(18) Z. Goldschmidt and U. Gutman, *Tetrahedron*, **30**, 3327 (1974).
(19) Z. Goldschmidt and Y. Bakal, *Tetrahedron Lett.*, 2809 (1974).
(20) This may actually be more common; however, in many systems the same product would arise regardless of which chromophore contained the excitation energy. Furthermore, the di-π-methane process in most molecules does not usually occur from both multiplicites of the excited state.
(21) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1965, pp 132, 214, and 220.
(22) (a) E. J. Bowen, *Adv. Photochem.* 1, 1 (1963); (b) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); (c) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1967, p 494.
(23) Alternately one could consider a rationale involving the energetics of bonding in the transition state [see H. E. Zimmerman and J. A. Pincock, *J. Am. Chem. Soc.*, **94**, 6208 (1972)]. Since exact singlet and triplet energies for the requisite interacting chromophores of **5** are not available, this point does not merit further discussion at this time.
(24) (a) P. S. Mariano and J. K. Ko, *J. Am. Chem. Soc.*, **94**, 1766 (1972); (b) S. S. Hixson and J. C. Tausta, *Tetrahedron Lett.*, 2007 (1974).
(25) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetahedron Lett.*, 3895 (1970).
(26) H. E. Zimmerman, D. W. Kurtz, and L. M. Tolbert, *J. Am. Chem. Soc.*, **95**, 8210 (1973).
(27) H. Hart and M. Kuziuja, *J. Am. Chem. Soc.*, **96**, 3709 (1974).
(28) I. Murata and Y. Sugihara, *Chem. Lett.*, 625 (1972). For this system an additional factor on reactivity could be the bicyclic conjugation as discussed for **2**.
(29) H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.*, **92**, 6259 (1970).
(30) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Am. Chem. Soc.*, **95**, 2155 (1973).
(31) H. E. Zimmerman and J. A. Pincock, *J. Am. Chem. Soc.*, **94**, 6208 (1972).
(32) This does not appear to be nearly so important in the singlet since **29b** has a quantum efficiency of 0.097[26] and **29a** an efficiency of 0.076[29] in their direct irradiations.
(33) General procedures: melting points were taken in open capillaries in a Thomas-Hoover "Unimelt" apparatus and are uncorrected. Infrared spectra were taken in the indicated phase on Perkin-Elmer Model 137 or 467 spectrophotometers. Nuclear magnetic resonance spectra were recorded in the indicated solvent at 60 mHz on Varian A60-A, Jeolco MH-100, or Bruker XL-90 instruments; spectra are reported in ppm τ units with reference to internal tetramethylsilane. Mass spectra were obtained with an AEI-MS9 spectrometer using an ionizing potential of 70 eV. VPC analyses were performed on a Varian Model 1200 or 1400 flame ionization gas chromatograph, and preparative VPC work was conducted on a Varian Model 700 thermal conductivity instrument using the following columns: column A, 5 ft × ⅛ in., 3% SE-30 on 60–80 mesh DMCS treated Chromosorb G; column B, 25 ft × ⅛ in., 5% SE-30 on 60–80 mesh DMCS treated Chromosorb G; column C, 13 ft × ⅛ in., 5% SE-30 on 60–80 mesh DMCS treated Chromosorb G; column D, 10 ft × ⅛ in., 3% Carbowax 20 M on 60–80 mesh DMCS treated Chromosorb G; column E, 10 ft × 0.25 in., 10% SE-30 on 60–80 Chromosorb W; and column F, 25 ft × 0.25 in., 5% SE-30 on 60–80 Chromosorb W. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.
(34) A. P. Krapcho and A. J. Lovey, *Tetrahedron Lett.*, 957 (1973).
(35) For further details concerning this reductive elimination, see: M. Fetizon, M. Jurion, and N. T. Anh, *J. Chem. Soc., Chem. Commun.*, 112 (1969); R. E. Ireland and G. Pfester, *Tetrahedron Lett.*, 2145 (1969); R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94**, 5098 (1972).
(36) While ir analysis of this material showed no saturated ketone absorption, conversion to **5** followed by VPC analysis (Column D at 140°) showed that ~5% of the saturated ketone 11 must have contaminated this conjugated ketone.
(37) K. A. Burdett, L. Shenton, D. H. Yates, and J. S. Swenton, *Tetrahedron*, **30**, 2057 (1974).

Mechanistic Studies on the Photocyclization of γ,δ-Unsaturated Ketones[1]

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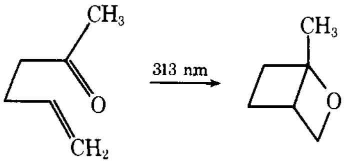
Abstract: Quantum yield studies of the photocyclizations of a series of aliphatic derivatives of *endo*-5-acylnorbornenes have shown that the efficiency of oxetane formation (eq 2) is a function of the steric bulk of the substituent. From an analysis of quenching and sensitization data, it is concluded that singlet states of the carbonyl groups are the reactive excited states. Similar studies with naphthoylnorbornenyl ketones have been interpreted in terms of two reactive states, $(n,\pi^*)_{S_1}$ and $(\pi,\pi^*)_{T_1}$. Although typical triplet state quenchers did not affect the photocyclization of 5-*endo*-benzoylnorbornene, it was concluded that the reaction proceeded via a very short-lived triplet state.

The first example of an intramolecular photocycloaddition of a carbonyl group to an olefin was reported by Srinivasan[2] in 1960 (eq 1). Yang[3] and Morrison[4] and their coworkers subsequently provided additional examples of this reaction with acyclic systems. Since that time, the reaction has found applications in ever more complex molecules with the production of some remarkable oxetanes.[5-21] Our early results with 5-acylnorbornenes[8] (eq 2) included the first examples of intramolecular photocycloadditions of phenyl and naphthyl ketones. The fact that high chemical yields of oxetanes were obtained from a wide variety of acylnorbornenes stimulated our interest in undertaking a more systematic study of this reaction.



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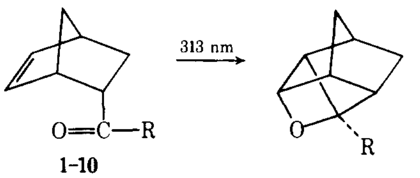

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(2)

Our first objective was to assess the importance of the nature of the acyl group on the quantum efficiencies of these reactions in an effort to delineate the overall importance of steric and electronic factors. In addition, we wished to obtain information on the nature and lifetimes of the reactive state(s) for comparison with the analogous intermolecular reactions. We report here our studies with an extended series of acylnorbornenes and some derivatives of acylbicyclo[2.2.2]octenes.

Results

Syntheses. The following series of R-substituted norbornenyl ketones was prepared by direct Diels-Alder reactions

Table I. Photocyclization Quantum Yields and Absorption Data for Acylnorbornenes and 11

Compd No.	Compd R	Concn, M	ϕ_{oxetane}[a,b] (±10%)	ϕ	$\lambda_{\max}$ (ϵ),[b] nm
1	H	0.155	0.10		
2	CH_3	0.20	0.14	0.14[c]	
3	C_2H_5	0.23	0.17		
4	i-C_3H_7	0.205	0.16		
5	t-C_4H_9	0.092	0.22		
6	i-C_5H_{11}	0.178	0.17	0.0008[d]	
7	c-C_3H_5	0.485	0.18	0.18[c]	
8	C_6H_5	0.10		0.19[c,e]	326 (71)
9	α-$C_{10}H_7$	0.008	0.128	0.130[c]	296 (6380)
10	β-$C_{10}H_7$	0.010		0.175[c]	284 (8700) 342 (1500) 327 (1550)
11	CH_3	0.20	0.14	0.14[c]	

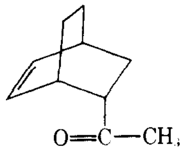
[a] Average of two or more determinations. [b] Benzene solutions. [c] Quantum yield of ketone disappearance. [d] Quantum yield of formation of 2. [e] Unchanged in the presence of 3.5 M 2,5-dimethyl-2,4 -hexadiene.

Table II. Quantum Yields for Formation of Oxetane 13 (R = CH_3) in the Presence of Quenchers and Sensitizers[a,b]

Additive	Concn, M	E_T, kcal/mol	ϕ_{oxetane} (±10%)
None	0		0.14
2,5-Dimethyl-2,4-hexadiene	4.0		0.14
trans-Dicyanoethylene	0.25		0.14
Triethylamine	1.0		0.15
Acetophenone	0.11	73.6[24]	0.007
Xanthone	0.001	74.2[24]	0.005
Butyrophenone[c]	0.10	72.0[25]	0.006

[a] Degassed benzene solutions, filter no. II. [b] Sensitizers absorbed >98% of incident light; ketone concentration 0.1–0.49 M. [c] Acetophenone formation quenched (ϕ_0/ϕ = 3.4).

or by oxidations of the carbinols formed from the reactions of *endo*-5-norbornenecarboxaldehyde (**1**, R = H) with the appropriate Grignard reagent: CH_3 (**2**); C_2H_5 (**3**); i-C_3H_7 (**4**); t-C_4H_9 (**5**); i-C_5H_{11} (**6**); c-C_3H_5 (**7**); C_6H_5 (**8**); α-$C_{10}H_7$ (**9**); and β-$C_{10}H_7$ (**10**). The bicyclooctyl system **11**



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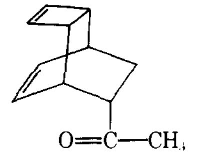

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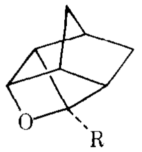
was prepared by a Diels-Alder condensation,[9] and the tricyclic ketone **12** was prepared from the corresponding nitrile[22] by hydrolysis of the methyllithium adduct.

Preparative Photolyses. All of the carbonyl derivatives gave oxetanes upon irradiation in benzene solutions with Pyrex-filtered light. Rigorous structure proofs have been published for **13**[8] (R = H or CH_3) and **14**,[9] and the other



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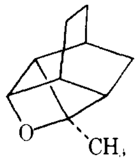

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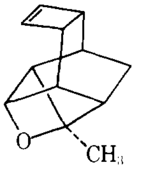

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structures are assigned by analogy. In all cases, NMR and infrared spectral data were consistent with the assignments.

Quantum Yields. Freshly purified samples of the carbonyl compounds were irradiated with 313-nm light in degassed benzene. Ketone disappearance and/or oxetane formation was monitored by quantitative absorption spectroscopy or gas chromatography. Quantum yields were calculated using benzophenone-benzhydrol actinometry.[23] The results of these measurements and some related data are presented in Table I.

Table III. Quenching of Naphthoylnorbornene Photocyclizations by 1,3-Cyclohexadiene

9 (0.010 M)		10 (0.0040 M)	
[Diene], M	Φ_{-K}[a]	[Diene], M	Φ_{-K}[b]
0	0.135	0	0.175
0.000025	0.120[c]	0.000020	0.150[e]
0.000050	0.107[c]	0.000040	0.144[e]
0.00010	0.100[c]	0.000060	0.136[c]
0.000125	0.096[c]	0.00010	0.125
0.00050	0.089[c]	0.050	0.119
0.00150	0.082	1.00	0.105[a]
0.0020	0.084[c]		
0.02–2.0	0.072[d]		

[a] Irradiated in degassed benzene using filter no. I. [b] Irradiated in degassed benzene using filter no. III. [c] Average of two determinations. [d] Average of three determinations. [e] Average of four determinations.

Table IV. Intersystem Crossing Efficiencies (ϕ_{isc})[a]

Ketone	M	[Diene], M	ϕ_{isc}
2 (R = CH_3)	0.23	0.10	$\leqslant$0.007[b]
8 (R = C_6H_5)	0.06	0.10	$\leqslant$0.006[b]
9 (R = α-$C_{10}H_7$)	0.01	0.10–0.010	0.165[c]
10 (R = β-$C_{10}H_7$)	0.01	0.050	0.135

[a] Measured in degassed benzene solutions using filter no. I and monitored by the extent of isomerization of *cis*-piperylene.[26] [b] Upper limits. [c] Independent (±20%) of concentration in this range.

The results of several quenching and sensitization experiments are given in Tables II, III, and IV.

Sensitization Experiments. Sensitization experiments were carried out on the α-naphthyl system (**9**) using Michler's ketone as the donor. Irradiations were carried out at 366 nm to minimize light absorption by the naphthoyl group in which case the sensitizer absorbed ≥98% of the light at the lowest concentration used. Quantum yields for ketone disappearance were determined by isolation of the unreacted ketone by quantitative thin layer chromatography. In general, these values agreed to within 15% of the quantum yield of oxetane formation, but the latter values are less reliable since these oxetanes are prone to undergo rearrangements in the presence of trace amounts of acid. The results are presented in Table V.

Emission Spectra. Total emission spectra for several ketones were measured in ethanol glasses at 77 K. Very weak emission centered at ca. 390 nm was observed for *endo*-5-acetylnorbornene (0.22 M). This emission is presumed to be fluorescence since typical aliphatic ketones emit at 405 nm in methanol.[27] Since the intensity of this emission was ca. 100-fold less intense than the total emission from acetone[27,28] (0.044) under similar conditions, an upper limit of 4×10^{-4} may be calculated for ϕ_f. Similarly, it was estimated that the total emission from *endo*-5-benzoylnorbornene (5×10^{-3} M) was less than 100-fold as intense as that from acetophenone under similar conditions. An upper limit for emission of 6×10^{-3} can be calculated from the known phosphorescence yield of acetophenone (0.62).[29]

By contrast, *endo*-5-α-naphthoylnorbornene (10^{-4} M) showed a fairly intense emission with a 0–0 band at 57.5 kcal/mol and a general appearance very similar to that of α-acetonaphthalene taken under similar conditions. The

Table V. Michler's Ketone Sensitization of Photocyclization of *endo*-5-(1-Naphthoyl)norbornene[a,b]

[Michler's ketone], M	Quantum yield of ketone disappearance (ϕ_{-K})
0.0005	0.255
0.0005	0.291
0.0010	0.266
0.0010	0.256
0.0020	0.167
0.0020	0.182
0.0040	0.115
0.0060	0.089

[a] 0.0080 M in benzene solution. [b] Filter number IV used throughout.

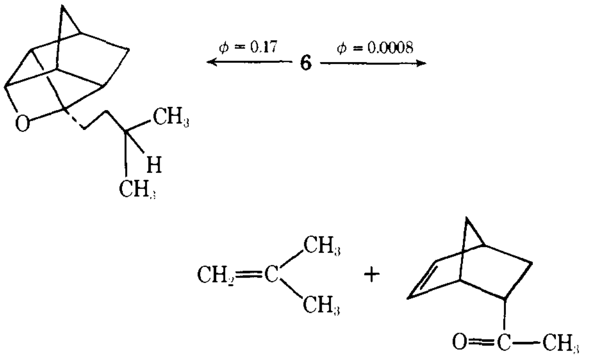
decay rate of this emission (τ_p = ca. 0.52 sec) assures that this emission is phosphorescence.

Discussion

It is convenient to consider separately the three distinct carbonyl types which have been studied. In the sequel, the results will be discussed in a more general context.

Aliphatic Systems. The results which we have obtained thus far are most consistently interpreted in terms of a mechanism which involves singlet states as the reactive excited states. The evidence for this conclusion follows from quenching and sensitization studies and our interpretations of the behavior of systems in which well-known side reactions are competitive. Thus, the absence of significant quenching (Table II) of the formation of oxetane **13** (R = CH_3) by high concentrations of typical singlet state and triplet state quenchers allows limits to be placed on excited state lifetimes. Assuming a quenching rate constant of $5 \times 10^9\ M^{-1}\ sec^{-1}$ in both cases[26a,30] and a ±10% uncertainty in the measurement of the quantum yields, the maximum lifetimes are 10^{-10} (τ_S) and 5×10^{-12} sec (τ_T). Since typical intersystem crossing rates for aliphatic ketones range from ca. 10^8 to $5 \times 10^8\ sec^{-1}$,[31-33] the overall triplet yield is expected to be no greater than 0.05 under these circumstances.

This analysis is consistent with the results obtained on irradiation of the isoamyl ketone **6** (eq 3) in which type II photoelimination competes with oxetane formation.[4b] If the rate of the former reaction from the singlet state is comparable to that in simpler analogs[33] ($2.4 \times 10^8\ sec^{-1}$), a maximum singlet state lifetime for **6** may be calculated from the equation $\tau_S = \phi_{II}/k_S{}^{II}$. The value thus obtained, 3×10^{-12} sec, effectively precludes intersystem crossing.[34]



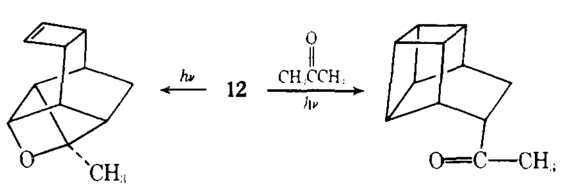
(3)

The triplet sensitization experiments in Table II demonstrate that triplets, once formed, are reactive, but the results are difficult to interpret quantitatively. Thus, the sensitizers used are all capable of promoting dimerization of norbornene (E_T ~ 72 kcal/mol), but it has been shown that quenching of butyrophenone triplets by norbornene probably does not involve efficient energy transfer.[25] It is significant that a new photoproduct was formed in the sensitization experiments (ϕ ~ 0.003). This material was not isolated but, since its GC retention time was similar to that of the oxetane, dimeric structures can be eliminated.

Table VI. Cyclization:Cleavage Efficiencies as a Function of R

R	Oxetane formation (eq 4) (±10%)	Type II reaction (eq 5) $k_c/(k_c + k_e)$
H	0.10	0.12
CH_3	0.14	0.18
C_2H_5	0.17	0.20
i-C_3H_7	0.16	0.23
t-C_4H_9	0.22	0.28

These data do not preclude the possibility of direct energy transfer from the $^1(n,\pi^*)$ state of the carbonyl group to the $^3(\pi,\pi^*)$ state of the olefin via an intermediate oxetane-like exciplex.[34] In a series of experiments designed to test for this kind of intramolecular energy transfer, we prepared and irradiated the tricyclic ketone **12**. It was reasoned that the formation of olefin triplets in this system would produce the pentacyclic ketone **16** to some extent since the latter is the major product of acetone-sensitized photolysis. The direct photolysis of **12** did not produce **16**, and we conclude that no intramolecular triplet energy transfer occurred.



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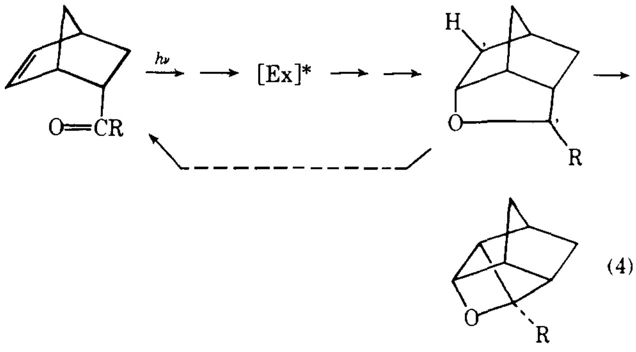
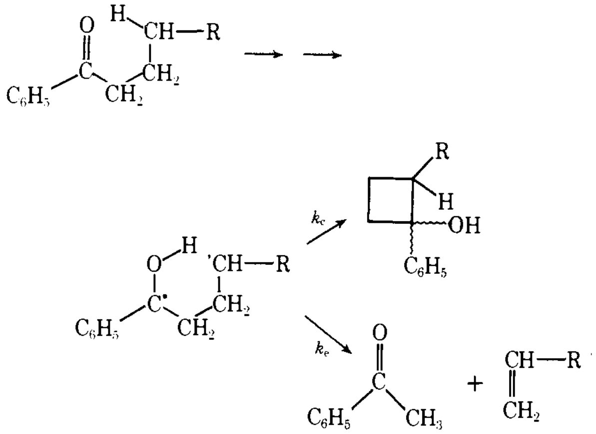
In summary, the above results are consistently interpreted in terms of a mechanism which involves rapid deactivation of carbonyl singlet states by the internal double bonds. Kurowsky and Morrison[4] reached this conclusion independently and postulated that the initial interaction involved formation of an exciplex by analogy with the intermolecular counterpart of these reactions.[25,30,35-37] Although the detailed fate of exciplexes is unknown, it is generally agreed that at least part of the time they produce singlet 1,4 biradicals which may then partition between oxetane and ground state components (eq 4).[35-38] A question of major importance concerns the role that structural factors play in these partitionings between oxetane and reactant. At this juncture, however, the only experimental information available represents the total partitioning of all intermediates. Despite this limitation, it is of some interest to note the trend in cyclization efficiency in the aliphatic series in which R varies from H through *tert*-butyl (Table VI). It is seen that oxetane formation is favored by bulky substituents despite the increased steric strain in the oxetanes. In the same table are presented data which pertain to the cyclization:cleavage



(4)

ratios of a series of phenyl alkyl ketones which undergo type II reactions upon irradiation (eq 5).[39] Although the biradi-

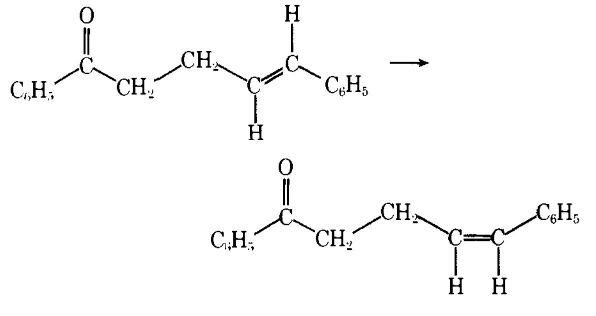


(5)

cals in these processes are initially in the triplet manifold, it is presumed that the partitioning takes place after spin inversion.

Thus, in both examples, the cyclization step is seen to be favored by increased bulk in the substituent despite adverse steric interactions. As a tentative hypothesis, we have interpreted these results to mean that the primary role of the substituents is to serve as energy sinks. The ability of the substituent to rapidly dissipate thermal energy may be more important for cyclization than cleavage since the former process is more exothermic than the latter and because the energy liberated is initially more localized for single bond formation. Ultimately, solvent-solute interactions remove the excess energy, but the partitioning in question involves relatively slight atomic motions, and the crucial stage may be reached before solvent interactions become significant. In view of the importance of 1,4 biradicals,[35-43] the generality of the substituent effect should be explored more extensively in order to assess the importance of other variables, e.g., radical stability and/or conformational effects.

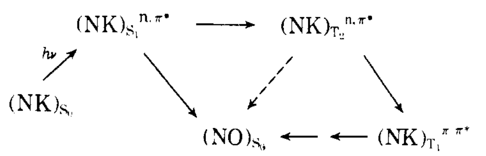
5-*endo*-Benzoylnorbornene (8). The results (Tables I and IV) of the quenching and triplet counting experiments with **8** were qualitatively similar to those with the aliphatic systems. The finding that no detectable quenching of the photocyclization was observed in the presence of 3.5 *M* 2,5-hexa-2,4-diene is indicative of a singlet state reaction or a triplet state reaction which proceeds at a rate faster than 1.6×10^{11} sec^{-1}. Singlet state reactions are more problematical in this system, however, since intersystem crossing rates are expected to exceed 10^{11} sec^{-1} for aromatic ketones.[44] In this context, the results of Cowan and Baum with the acyclic γ,δ-unsaturated aromatic ketone shown in eq 6 are of interest.[45] These workers found that the triplet



(6)

yields in the trans isomer were essentially unity and that intramolecular energy transfer ($k_{\mathrm{et}} = 7.2 \times 10^{10}$ sec^{-1}) was the sole mode of decay of the triplets. It can be argued that this intramolecular energy transfer rate represents the minimum rate of "contact" of the chromophores. Since the transfer is highly exothermic, the rate of transfer may be considered to be controlled by the internal "diffusion" rate of the components. Since the comparable rate of interaction in **8** is expected to be at least 25 times faster[46] as a result of the decreased conformational mobility of the components, a lower limit to the analogous contact rate in the bicyclic system is 1.8×10^{11} sec^{-1}. This value is compatible with the minimum triplet rate required by the quenching data.

Scheme I



NK = naphthyl ketone NO = naphthyl oxetane

Naphthoyl Ketones. The behavior of the two naphthyl ketones **9** and **10** contrasts in several important ways with that of the aliphatic and phenyl ketones. For example, the data in Table III show that partial quenching of oxetane formation can be effected by relatively low concentrations of dienes. In addition, the photocyclization of **9** can be efficiently sensitized by Michler's ketone. These results are conveniently discussed by reference to Scheme I in which some of the excited state energy levels of the naphthyl ketones have been ordered. The basis for this diagram has been discussed extensively, and our assignments are made (in part) by analogy.[47-49] We interpret the results of the sensitization and quenching experiments as manifestations of the behavior of the $(\mathrm{NK})_{\mathrm{T}_1}{}^{\pi,\pi^*}$ state. This conclusion is based on the relative triplet energy levels of Michler's ketone[24] (61 kcal/mol), ketone **9** (57.5 kcal/mol), and 1,3-cyclohexadiene[50] (53 kcal/mol) from which it can be seen that both energy transfer and quenching should be diffusion-controlled processes.[51]

The quenching data (Table III) and the intersystem crossing efficiencies (Table IV) can be used to estimate the lifetimes of the quenchable states by means of Shetlar's method.[52] In this treatment, a modified Stern-Volmer equation (eq 7)

$$(\phi_0 - \phi)/(\phi - \phi_0^{\mathrm{s}}) = k_{\mathrm{q}}\tau[\mathrm{Q}] \qquad (7)$$

has been derived in which ϕ_0 represents the maximum total quantum yield, ϕ_0^{s} is the quantum yield of the unquenchable portion of the reaction, and ϕ is the quantum yield of the reaction at a given quencher concentration Q. The lifetimes of the quenchable states can then by calculated from the slopes[53] of the plots (Figure 1) if a diffusion-controlled quenching rate is assumed ($k_{\mathrm{q}} = 5 \times 10^9$ M^{-1} sec^{-1}). The following lifetimes were calculated for the quenchable states of ketones **9** and **10**: 2.5×10^{-6} and 4.8×10^{-6} sec, respectively. By comparison, typical triplet lifetimes of simple naphthoyl systems range from 10^{-3} to 5×10^{-4} sec.[54-57] We conclude that the lifetimes of the lowest triplet states of **9** and **10** are limited mainly by the rates of reactions at the double bonds.

The efficiencies of the cyclizations of the quenchable triplet states ($\phi_{\mathrm{T}_1}/\phi_{\mathrm{isc}}$) are the highest values obtained for any of the acylnorbornenes studied: 0.39 (**9**) and 0.52 (**10**). These results contrast markedly with those obtained for intermolecular photocycloadditions of naphthoyl ketones ($\phi < 0.04$).[58] Since the recent results have demonstrated that, in at least one case, naphthoyl triplets were not involved in the intermolecular cycloaddition reaction, our results represent the only documented examples of oxetane formation from naphthoyl triplet states. While this finding may not be unique, it is clear that the intramolecularity is advantageous in this context in that there can be many more "collisions" between the excited carbonyl group and the double bond during the lifetime of the excited state.

On the other hand, the cyclization efficiencies from the nonquenchable states are defined by the ratio ($\phi_{\text{total}} - \phi_{T_1})/(1 - \phi_{\text{isc}})$ and are seen to be smaller by factors of ca. 4 [0.086 (**9**) and 0.12 (**10**)] than those calculated for the reactions from the lowest triplet states. It is unlikely that these disparities arise from unequal partitionings of biradical intermediates derived from upper and lower triplet states since vibrational relaxation ($k \sim 10^{12}$ sec^{-1}) is expected to dominate the behavior of the upper state intermediate. This contention is supported by recent estimates of the lifetimes of triplet 1,4 biradicals[39,41,59,60] (10^{-4} to 10^{-7} sec), but we are unable to exclude the possibility that some of the inefficiencies involve decay of exciplexes.[35-38] It is important to note, however, than *any* differences in partitionings are significant since the immediate precursors of oxetanes and ground state components are presumed to be singlet states.[37] Since the singlet state formed via the lowest triplet is likely to be thermally equilibrated,[42] there is no reason to expect it to undergo an identical partitioning with a species which may initially possess as much as ~15 kcal/mol excess energy.[48] The partitioning of a "hot" singlet species would tend to be more selective toward the less exothermic pathway, i.e., cleavage, for the reasons discussed above.

Sensitization Experiments. The success of the sensitization experiments (Figure 1) lends further support to the above proposals concerning the nature of the quenchable reactive state in these reactions. Specifically, Michler's ketone would be expected to populate only the lowest triplet level (vide infra) of the acceptor. The dependency of sensitization efficiency on sensitizer concentration (Table V) is a relatively new phenomenon which may involve additional quenching processes, e.g., self-quenching.[61-64] In any event, a maximum value for the quantum yield of the triplet cycloaddition may be obtained from a plot of the reciprocal of the sensitized quantum yield vs. sensitizer concentration. This value (0.37) is in good agreement with that obtained (0.39) by independent means (vide supra).

Summary and Conclusions

We have interpreted the photochemistry of the aliphatic systems in terms of rapid exciplex formation between the $(n,\pi^*)_{S_1}$ states of the carbonyl groups and the double bonds. The facility of this step is limited by rotation about one single bond and probably proceeds at rates in excess of 10^{11} sec^{-1}, i.e., faster than intersystem crossing, Norrish cleavages, and intermolecular quenching processes. It was noted that bulkier aliphatic groups promoted more efficient cyclization despite the adverse steric interactions created in the oxetanes. These results were rationalized in terms of the ability of the alkyl groups to dissipate the energy of bond formation, the larger groups being better energy sinks. The naphthoyl ketones underwent photocyclization from two excited states. The quenchable state is believed to be the π,π^* triplet since it can be populated by energy transfer from Michler's ketone triplets. The nonquenchable reactive state is believed to be in the singlet manifold but, in these cases, intersystem crossing is competitive.[58a] Finally, the benzoyl ketone **8** was shown to undergo cyclization which could not be quenched by high concentrations of dienes. In view of the very fast rate of intersystem crossing of aromatic ketones,[44] it is concluded that the reactive state in this system is the triplet state. This conclusion provides for a self-consistent rationalization of the contrasts in the behavior of the three types of carbonyl systems. No doubt, there are small differences in the rates of exciplex formation for the three types of systems, but the major factor which controls the partitioning between singlet and triplet reaction is k_{isc} which is expected to vary in the order: benzoyl > naphthoyl > aliphatic ketones.[31-33,44,58]

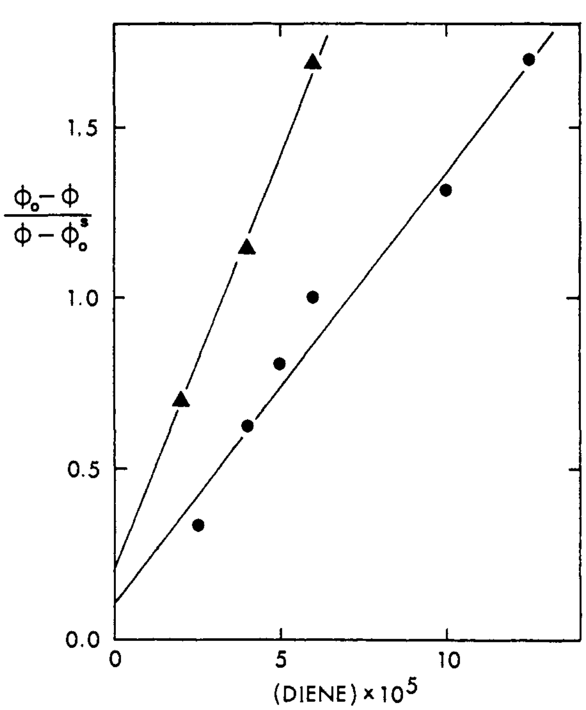


Figure 1. Shetlar plot of quenching of naphthoylnorbornene cyclizations by 1,3-cyclohexadiene: circles, **9** (α); triangles, **10** (β).

Experimental Section

Proton magnetic resonance spectra were determined on a Varian Model T-60 spectrometer in carbon tetrachloride using tetramethylsilane as an internal standard. Gas chromatograms were determined on an Aerograph Model A90P or a Barber-Coleman Model 5000 chromatograph. Columns used were Carbowax 20M (5-7 ft × 0.25 in.) and UCON 50-HB-2000 (150 ft × 0.1 in.). Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer.

Preparation and Purification of Starting Materials. a. Norbornenes. The following derivatives were prepared according to published procedures: **1**;[65] **2**;[66] **8**;[21] **9**;[21] and **11**.[9] Samples of these materials were rigorously purified by preparative gas chromatography or recrystallization. The following acylnorbornenes were prepared by the reaction of 5-*endo*-norbornene carboxaldehyde (>97% endo) with the appropriate Grignard reagent followed by chromic acid oxidation according to published procedure:[21] **4**; **5**; **6**; **7**; **10**. The products were distilled or chromatographed until pure. Physical constants for these ketones are given in Table VII.

b. Tricyclo[4.2.2.$0^{2,5}$]deca-7,9-dien-7-yl Methyl Ketone (12). Ketone **12** was prepared by the reaction of methyllithium with 9-cyanotricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene.[22] A solution of 1.30 g (0.0082 mol) of this ketone in 50 ml of anhydrous ether was cooled to −78°. A solution of ethereal methyllithium (11 ml, 0.018 mol) was injected through a serum cap over a period of 15 min. The resulting mixture was stirred for 1 hr at −78° and then allowed to warm to room temperature over 19 hr. The reaction mixture was then heated at reflux for 4.5 hr with 0.5 *N* hydrochloric acid. The resulting mixture was neutralized with aqueous sodium carbonate and extracted with ether. Evaporation of the dried extracts gave 0.95 g (66%) of ketone **12**. Physical properties are given in Table VII.

Oxetanes. Preparative irradiations were generally carried out on the exo,endo mixtures of the ketone as originally obtained. Benzene solutions (1-3%) were purged with dry nitrogen in an immersion apparatus and were irradiated through Pyrex or Corex filter sleeves with a 450-W Hanovia lamp. The course of the cyclizations was followed by gas chromatography or TLC, and most reactions went to completion. Evaporation of the benzene followed by distil-

Table VII. Physical Constants for Ketones and Oxetanes

					Oxetanes		
Ketone	Bp (mmHg) or mp, °C	Calcd % C, H	Found C, H	^{1}H NMR data[a]	Bp (mmHg) or mp, °C	Found C, H	^{1}H NMR[a]
3[b]	106 (26)	C, 79.95; H, 9.39	C, 80.25; H, 9.65	5.95 (m, 2 H)	100 (48)	C, 79.73; H, 9.58	4.48 (dd, 1 H)
4	38 (0.06)	C, 80.49; H, 9.76	C, 80.28; H, 9.97	5.90 (q, 2 H) 1.05 (dd, 6 H)		C, 80.79; H, 10.00	4.46 (dd, 1 H) 1.05 (dd, 6 H)
5	82 (2.4)	C, 80.85; H, 10.18	C, 80.86; H, 9.88	5.87 (q, 2 H) 1.15 (s, 9 H)	70 (15)	C, 80.91; H, 10.16	4.37 (dd, 1 H) 0.97 (s, 9 H)
6	79.5 (1)	C, 81.20; H, 10.48	C, 81.40; H, 10.47		70–80 (9)	C, 80.93; H, 10.25	4.48 (dd, 1 H) 0.88 (d, 6 H)
7	60 (0.1)	C, 81.48; H, 8.64	C, 81.39; H, 8.82	5.96 (q, 2 H)	48 (0.1)	C, 81.77; H, 8.96	4.43 (dd, 1 H)
10	49–51	C, 87.07; H, 6.50	C, 86.93; H, 6.57	5.91 (o, 2 H)	97–98	C, 87.13; H, 6.58	4.60 (dd, 1 H) 1.30–2.73 (m, 7 H)
12	70 (0.03)	C, 82.72; H, 8.10	C, 82.58; H, 8.32	5.88[c] (m, 4 H)	39–41 (1.0)	C, 82.78; H, 7.97	4.44 (m, 1 H) 1.38 (s, 3 H) 6.08 (m, 2 H)

[a] q = quartet; dd = doublet of doublets; o = octet; s = singlet. [b] Prepared from cyclopentadiene and ethyl vinyl ketone. [c] Determined in benzene.

lation (silica chromatography for **10**) served to isolate the oxetanes. With the exception of **6**, these irradiations produced no observable side products either by GC or TLC.

Quantum Yields. a. Purification of Materials. Benzene was purified by repeated washing with concentrated sulfuric acid, followed by washings with water and sodium carbonate solution. After drying over calcium chloride, it was distilled from phosphorus pentoxide. The middle fraction was collected and stored over calcium hydride or sodium carbonate. The following internal standards were purified by a similar procedure: tetradecane, pentadecane, and hexadecane. *cis*-1,3-Pentadiene was freshly distilled prior to use. 1,3-Cyclohexane was distilled from hydroquinone under a blanket of nitrogen prior to use. 2,5-Dimethyl-2,4-hexadiene was recrystallized twice from itself prior to use. Acetophenone was used as received from Matheson Coleman and Bell. Butyrophenone was distilled under vacuum. Both ketones were homogeneous by GC analysis. Xanthone was recrystallized from benzene and gave the literature absorption spectrum. TLC on silica plates showed no impurities. Michler's ketone was recrystallized four times from 95% ethanol. The absorption spectrum agreed with that in the literature[67] ($\epsilon^{333}_{C_6H_{12}}$ 40,000), and the spectrum of 4 μ of 5 $\times$ 10^{-2} *M* solution in benzene was virtually identical with that of 1 cm of a 10^{-5} *M* solution. All carbonyl compounds were freshly chromatographed or recrystallized prior to use.

b. General Procedure. The solutions to be irradiated were placed in 13 × 100 mm Pyrex culture tubes which had been fused to ground joints. These assemblies were attached to a vacuum line and degassed at 0.05 mm by the freeze–thaw technique. They were sealed off with a torch after three or four cycles. With the exception of the naphthyl ketones, irradiations were carried out on a merry-go-round apparatus. The emission from a 450-W Hanovia lamp was filtered through a solution of potassium chromate (0.270 g/l.) and potassium carbonate (1.38 g/l.) to isolate the 313-nm band. The entire apparatus was kept at 25 ± 1° by means of a water bath.

Some experiments with the naphthyl ketones were carried out on an optical bench using the light from a 200-W Osram lamp (HBO W/2) and a condensing lens assembly (f/1.0, 35 mm-aperture). The power supply was obtained from Oriel Optics Corp., and the voltage output was regulated to ±1% for a 10% line voltage change. Four filter systems were utilized on the bench. Filter I (313 nm) consisted of 5 cm of a solution 4 $\times$ 10^{-4} *M* in K_2CrO_4 and 1% Na_2CO_3 in conjunction with 0.3 cm of Corning glass 7-54 (9863). Filter II (336 nm) consisted of 1 cm of 0.10 *M* naphthalene solution in benzene, 5 cm of $NiSO_4 \cdot 6H_2O$ (10 g/100 ml of H_2O), and Corning glass filter 7-51 (5970). Filter III (334 nm) consisted of 5 cm of a solution of 10 g of $NiSO_4 \cdot 6H_2O$ in 100 ml of water, 1 cm of a solution prepared by diluting a solution of 46 g of $SnCl_2$ and 52 ml of concentrated H_2SO_4 in 500 ml of water with an equal volume of 10% aqueous HCl, and 0.5 cm of Corning glass filter 7-51 (5970). Filter number IV (366 nm) consisted of 5 cm of copper sulfate solution (15.0 g, of pentahydrate per 100 ml of H_2O) and 0.5 cm of Corning glass 7-37 (5860).

Filters I or III were used in the work with the aromatic ketones. Filter IV was shown to transmit light to the extent of about 6% between 334 and 340 nm.

c. Actinometry. The majority of the runs were calibrated using the benzophenone (0.10 *M*)-benzhydrol (0.05 *M*) actinometer system of Moore and Ketchum.[23] Degassed benzene solutions were irradiated concurrently with samples on the merry-go-round or were used to calibrate the output of the Osram lamp by averaging the flux before and after irradiations. The aliphatic systems were measured relative to the methyl ketone which was determined first by the above method. All solutions were optically dense ($A \geq 2$), and conversions were kept to less than 15%. Duplicate runs were averaged.

d. Analytical. The conversions of the aliphatic systems were measured by quantitative gas chromatography using the internal standards mentioned above. Peak areas were cut out and weighed, and averaged values from seven or more injections were used in the calculations.

The concentrations of aromatic ketones were monitored by absorption spectroscopy at several wavelengths between 320 and 345 nm. In certain experiments, the photosylates were subjected to preparative TLC (silica, Eastman 6061), and the isolated spots were examined individually for oxetane and ketone content.

Sensitization Experiments. Solutions of ketone **9** (0.008 *M*) and Michler's ketone (see Table V) in degassed benzene were irradiated for sufficient time to effect ca. 15% conversion of ketone to oxetane. The optical bench was used with filter combination number IV. The percentage conversion of ketone 9 was determined by quantitative TLC (Eastman sheets, No. 6061) of 90 μl of photolysate, using solutions of cyclohexane-benzene-chloroform in the ratios 7:2:1 for development and uv analysis. In a typical experiment, four plates were used, and the results were averaged.

The method was checked on unphotolyzed solutions from which 92 ± 3% of the starting ketone could be recovered. Attempts to routinely analyze for oxetane formation usually gave somewhat lower values probably the result of isomerization of the oxetane by traces of acids.

8-Cyanopentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane. A solution of 6.87 g (0.0437 mol) of 9-cyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene[21] in 1.2 l. of benzene which contained 12 ml of acetone[68] was irradiated in an immersion apparatus (Corex filter) for 126 hr with a 450-W lamp. A nitrogen atmosphere was maintained throughout the course of the irradiation. The solvents were evaporated and the residue distilled at 97-99° (0.75 mm): yield, 2.5 g (36%); NMR δ 3.00 (multiplet, 9 H), 1.80 (t, 1 H), 1.70 (dd, 1 H); ir (neat) 2250 cm^{-1} (C≡N).

Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 6.98; N, 8.92. Found: C, 84.04; H, 7.05; N, 8.91.

8-Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decyl Ketone (16). The above nitrile (1.70 g, 0.0108 mol) was treated with 0.105 mol of ethereal methyllithium at −78° by the procedure described earlier. There was obtained 0.96 g (51%) of a colorless oil: bp 100° (0.5 mm); NMR δ 3.00 (m), 1.84 (s, CH_3), 1.40 (m); ir (neat) 1705 cm^{-1}

(C=O). The sample decomposed rapidly on standing.

Sensitized Photolysis of Ketone 12. A solution of 0.0175 g of ketone **12** in 1 ml of reagent grade acetone was placed in a quartz NMR tube and was purged with a dry nitrogen stream. The tube was tightly capped and irradiated with the 300-nm source in a Srinivasan-Griffin photoreactor. After 3 hr, GC analysis showed that 0.7% of **12** had been converted to oxetane **15** and 13% had been converted to **16**. On longer irradiation, ketone **16** began to decrease in concentration.

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References and Notes

(1) (a) Presented in part at the XXIIIrd IUPAC Meeting, Boston, Mass., July 1971; Abstracts, p 96; (b) R. R. Sauers and A. D. Rousseau, *J. Am. Chem. Soc.*, **94**, 1776 (1972).

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960).

(3) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965).

(4) (a) H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965); (b) S. R. Kurowsky and H. Morrison, *ibid.*, **94**, 507 (1972).

(5) P. Bladon, W. McMeekin, and I. A. Williams, *J. Chem. Soc.*, 5727 (1963).

(6) R. R. Sauers and A. Shurpik, *J. Org. Chem.*, **32**, 3120 (1967).

(7) J. Meinwald and R. A. Chapman, *J. Am. Chem. Soc.*, **90**, 3218 (1968).

(8) R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969).

(9) R. R. Sauers and J. A. Whittle, *J. Org. Chem.*, **34**, 3579 (1969).

(10) K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Lett.*, 3399 (1969).

(11) J. Meinwald and A. T. Hamner, *Chem. Commun.*, 1302 (1969).

(12) T. Mori, K. H. Yang, K. Kimoto, and H. Nozaki, *Tetrahedron Lett.*, 2419 (1970).

(13) Y. Bahurel, F. Pautet, and G. Descotes, *Bull. Soc. Chim. Fr.*, 2222 (1971).

(14) M. L. Mihailović, L. Lorenc, N. Popov, and J. Kalvoda, *Helv. Chim. Acta*, **54**, 2281 (1971).

(15) J. A. Marshall and J. P. Arrington, *J. Org. Chem.*, **36**, 214 (1971).

(16) J. Morizur, B. Furth, and J. Kossanyi, *Bull. Soc. Chim. Fr.*, 1959 (1970).

(17) G. L. Lange and M. Bosch, *Tetrahedron Lett.*, 315 (1971).

(18) R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem. Commun.*, 809 (1972).

(19) R. R. Sauers and T. M. Henderson, *J. Org. Chem.*, **39**, 1850 (1974).

(20) J. C. Dalton and H.-F. Chan, *Tetrahedron Lett.*, 3351 (1974).

(21) R. R. Sauers, W. Schinski, M. M. Mason, E. O'Hara, and B. Byrne, *J. Org. Chem.*, **38**, 642 (1973).

(22) R. E. Benson and T. L. Cairns, *J. Am. Chem. Soc.*, **72**, 5355 (1950).

(23) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962); W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

(24) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(25) I. E. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, **94**, 3859 (1972).

(26) (a) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965); (b) G. F. Vesley, *Mol. Photochem.*, **4**, 519 (1972).

(27) M. O'Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, **92**, 5842 (1970).

(28) M. O'Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, **92**, 258 (1970).

(29) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1967, p 297.

(30) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Am. Chem. Soc.*, **90**, 3274 (1968).

(31) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2503 (1967).

(32) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Am. Chem. Soc.*, **92**, 6974 (1970).

(33) N. C. Yang, S. P. Elliott, and B. Kim, *J. Am. Chem. Soc.*, **91**, 7551 (1969).

(34) D. A. Hansen and E. K. C. Lee, *J. Am. Chem. Soc.*, **95**, 7900 (1973).

(35) (a) N. C. Yang and W. Eisenhardt, *J. Am. Chem. Soc.*, **93**, 1277 (1971); (b) N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971).

(36) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973).

(37) N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, **92**, 320 (1970).

(38) A test for the intermediacy of biradicals was designed which takes cognizance of the tendency of cyclopropylcarbinyl radicals to undergo isomerization [J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, **91**, 1877 (1969); D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968)]. Thus, the cyclopropyl ketone **7** was expected to reveal the presence of long-lived ($>10^{-8}$ sec) biradicals in the form of rearranged products and/or lowered quantum yields. In the event, no rearranged products were detected, and the quantum yield appeared to be consistent with those of the other compounds studied. A successful application of this technique was recently reported in an intermolecular oxetane reaction [N. Shimizu, M. Ishikawa, K. Ishijura, and S. Nishida, *J. Am. Chem. Soc.*, **96**, 6456 (1974)]. In fact, there may be no real distinction between the singlet exciplex and a singlet diradical; the species shown in eq 4 may represent a vibrationally excited extremum.

(39) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7506 (1972).

(40) (a) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7091 (1970); (b) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1970).

(41) P. J. Wagner and K.-C. Liu, *J. Am. Chem. Soc.*, 96, 5952 (1974).

(42) L. M. Stephenson and T. A. Gibson, *J. Am. Chem. Soc.*, **96**, 5624 (1974).

(43) C. P. Casey and R. A. Boggs, *J. Am. Chem. Soc.*, **94**, 6457 (1972).

(44) P. M. Rentzepis and C. J. Mitschele, *Anal. Chem.*, **42**, (14), 20A (1970).

(45) D. O. Cowan and A. A. Baum, *J. Am. Chem. Soc.*, 93, 1153 (1971).

(46) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *J. Am. Chem. Soc.*, **94**, 4292 (1972); F. D. Lewis, R. W. Johnson, and D. R. Kory, *ibid.*, **96**, 6100 (1974).

(47) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949); V. Ermolaev and A. Terenin, *J. Chim. Phys. Phys.-Chim. Biol.*, **55**, 698 (1958).

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

(49) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **62**, 3375 (1966).

(50) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965).

(51) A. A. Lamola in "Energy Transfer and Organic Photochemistry" "Technique of Organic Chemistry", Vol. 14, P. A. Leermakers and A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1969, p 17.

(52) M. D. Shetlar, *Photochem. Photobiol.*, **10**, 407 (1969).

(53) The lines shown on Figure 1 are least-square plots. The fact that the intercepts are not zero is an indication of the sensitivity of the function plotted to small errors in the quantum yield determinations. Inclusion of the origin in the calculations gives the following values of τ: 9, 2.8×10^{-6} sec; **10**, 6×10^{-6} sec. Use of the values given in the text gives a good fit of ϕ_0/ϕ vs. (diene) plots: A.D.R., Ph.D. Thesis, Rutgers University, 1972. A referee has questioned the validity of this treatment for naphthalenic systems in view of the known ability of dienes to quench naphthalene singlets; see L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969). However, since the lifetimes in question were calculated from slopes determined by very low concentrations of quenchers ($<10^{-4}$ *M*), we believe that complications attributable to singlet quenching are insignificant. In addition, the values of ϕ_{isc} may be slightly low although, in the case of **9**, we found only a slight dependency on diene concentration.

(54) S. G. Cohen, G. A. Davis, and W. D. K. Clark, *J. Am. Chem. Soc.*, **94**, 869 (1972).

(55) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

(56) C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1969).

(57) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

(58) (a) N. C. Yang, M. Kimura, and W. Eisenhardt, *J. Am. Chem. Soc.*, **95**, 5058 (1973); (b) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, 3657 (1964).

(59) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Am. Chem. Soc.*, **96**, 3351 (1974).

(60) L. M. Stephenson and J. I. Brauman, *J. Am. Chem. Soc.*, **93**, 1988 (1971).

(61) O. L. Chapman and G. Wampfler, *J. Am. Chem. Soc.*, 91, 5390 (1969).

(62) A. G. Schultz, D. D. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, *J. Am. Chem. Soc.*, **92**, 6086 (1970).

(63) T. H. Koch and A. H. Jones, *J. Am. Chem. Soc.*, 92, 7503 (1970).

(64) R. W. Yip, A. G. Szabo, and P. K. Tolg, *J. Am. Chem. Soc.*, **95**, 4471 (1973).

(65) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 117 (1928).

(66) J. G. Dinwiddie, Jr., and S. P. McManus, *J. Org. Chem.*, **30**, 766 (1965).

(67) "U. V. Atlas of Organic Compounds", Vol. III, Plenum Publishing Co., New York, N.Y., 1967, pp D11, T9.

(68) (a) G. O. Schenck, J. Kuhls, and C. H. Krauch, *Z. Naturforsch., Teil B*, **20**, 635 (1965); (b) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966); (c) W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966).