can satisfactorily account for these results.[10]

Evidence for triplet energy transfer from sensitizers having triplet energies above 62 kcal/mol could not be obtained by the double sensitization studies due to inefficient triplet energy transfer from triphenylene to the second sensitizer. However *trans*-piperylene was found to quench the hydrogen abstraction reactions in the presence of the higher energy sensitizers (Table IV). Since the concentration of the piperylene employed (2×10^{-2} *M*) was insufficient to cause efficient quenching of singlet states,[11] triplet sensitization is again implicated. Piperylene appears to quench sensitizer triplets rather than lactone triplets since the quenching efficiency drops with the sensitizer triplet energy, and quenching of the hydrogen abstraction reaction of I during direct irradiation is inefficient.

Another alternative to diffusion-controlled triplet energy transfer that could conceivably explain the unexpected sensitization results is ground-state complex formation. For this reason careful Beer's law dependence studies were conducted on the individual lactones I and II and on equimolar solutions of I with both naphthalene and phenanthrene. However, no deviations from strictly additive spectra could be discerned even over a large concentration range (10^{-6}–10^{-3} *M*).

Discussion

The conclusion that the sensitized reactions proceed by triplet energy transfer to the lactones indicates that triplet intermediates can give rise to both the hydrogen abstraction and isomerization reactions. As certain of the sensitizers were *selective* and sensitized only the isomerization reactions of lactones I and II, whereas others were *unselective* and sensitized both reactions, it follows that I and II each have two reactive triplets. One of these undergoes exclusively the isomerization reaction and the other undergoes the hydrogen abstraction reaction, although competing isomerization from the latter state is not excluded.[12] Based on the concentration quenching studies the triplet giving rise to hydrogen abstraction appears to be a long-lived T_2 state and that giving rise to isomerization is T_1. Although this conclusion is admittedly based on a hypothetical mechanism for self-quenching, alternative mechanisms are difficult to formulate and *energy conservation requirements related to the sensitizer selectivity phenomena demand these excited state assignments* (*vide infra*).

The presence of a long-lived T_2 state in the lactones I and II implies that there is a barrier to $T_2 \rightarrow T_1$ internal conversion. Moreover the failure to populate T_2 (that is, cause the hydrogen abstraction reaction) on population of S_2 (with 3650-Å light) implies barriers to $S_2 \rightarrow S_1$ and $S_2 \rightarrow T_2$ crossings. We believe the origins of these inefficiencies lie in large geometrical differences between the initial and final states. The probability of crossing between states depends on the magnitudes of both the electronic and vibrational overlap integrals of

---

[9] A double sensitization experiment using lactone II and triphenylene with naphthalene as the second sensitizer gave similar results (see Table V).

[10] The double sensitizer experiment with fluoranthene, which yielded different results from direct fluoranthene sensitization, is an exception which demonstrates the validity of the technique. The failure to observe the hydrogen abstraction reaction when the triphenylene–fluoranthene sensitizer combination was used implies that fluoranthene triplets do not sensitize this reaction. Nontriplet energy transfer is therefore involved in the direct sensitization experiment. This was demonstrated by showing that fluorescent light emitted by fluoranthene initiates the hydrogen abstraction reaction (see Experimental Section).

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

[12] An alternative interpretation of the sensitization data assumes that the lactones form excited state complexes with the triplets of *selective* sensitizers but not with the triplets of *unselective* sensitizers. The latter are assumed to transfer energy in the usual manner to initiate both reactions from T_1 of the lactones, while the complexes react exclusively by geometrical isomerization. While none of the data directly exclude these processes, the hypothesis is uneconomical as it does not eliminate the need to postulate two reactive excited states to account for the wavelength sensitivity in the unsensitized reactions.

the two states in question.[13] Any large geometrical distortion of either the initial or final state would reduce the vibrational overlap and result in an abnormally slow crossing rate. The present T_2 states likely have $^3(n,\pi^*)$ symmetry as suggested by their ability to abstract hydrogen from solvent, and it is therefore expected that they will have planar arrangements of atoms about their carbon–carbon double bonds. On the other hand the T_1 states undergo geometrical isomerization and are thus probably $^3(\pi,\pi^*)$ states which relax to preferred perpendicular carbon–carbon double bond geometries. Crossing between these states might therefore be expected to be very inefficient. Moreover 3650-Å light excites a highly allowed transition in both lactones which gives rise almost exclusively to the isomerization reactions. The resulting S_2 state is thus almost certainly a $^1(\pi,\pi^*)$ state. Provided this state undergoes relaxation directly to the perpendicular geometry, crossing from S_2 to a (n,π^*) S_1 state or to the (n,π^*) T_2 state would be inefficient for similar reasons. Similar reasoning can also be employed to account for the apparent inefficient internal conversion $S_2\,(n,\pi^*) \rightarrow S_1\,(\pi,\pi^*)$ in lactone III.

In this regard it is noteworthy that most of the compounds that have been reported to undergo reactions which may proceed through abnormally long-lived upper excited states[3,5,14] have a carbonyl group and a double bond capable of twisting in an excited state to a nonplanar geometry. The preceding discussion rationalizes why these groups are frequently present and permits predictions concerning other compounds which might be expected to show wavelength dependence or other photochemical behavior related to long-lived upper excited states. Thus a variety of unsaturated carbonyl compounds including sodium cinnamate,[5d] 2-benzalcyclopentanones, 2,5-bisbenzalcyclopentanone, chalcone, and methyl β-styryl ketone have recently been found to display wavelength dependence.[15,16]

There remains for consideration the unusual behavior of the sensitizers. As already noted, the sensitizers fall into two groups, *selective* sensitizers which only initiate the isomerization reactions and *unselective* sensitizers which initiate both isomerization and hydrogen abstraction.[17] Since the two reactions of lactones I and II proceed separately from the T_1 and T_2 states, energetic considerations would suggest that sensitizers with triplet energies above that of T_2 of the acceptor should be *unselective* and cause population of both T_1 and T_2, whereas lower triplet energy sensitizers should be *selective* and be capable of populating only T_1. Table VI, which summarizes the behavior of the sensitizers, reveals that below specific critical energies (56.6 kcal/mol for I and 58.9 kcal/mol for II) all the sensitizers indeed become *selective*. These critical triplet energies are probably near the lactone T_2 energies. The initiation of only the isomerization reactions with the lower energy sensitizers demonstrates that it is the T_1 states that give this reaction while the T_2 states give rise to the hydrogen abstraction processes.

Table VI. Summary of Sensitizer Selectivities in the Sensitized Reactions of Lactones I and II in Isopropyl Alcohol

Sens E_T, kcal/mol	Sensitizer	Lactone		Predicted
		I[a]	II[a]	
84.0	Benzene	U	U	U
68.0	Triphenylene	S	S	S
67.9	Fluorene	U	U	U
65.5	Biphenyl	U	U	U
61.8	Phenanthrene	S	S	S
61.7	*o*-Terphenyl	S	S	S(?)[c]
60.9	Naphthalene	U	U	U
			...[b]	
58.9	1-Phenylnaphthalene	S	S	S
58.8	2-Phenylnaphthalene	U	S	U
58.4	*p*-Terphenyl	U	S	U
		...[b]		
56.6	Chrysene	S	S	S
52.7	Fluoranthene	S	S	U
48.0	Pyrene	S	S	S(?)[d]

[a] U stands for *unselective*, S for *selective*. [b] Dotted line represents probable energy of T_2 state, but see ref 22. [c] See ref 21. [d] See ref 20.

The fact that certain of the sensitizers with triplet energies above the T_2 energies of the lactones are also *selective* demands further explanation. Energy considerations alone would suggest that all the high energy sensitizers should excite the lactones to both their T_1 and T_2 states, hence selective excitation to T_1 must be controlled by some factor in addition to sensitizer triplet energy. This selectivity factor does not appear to be sensitive to the small structural differences between I and II since each sensitizer with triplet energy above the T_2 levels of both I and II has the same selectivity behavior with both lactones.

Molecular orbital calculations on the lactones and sensitizers provide a possible explanation of the selectivity phenomenon. Orbital symmetries of the lowest unfilled orbitals of the lactones were compared with the symmetries of the highest filled orbitals of the sensitizers. Only the symmetries at the nonbenzenoid sp^2-hydridized atoms of the lactones were considered since SCF calculations demonstrated that the transition densities for the lowest energy transitions were localized at these atoms.[18] The symmetries were obtained by HMO calculations and are given in Chart III.[18,19] Those atoms of the sensitizers pictured in heavy type have orbital symmetries that closely match atom-for-atom the symmetries at geometrically related atoms in the lactones. The remaining sensitizers have no set of atoms properly oriented for symmetry matching. Each sensitizer which permitted good symmetry matching is "predicted" in Table VI to be *selective* and those sensitizers in which no symmetry matching is possible are "predicted" to be *unselective*.[20]

The exact coincidence between the "predicted" and observed selectivities (Table VI) for sensitizers above the T_2 levels of the lactones is striking. This correla-

---

(13) G. W. Robinson, *J. Mol. Spectrosc.*, **6**, 58 (1961); G. W. Robinson and R. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); *ibid.*, **38**, 1187 (1963); M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968).

(14) Possible exceptions include: (a) J. E. Alexander and S. P. Pappas, Abstracts, 157th National Meeting of the American Chemical Society, April 1969, ORGN 87; (b) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, **91**, 5038 (1969).

(15) R. Weinkam and N. Baumann, unpublished observations.

(16) E. F. Ullman and R. Weinkam, in press.

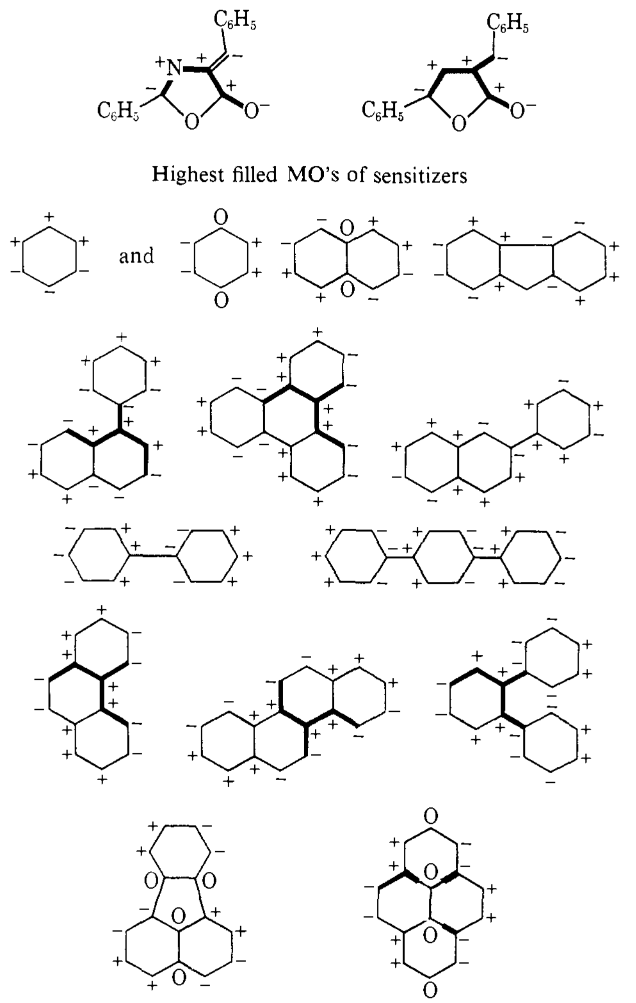
(17) Note that fluoranthene properly falls in the former category as a consequence of the double sensitization results (*cf.* ref 10).

(18) We are indebted to Professor W. Little, Stanford University, for the SCF and HMO calculations.

(19) Most of these data are given in E. Heilbronner and P. A. Straub, "Hückel Molecular Orbitals," Springer-Verlag, New York, N. Y., 1966.

(20) The prediction concerning pyrene is questionable since the matching is neither good nor bad due to the presence of orbital nodes at two key atoms.

Chart III



Lowest unfilled MO's of lactones I and II

Highest filled MO's of sensitizers

tion suggests that the sensitizer triplets might transfer energy to the acceptor in a collision complex which survives long enough for the two molecules to explore all possible face-to-face orientations. Upon achieving a geometry in which orbital symmetry matched atoms become nearest neighbors, rapid excitation of the lactone T_1 (π,π^*) state might then occur. If no geometry permitting orbital symmetry matching is available, slower unselective energy transfer could lead to excitation of any of the energetically accessible lactone triplet states.[21,22]

The reason for the success of the predictions based on orbital symmetry matching remains incompletely explained. Similar relationships have been suggested to explain the rates of singlet quenching of naphthalene by dienes.[11] A rationale which might explain both observations is based on the construction of correlation diagrams that predict that sensitizers with π,π^* excited states should selectively excite energetically accessible π,π^* states of acceptors when orbital symmetry matching is possible. A description of this concept has been given previously.[1b] The present results suggest that selective sensitized excitation of acceptor π,π^* states might be a common phenomenon but is seldom observable due to the usually rapid decay of upper excited states.

Experimental Section

Materials. 4-Benzal-2-phenyl-5-oxazolone (I) and α-benzyl-γ-phenylbutenolide (II) were synthesized by published procedures[23,24] and α-benzal-γ-butyrolactone was purchased from K & K Laboratories. The compounds were purified by recrystallization to constant melting point and until no impurities could be detected by tlc. Mallinckrodt Analytical Reagent grade isopropyl alcohol was distilled prior to use as solvent. Purities of the sensitizers were checked by vpc, tlc, and ultraviolet spectroscopy. Most sensitizers were purified by recrystallization and where necessary by column chromatography. 1-Phenylnaphthalene was purified by preparative vpc on an SE-30 column. 2-Phenylnaphthalene and phenanthrene were freed of anthracene by the method of Kooyman and Farenhorst[25] and subsequently recrystallized to constant melting point. Mallinckrodt Analytical Reagent grade benzene was used as sensitizer without further purification.

Spectra. The spectra of lactones I and III and their photoisomers in isopropyl alcohol are recorded in Figures 1 and 2. Maxima were observed at λ_{I} 259 (ϵ 16,000), 344 (31,000), 360 (40,800), and 380 mμ (28,800); $\lambda_{\mathrm{I(photoisomer)}}$ 224 (ϵ 10,800), 238 (11,200), 243 (10,200), and 362 mμ (38,400); λ_{III} 218 (ϵ 12,400), 224 (10,700), and 281 mμ (24,000); $\lambda_{\mathrm{III(photoisomer)}}$ 220 (ϵ 9500) and 288 mμ (14,700). Lactone II was studied as a mixture of geometrical isomers which changed in composition on irradiation. The spectrum of this mixture is given in Figure 2, λ_{II} 245 (ϵ 17,000), 252 (16,800), and 385 mμ (27,800). The spectra were invariant with concentration as shown by spectral comparison of several solutions of tenfold different concentrations in cells having corresponding differences in light path.

Singlet–triplet absorption spectra were determined using 10–20% solutions of the lactones in chloroform. Under 2100 psi oxygen pressure new absorption maxima with vibrational structure were observed which disappeared on releasing the pressure. The data given in Table III are calculated from the longest wavelength maxima.

Irradiations. Quantum yield studies were carried out with a Hanovia 100-W U-shaped medium-pressure mercury arc equipped with the filter systems for 2537 and 3130-Å light described by Calvert and Pitts.[7b] Corning filter combinations were used for isolation of 3650- and 4050-Å light. Measurements using 3800-Å light were made with a GE B-H6 1000-W ultra high pressure mercury arc equipped with Corning 3060 and 5860 filters. Solutions of the lactones in isopropyl alcohol were prepared by degassing by the freeze–thaw technique. Because of oxygen inhibition of the hydrogen abstraction reaction very careful degassing was necessary to obtain suitable kinetics for quantum yield measurements. Potassium ferrioxalate was used for actinometry according to the method of Hatchard and Parker.[26] In measurements employing low lactone concentrations the quantum yields were corrected for unabsorbed light.

Except where otherwise indicated preparative experiments were carried out using the B-H6 lamp fitted with a 3650-Å band pass Corning filter combination or using a Southern New England Ultraviolet Co. Rayonet photochemical reactor equipped with low-pressure mercury lamps (>90% output at 2537 Å). The solutions were bubbled with nitrogen prior to irradiation. The hydrogen abstraction products obtained in these reactions were identical, as shown by tlc, with those formed during irradiation with sensitizers and at the different wavelengths.

Oxazolone I Photoproducts. The geometrical isomer of I was prepared by irradiation of 110 mg of I in 100 ml of tetrahydrofuran (purified by distillation from lithium aluminum hydride) over 1.5 hr with 3650-Å light. Evaporation of the solvent and dry column chromatography of the residue on silica gel using 90% chloroform–10% hexane yielded 49 mg of each isomer. Similar results were

---

[21] This model leaves some doubt about the validity of the prediction concerning *o*-terphenyl as this sensitizer cannot be completely planar. Possibly some of the symmetry-matched atoms in the collision complexes can interact at relatively large distances.

[22] The predictions based on orbital symmetries suggest that chrysene would behave selectively even if its triplet energy was above the T_2 energy of I. Accordingly the T_2 energy of I should be revised downward to include the range 53–58 kcal/mol.

[23] H. B. Gillespie and H. R. Snyder in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 489.

[24] R. Filler, E. J. Piasek, and H. A. Leipold, *Org. Syn.*, **43**, 3 (1963).

[25] E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1943).

[26] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

obtained when isopropyl alcohol was used as solvent for the photolysis.

The previously unknown photoisomer melted at 149–150° and was converted to the starting material on heating for a few minutes above its melting point. The infrared carbonyl absorption of the photoisomer was similar to that of I with peaks at ν_{KBr} 1817, 1772, and 1795 cm^{-1}. Its nmr (CDCl$_3$) showed signals at τ 1.87 (4 *o*-ArH) and 2.5 (11 H, m) whereas I displayed a resolved higher field olefinic signal at 2.79. This suggests that the olefinic hydrogen of the photoisomer is deshielded relative to that of I. Since the relative deshielding effects of the C═N and C═O groups are not readily predictable, the *syn* geometry assigned to the photoisomer is based solely on its tendency to isomerize thermally to I.

On irradiation of 300 mg of I in 300 ml of isopropyl alcohol with 2537-Å light and subsequent evaporation of the solvent, a yellow oil was obtained. On standing in 100 ml of carbon tetrachloride the oil crystallized to give 61 mg (17%) of IV. Two recrystallizations from ethanol gave 50 mg, mp 230° dec.

Anal. Calcd for $C_{19}H_{19}NO_3$: C, 70.40; H, 6.43; N, 4.54. Found: C, 70.59; H, 6.43; N, 4.79.

The mass spectrum of IV displayed major peaks at *m/e* 309 (M$^+$), 265 (M$^+$ − CO$_2$), 223 [M$^+$ − CO − (CH$_3$)$_2$CO], and 105 (C$_6$H$_5$CO$^+$) consistent with a γ,γ-dimethyl-γ-butyrolactone. The infrared spectrum showed characteristic maxima at ν_{KBr} 3430 (NH), 1757 (OC═O), and 1667 cm^{-1} (NC═O), and nmr signals (CDCl$_3$) appeared at τ 1.06 (NH, d, J = 8 Hz), 7–8 (10 ArH, m), 4.50 (CHC═O, d of d, J_1 = 8, J_2 = 13 Hz), 6.20 (PhCH, d, J_2 = 13 Hz), 8.48 (CH$_3$, s), and 8.92 (CH$_3$, s). Hydrolysis of IV with hot 20% aqueous sodium hydroxide for 6 hr yielded benzoic acid in 99% yield.

Benzalbutyrolactone III Photoproducts. A solution of 560 mg of III in 120 ml of isopropyl alcohol was irradiated with 3650-Å light for 4 hr. The residue obtained on evaporation was purified by preparative thin layer chromatography on silica gel with 5% acetic acid in benzene. About 25% of the faster moving photoisomer was obtained which, after recrystallization from 9:1 benzene–ether, melted at 91°. Upon heating to 160° the starting isomer III was regenerated.

The photoisomer had an identical mass spectrum with that of III, *m/e* 174 (M$^+$), and similar carbonyl and olefinic infrared absorption at 1736 and 1647 cm^{-1}. The nmr spectrum (CDCl$_3$) displayed signals at τ 2.2 (2 *o*-ArH, m), 2.65 (3 ArH, m), 3.01 (C═CH, t, J = 2 Hz), 5.62 (OCH$_2$, t, J = 8 Hz), and 6.88 (CH$_2$C═C, m). The starting material III has a similar spectrum but with unresolved aromatic hydrogen signals at τ 2.55 (m) and a vinyl hydrogen signal at 2.45 (t, J = 3 Hz) which was deshielded relative to that of the photoisomer. This deshielding and the relative thermal stabilities of the two isomers support the assigned geometries.

Irradiation of 400 mg of III in 1.2 l. of isopropyl alcohol for 12 hr with the B-H6 lamp fitted with a Vycor filter yielded, after evaporation of the solvent, 504 mg of an oil. Pinacol and polymeric products were readily removed by chromatography to give about a 30% yield of a mixture of lactones, $\nu_{\max}$ (CHCl$_3$) 1760 cm^{-1}. Repeated thin layer chromatography on Merck GF-254 silica gel with 5% acetic acid in benzene gave four products. One of these was purified by molecular distillation [100° (10^{-3} mm)] to give 30 mg of solid VIII which, after recrystallization from ether–hexane, melted at 98°. A second component was purified by molecular distillation [45° (10^{-3} mm)] to give 23 mg of oily VI. The other two components could not be completely separated and were not identified.

Product VIII displayed infrared maxima at $\nu_{\mathrm{CHCl_3}}$ 3640 (OH), 1760 (C═O), 1390 and 1380 [C(CH$_3$)$_2$], and 1107 cm^{-1} (C—O). The mass spectrum was consistent with a γ,γ-dimethyl-γ-butyrolactone with major fragments at *m/e* 234 (M$^+$), 176 [M$^+$ − (CH$_3$)$_2$CO], 148 [M$^+$ − CO − (CH$_3$)$_2$CO], and 132 [C$_6$H$_5$CH═C(CH$_3$)$_2$]. Only a weak peak due to loss of water (M$^+$ − 18) was observed contrary to the expected behavior of a tertiary alcohol. The presence of a primary hydroxyl group in VIII was established by the appearance of an nmr signal (CDCl$_3$) at τ 6.30 (CH$_2$O, q) which sharpened on addition of D$_2$O and a signal at 7.49 (OH) which disappeared. The appearance of additional signals at τ 2.78 (5 ArH, m), 6.71 (2 electronegatively substituted CH groups, m), 8.16 (CH$_2$, m), 8.50 (CH$_3$, s), and 8.91 (CH$_3$, s) further support structure VIII.

The oily product VI was found to be identical with the product obtained by hydrogenation at atmospheric pressure of the lactone III in ethyl acetate over palladium on charcoal. The two samples had identical chromatographic behavior, and they displayed maxima in the infrared at $\nu_{\mathrm{CHCl_3}}$ 1760 cm^{-1} (C═O) and nmr (CCl$_4$) signals at τ 2.78 (5 ArH, m), 5.91 (OCH$_2$, m), 6.8 (CHC═O, m), 7.2 (PhCH$_2$, m), and 8.0 (CH$_2$, m). The mass spectra showed major fragments at *m/e* 176 (M$^+$), 148 (M$^+$ − CO), and 91 (C$_7$H$_7$$^+$).

Sensitization. Sufficient concentrations of the sensitizers were employed to absorb >99% of the light. Like the other quantitative studies, the rates of the sensitized reactions were followed by monitoring the ultraviolet absorption at a long-wavelength isosbestic point. This procedure could not be followed in the case of the lactone III because its short-wavelength absorption was obscured by most of the sensitizers. As the reaction could therefore only be followed by tlc (vpc caused decomposition), only qualitative studies were carried out.

Sensitization of I and II with fluoranthene was carried out differently than with the other sensitizers because absorption by fluoranthene interfered with spectral monitoring. Accordingly 3650-Å light was used with only enough fluoranthene to absorb 20% of the light. Although much of the light was absorbed by the lactones, the hydrogen abstraction reactions produced by direct light absorption proceeded at a negligible rate at this wavelength.

Fluoranthene-induced hydrogen abstraction by the oxazolone I was demonstrated to be due to reabsorption of fluorescent light emitted by the fluoranthene. This was established by positioning a cell containing a solution of fluoranthene directly between the 3650-Å light source and a cell containing an isopropyl alcohol solution of I. The disappearance of I was found to occur at a rate in excess of that without the fluoranthene solution present.