

Molecular Photochemistry of Alkanones in Solution: α -Cleavage, Hydrogen Abstraction, Cycloaddition, and Sensitization Reactions¹

NICHOLAS J. TURRO,* J. CHRISTOPHER DALTON,^{2a} KEITH DAWES,^{2b} GEORGE FARRINGTON,^{2c} RICHARD HAUTALA,
DOUGLAS MORTON,^{2a} MARK NIEMCZYK, AND NEIL SCHORE^{2a}

Department of Chemistry, Columbia University, New York, New York 10027

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Excitation by absorption of ultraviolet or visible light provides a convenient, but by no means unique, method for generating electronically excited molecules in the laboratory.³ Following absorption, two electrons become orbitally decoupled. Generally, the spins of these electrons remain antiparallel, *i.e.*, absorption of ultraviolet or visible light by an organic molecule will generally produce an electronic isomer of the ground state. This electronic isomer is called an excited singlet state, which we shall hereafter designate as S_1 , in contradistinction to S_0 , the electronic ground state. A "spin isomer" of S_1 results if the spins of the orbitally decoupled electrons are parallel. This triplet state we shall designate as T_1 ; it is an electronic and spin isomer of S_0 . In general, because of quantum mechanical constraints (the Pauli principle), the T_1 state is more stable than S_1 .

In formaldehyde,⁴ the S_1 and T_1 states are well characterized and are saliently different from the ground state (Figure 1). The electronic isomers of formaldehyde are pyramidal species possessing a very long, essentially single, CO bond and a substantially reduced dipole moment.⁵ Indeed, H_2CO electronic isomers undergo rapid inversion (at about 10^{10} sec^{-1}) through a mirror plane, analogous to the behavior of the ammonia molecule.

This beautifully detailed description of S_1 and T_1 in H_2CO is possible because of its amenability to spectroscopic analysis. Although S_1 and T_1 possess about 80 kcal of energy above that of the ground-state formaldehyde, these species last long enough to be characterized by their spectra. The S_1 and T_1 states are generally the only photochemically reactive states (Kasha's rule) which need be considered in solution.⁶

The diffuse absorption and emission spectra of alkanones, on the other hand, are not amenable to such detailed analysis. As a result, we must employ a strongly coupled combination of spectroscopic and chemical evidence in order to infer the nature and be-

havior of the electronic isomers of the alkanones at the molecular level.

An abundance of theoretical and experimental evidence leads to the working hypothesis that the configuration of S_1 and T_1 in alkanones is $(n_0)^1(\pi^*)^1$, where n is an orbital more or less localized on the carbonyl oxygen atom and π^* is an orbital delocalized over both the carbonyl atoms.⁷ We shall designate both S_1 and T_1 as " n, π^* states," thereby emphasizing the approximate electronic configuration of these states. This model⁸ suggests that both states will be amphoteric reagents, *i.e.*, electrophilic and radical-like in the vicinity of the half-vacant n orbital on oxygen, and nucleophilic (and possibly radical-like) above and below the carbonyl faces because of the presence of a π^* electron (Figure 2).

In this Account, we test the usefulness and validity of the above model as a means of predicting and understanding how structural changes influence the reactivity, specificity, and efficiency of photoreactions of alkanones. We shall attempt to show how studies of quantum yields and photochemical kinetics have led to a considerable increase in our confidence in the understanding of the behavior of electronically excited alkanones. In addition, we shall show how biradical intermediates, concerted rearrangements, cycloadditions, and other topics of wide interest to chemists are involved in the photochemistry of alkanones.

Chemistry of the S_1 and T_1 States of Alkanones^{9a, b}

The overwhelming majority of known photochemical reactions of alkanones falls in three typical classes:

(1) Molecular Photochemistry. L. Paper XLIX: A. Yekta and N. J. Turro, *Mol. Photochem.*, **3**, 307 (1972). (b) This work was generously supported by the Air Force Office of Scientific Research by Grant AFOSR-70-1848.

(2) (a) NIH Predoctoral Fellow; (b) NATO Postdoctoral Fellow, (c) NSF Predoctoral Fellow.

(3) For example, electronically excited alkanones are produced by thermal decomposition of 1,2-dioxetanes: E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

(4) J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963).

(5) D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966).

(6) M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).

(7) M. Kasha in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins University Press, Baltimore, Md., 1961, p 31.

(8) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(9) For recent reviews see (a) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Interscience, New York, N. Y., 1969, p 191 ff; (b) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970); (c) P. J. Wagner and R. W. Spierke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

Nicholas Turro has authored several books in the general area of photochemistry. He received his Ph.D. in 1963 from Caltech, and after a year's postdoctoral work, joined the staff at Columbia University. Professor Turro supervises a large and active research group between or after working on their Ph.D.'s with him: Douglas R. Morton, Jr. (now a postdoctoral associate with William Johnson at Stanford University), J. Christopher Dalton (now Assistant Professor at the University of Rochester), George L. Farrington, Neil E. Schore, and Mark P. Niemczyk. Keith Dawes (Ph.D. from University of Manchester, England, and presently at Oxford University) and Richard R. Hautala (Ph.D. from Northwestern) were postdoctoral fellows in his group.

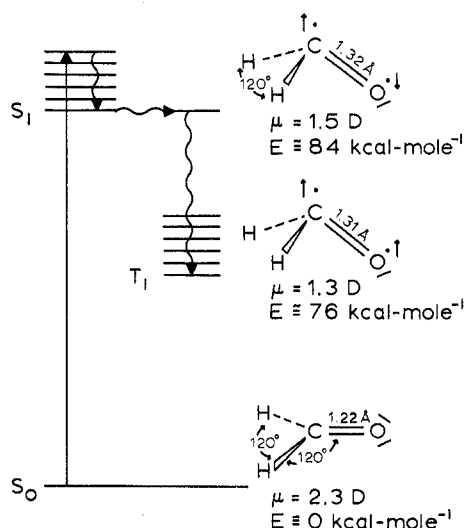
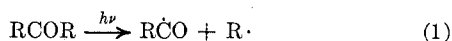
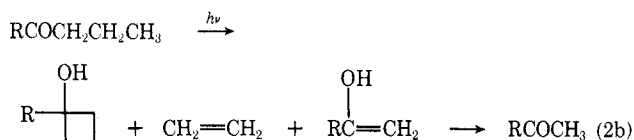
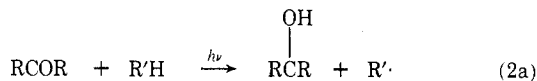


Figure 1. Properties of formaldehyde in its thermally equilibrated ground state, lowest excited singlet state, and lowest triplet state. It should be noted that, although the ground state is planar, the excited singlet possesses an angle of 20° intersecting the HHC plane and the CO axis. The triplet state is even more puckered, with a corresponding angle of 35° .

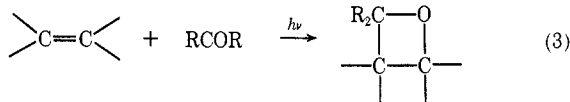
(a) cleavage of the C—C=O bond, known as α cleavage or type I cleavage (eq 1); (b) abstraction of a hydrogen atom by the carbonyl oxygen atom, which may occur intermolecularly (eq 2a) or intramolecularly (eq 2b); the latter case is known as type II reaction;



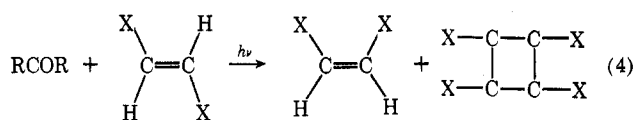
(c) cycloaddition to an unsaturated carbon-carbon linkage (eq 3). Reactions associated with (c) are



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sensitized isomerization and dimerization of ethylenes (eq 4).



We shall consider each of the above processes, emphasizing recent contributions from work done at Columbia and other laboratories. First, we must briefly review some of the important characteristics of photochemical reactions which will be crucial for a valid

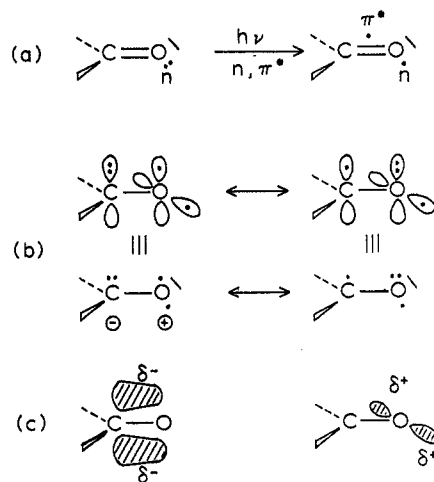


Figure 2. Description of an n, π^* excitation (a), the electronic distribution in an n, π^* S_1 or T_1 state (b), and the amphoteric nature of an n, π^* S_1 and T_1 state (c). Key concepts of the approximate model (which cannot differentiate between properties of S_1 and T_1 or predict their nuclear configurations) are (1) the nucleophilic character of the π faces, (2) the electrophilic character at the edges of the carbonyl oxygen atom, and (3) the radical-like character of both the π faces and the carbonyl edges.

and convincing extrapolation from the realm of laboratory observations into the realm of intellectual constructs of what occurs at the molecular level.

Efficiency and Yields of Photoreactions: Probability That an Absorbed Photon Will Result in the Formation of a Molecule of Product¹⁰

Simple and convenient methods are available for measuring the number of photons absorbed by an organic molecule. The *efficiency* of photoreaction, *i.e.*, the number of molecules of photoproduct formed divided by the number of photons absorbed, is known as the *quantum yield*, ϕ , of product formation. The "chemical yield" of a photoreaction depends upon the relative efficiencies of competing irreversible reactions which occur after photon absorption. The *reactivity* of S_1 and T_1 toward a given process is properly associated with the *rate constant*, k , for the process. The quantum yield is basically a measure of the rate of a process (from S_1 or T_1) divided by the rate of light absorption (I_a) leading to the reactive state, *i.e.*

$$\phi = \frac{\text{molecules reacting/sec}}{\text{photons producing reactive state/sec}} = \frac{k[M^*]}{I_a} \quad (5)$$

Thus, in order to measure k we must have information in addition to ϕ . In general, ϕ is a poor guide to reactivity, even in closely related cases, because of the nature of competing photochemical processes which determine ϕ .¹¹ As we shall see, however, measurement of ϕ will be useful in establishing certain aspects of photochemical reactions.

Knowledge of both efficiencies and reactivities of S_1 and/or T_1 allows us to make important conclusions

(10) N. J. Turro, *J. Chem. Educ.*, **44**, 536 (1967).

(11) For example, see P. J. Wagner and H. N. Schott, *J. Amer. Chem. Soc.*, **91**, 5383 (1969).

about "invisible chemical or physical processes," namely *radiationless energy loss mechanisms which lead to no net chemical change*.

Energetics and Dynamics of Alkanone S₁ and T₁ States

The chemically significant processes which interconnect S₀, S₁, and T₁ of acetone in an inert solvent provide a concise and informative model of the energetics and dynamics which will be crucial in understanding the photochemical reactions of alkanones. Excitation of acetone with light of wavelength 260–300 nm produces (after vibrational relaxation) S₁, the n,π* singlet state, in quantitative yield. The important features of S₁ for acetone are: (1) it possesses ~84-kcal/mole¹² excess electronic energy over S₀, acetone's ground state; (2) in the absence of external quenchers of S₁, only two important processes deactivate S₁: (a) intersystem crossing to T₁ and (b) fluorescence to yield S₀; (3) the rate constant for intersystem crossing (*k*_{ST}) is 5 × 10⁸ sec⁻¹ while the rate constant for fluorescence (*k*_F) is only ~10⁶ sec⁻¹; (4) both S₁ and T₁ are n,π* states.

The lifetime of S₁ (τ_S) is defined as the reciprocal of the rates of deactivation of S₁ (eq 6) and is inherently limited by the rate of intersystem crossing. Although the quantum yield of fluorescence from S₁ for acetone

$$\tau_S = (k_F + k_{ST})^{-1} = k_{ST}^{-1} \quad (6)$$

is quite low (~0.001), this emission is easily detected by sensitive fluorescence techniques. Fluorescence is a particularly versatile and valuable probe for quantitative study of the photoreactions of S₁ of alkanones.

If T₁ is produced, its major mode of deactivation is intersystem crossing to S₀.¹³ The latter process has a rate constant (*k*_D) which is considerably smaller (~10⁶ sec⁻¹) than the intersystem crossing process (*k*_{ST} ~ 5 × 10⁸ sec⁻¹), which serves as the major deactivation for S₁. The lifetime of T₁ (τ_T) is thus given by τ_T = (*k*_D)⁻¹.

Although the T₁ state possesses about the same amount of excess electronic energy (~78 kcal/mole) as S₁, quenching by electronic energy transfer to a qualified energy acceptor is generally more important for T₁ than for S₁ because of the longer lifetime of T₁.

Measurement of the Reactivity of S₁ and T₁

S₁ and T₁ of alkanones have certain "inherent" unimolecular paths for deactivation. If a molecule, Q, is capable of efficiently "robbing" S₁ or T₁ of its electronic excitation, then Q is called a "quencher." Experimentally, if the efficiency of a decay path of S₁ (*e.g.*, fluorescence) or T₁ (*e.g.*, photoreaction) is measured as a function of [Q], then one has obtained, in principle, information on the relative rates of quenching and excited-state deactivation. Equation 7, called the Stern-Volmer equation, is a convenient expression for re-

lating the deactivation of S₁ and/or T₁ to a quenching process. In this expression, φ⁰ is the quantum yield for a photoprocess (from either S₁ or T₁) in the absence

$$\frac{\phi^0}{\phi} = 1 + k_q[Q]\tau \quad (7)$$

of Q, φ is the quantum yield for the same process in the presence of Q, τ is the lifetime of the reactive state in the absence of Q, *k*_q is the bimolecular rate constant for quenching of the reactive state, and [Q] is the concentration of quencher. Thus, the slope of an experimentally linear plot of φ⁰/φ *vs.* [Q] yields *k*_qτ, which is simply *k*_q/*k*_d where *k*_d is the "inherent" rate constant for deactivation of the excited state; *k*_d is generally directly related to the reactivity of S₁ and/or T₁. Finally, if a plot of φ⁰/φ *vs.* [Q] is not linear (and experimental artifacts for the nonlinearity can be reasonably eliminated), then either the reaction or the quenching must be occurring from more than one excited state.¹⁴

Fluorescence quenching is an exceedingly specific and convenient technique for measuring the reactivity of alkanones toward various primary processes. In effect, the absorbed photon simultaneously "labels" and activates the alkanone S₁ state, while the emitted fluorescence photon serves as a built-in "clock" to tell us how fast our labeled ketone reacts or is quenched. We can use eq 7 by measuring the quenching of fluorescence as a probe of the reactivity of S₁ (*k*_q = *k*_F¹⁵).

Unfortunately, since phosphorescence from alkanones is generally too weak to be measured in fluid solution at room temperature, an indirect method, usually quenching of T₁ by 1,3-dienes, must be employed to monitor the reactivity of alkanone triplets.¹⁵ 1,3-Dienes are probably diffusion-controlled quenchers of T₁. Primary photochemical processes from T₁ can be made to compete with bimolecular diene quenching, and if Stern-Volmer kinetics are followed, the slope of the Stern-Volmer plot yields information on the reactivity of T₁.

The α-Cleavage (Type I) Reaction

Although irradiation of acetone in "inert" organic solvents does not lead to efficient photoreaction associated with α cleavage,^{16a} methyl *tert*-butyl ketone and di-*tert*-butyl ketone undergo photolysis to hydrocarbon and carbonyl fragments.^{16b}

Nearly all cyclopentanones and cyclohexanones have a tendency to photorearrange to an unsaturated aldehyde and/or a ketene (Scheme I).^{17a,b} These reactions are nicely correlated by the following simple working hypothesis: *photon absorption is followed by homolytic cleavage of a bond α to the excited carbonyl function*. In the case of acyclic ketones, the result of α cleavage is

(14) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970).

(15) For a recent review see ref 9a, p 96 ff.

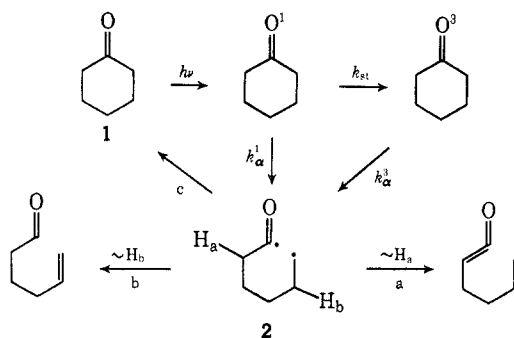
(16) (a) N. C. Yang in "Reactivity of the Photoexcited Organic Molecule," Interscience, New York, N. Y., 1967, p 145; (b) N. C. Yang and E. D. Feit, *J. Amer. Chem. Soc.*, **90**, 504 (1968).

(17) For reviews of recent work on the photochemistry of cyclic ketones see: (a) N. J. Turro, *et al.*, *Annu. Surv. Photochem.*, **2**, 1970; (b) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

(12) The energies of S₁ and T₁ are only approximate, since structure is essentially absent in the electronic spectra of acetone.

(13) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

Scheme I



production of a radical pair in a solvent cage. The observed products then follow naturally from the expected chemistry (in and out of the solvent cage) of an acylalkyl radical pair: disproportionation, decarbonylation, and hydrogen abstraction from solvent. For 5- and 6-ring ketones, a 1,5- and 1,6-biradical, respectively, are produced, and intramolecular disproportionation yields the observed predominant products.

Let us now ask the question: In which state or states, S_1 and/or T_1 , does α cleavage occur? In order to answer questions of this type there is a standard technique employed which takes advantage of the very fast rate of quenching of alkanone triplet states by 1,3-dienes. One measures the efficiency of formation of α -cleavage products as a function of 1,3-diene concentration. Since unimolecular α cleavage from T_1 will compete with bimolecular quenching by 1,3-diene (to regenerate S_0 of the alkanone), a Stern-Volmer plot, which obeys eq 7, will be observed experimentally if the reaction occurs only from T_1 and only T_1 is quenched by the diene. Results for methyl *tert*-butyl ketone^{16b} and for cyclohexanone^{9c} (1) reveal that, while the plot for cyclohexanone does indeed follow Stern-Volmer kinetics, the plot for methyl *tert*-butyl ketone is distinctly nonlinear, decreasing in slope at higher concentrations of 1,3-diene. This latter behavior is *prima facie* evidence for reaction from two different alkanone excited states.¹⁴ In addition, the quenching which occurs at high diene concentration is paralleled by quenching of ketone fluorescence.^{18,19} We can conclude that quenching of S_1 is occurring at high concentrations of diene, while at low concentrations of diene predominantly T_1 is being quenched. The data allow us to estimate the reactivity of both S_1 and T_1 of **2** toward α cleavage, while for **1** we can only estimate the reactivity for T_1 because no reaction from S_1 could be detected by diene quenching. However, since the lifetime of S_1 can be measured directly,²⁰ the total rate of deactivation of S_1 is available and an upper limit for the reactivity of S_1 toward α cleavage can be obtained.²¹

Analysis of such data^{9,16,20} has led to the following generalizations concerning the α -cleavage process: (1) there is a startling difference in reactivity toward α cleavage between T_1 and S_1 for alkanones, T_1 being generally more reactive; (2) substitution of α hydrogens by α -alkyl groups increases T_1 reactivity toward cleavage; (3) cleavage of the more substituted bond (which parallels radical stability) generally determines product structure; (4) a "loss" mechanism exists for dissipating the energy of absorbed photons without net product formation.

We can summarize the general pattern with cyclohexanone as an example (Scheme I). Path c in Scheme I is included in order to provide a "loss" mechanism for photon energy. This choice, rather than a more general "radiationless deactivation" of T_1 (no or very feeble phosphorescence is generally observed for alkanones in fluid solution), is preferred. A loss mechanism is required to explain that, although a relative reactivity difference of 100–1000 is observed experimentally,^{9,16,20} the efficiencies of net reaction are always significantly less than unity. Thus, the proposal that reactivity measures the rate of formation of an intermediate, and the product formation efficiency measures the stabilization of the intermediate, is an attractive model to help us understand the available data. The partitioning of the radical pair produced by α cleavage will depend on the ease of formation of transition states for transfer of H_a , H_b , and recyclization. Use of molecular models shows that intermediates such as **2** can be used to predict variations in the relative rates of paths a and b as a function of structure.²² Finally, strong support for the existence of an intermediate such as **2** and a general loss mechanism as suggested by path c comes from the observation that *cis*- and *trans*-2,3-dimethylcyclohexanones²³ undergo photoepimerization concomitant with photoisomerization by way of α cleavage.

The photochemistry of cyclobutanones differs significantly from that of most alkanones.²⁴ For example, three major products which do not have a general analogy in cyclopentanone or cyclohexanone photochemistry are generally formed. Indeed, product formation is both stereospecific and stereoselective (eq 8–10), and no photoepimerization occurs during the photolyses.²⁵ Furthermore, in contrast to the relatively facile quenching of cyclopentanone photochemistry by 1,3-dienes, even high concentrations ($>1 M$) of the latter do not measurably²⁵ inhibit cyclobutanone reactions. One can conceive of an intermediate, formed by α cleavage, which can be stabilized by reasonable paths which will lead to the observed products. However, one must impose a special quality on such an intermediate—

(21) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2564 (1970).

(22) G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, **4**, 211 (1965); *Pure Appl. Chem.*, **9**, 607 (1964).

(23) J. A. Barltrop and J. D. Coyle, *Chem. Commun.*, 1081 (1969).

(24) (a) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967); (b) N. J. Turro, E. Lee-Ruff, D. R. Morton, and J. M. Conia, *ibid.*, 2991 (1969); (c) D. R. Morton, E. Lee-Ruff, R. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

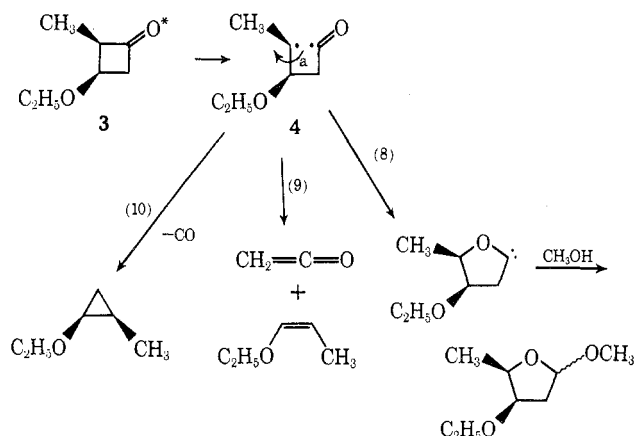
(25) N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970).

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

(19) F. S. Wettack, G. D. Renkes, M. G. Renkly, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970).

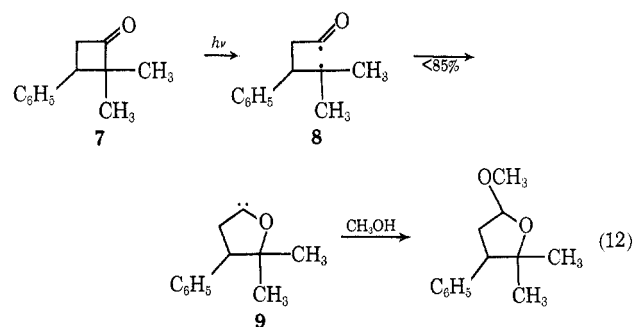
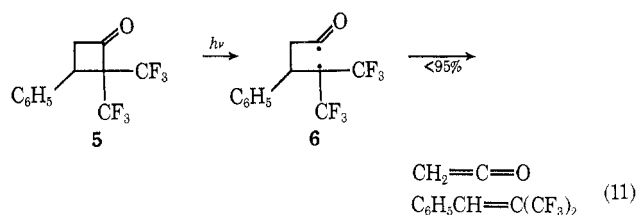
(20) D. S. Weiss, N. J. Turro, and J. C. Dalton, *Mol. Photochem.*, **2**, 91 (1970).

it must collapse to products without loss of stereochemistry. Thus, if we consider the "biradical" 4 as a species formed by α cleavage, 4 must undergo reaction *via* paths 8, 9, and 10 faster than rotation about bond "a."



Although such rapid unimolecular stabilization is conceivable, calling 4 a "biradical" does not sit well, if we expect such species to behave like two loosely intramolecularly connected monoradicals.²⁶ At any rate, we feel that either 4 exists briefly but then rapidly collapses to products or the transition states for product formation all have considerable biradical character. Since 1,3-dienes fail to quench the photoreactions of cyclobutanones, the reactive state might be S_1 or an unquenchable T_1 (or some mixture of both), although the stereospecificity might make a singlet reaction more attractive.^{25,27}

The striking contrast²⁸ in the photochemical behavior of 5 and 7 (eq 11 and 12) provides strong support for



an intermediate or transition state such as 6 and/or 8. Since the most substituted α bond breaks in both cases, in spite of considerably different electronic den-

sities of the α bond which is cleaved, it appears that the α bond must be nearly completely cleaved before the product-determining step occurs. On the basis of hypotheses of transition states or intermediates such as 6 and 8 we can understand why (a) the most substituted bond cleaves and (b) why the more nucleophilic alkyl carbon of 8 migrates preferentially relative to the electron-poor free-radical carbon of 6.

Hydrogen Abstraction Reactions of Alkanones

Only a handful of reactions concerned with intermolecular hydrogen abstraction reactions of S_1 and/or T_1 states of alkanones have been reported.²⁹ A report has appeared^{29a} in which evidence for a large reactivity difference between T_1 and S_1 states toward hydrogen abstraction from $(n\text{-Bu})_3\text{SnH}$ was presented. Later work, however, showed that complications,²⁷ *i.e.*, possible "quenching" of ketyl radicals by dienes and reactions of tin radicals with dienes,³⁰ can vitiate standard kinetic analyses. 2-Adamantanone fluorescence³¹ (*i.e.*, S_1) is quenched by $(n\text{-Bu})_3\text{SnH}$ with a rate constant of $5 \times 10^8 M^{-1} \text{sec}^{-1}$. This number is quite comparable to the reported rate ($\sim 8 \times 10^8 M^{-1} \text{sec}^{-1}$) for hydrogen abstraction from $(n\text{-Bu})_3\text{SnH}$ by T_1 of acetone.^{29a}

The intramolecular analog (type II abstraction) has been the focus of considerable recent investigation.³² Although here also complications of kinetic analyses have been found, several reactivity and efficiency trends appear to be clear-cut.

Since intermolecular hydrogen abstraction seems to clearly involve the intermediacy of ketyl radicals, an analogous model may explain the intramolecular counterpart. We shall assume a model in which reaction from both S_1 and T_1 of alkanones structurally capable of undergoing type II reactions proceeds with biradical-like transition states and then ask whether evidence exists to suggest that such a transition state will lead to actual biradical intermediates such as 11 (Scheme II). We will try also to inquire about the spin states of such intermediates.

It is generally found that k_d (which is the measure of all deactivation paths of S_1 and T_1) increases as the abstracted hydrogen goes from primary to secondary to tertiary in keeping with expectations of the effect of bond strengths of the γ C-H bonds.³² But again an inefficiency is noted, as measured by ϕ_{II} , which is maintained throughout the series even though rates go up by an order of magnitude.

Available data suggest that the T_1 reaction very probably proceeds *via* a relatively long-lived biradical; *e.g.*, racemization of the γ carbon of 10 ($R_1 = \text{CH}_3$; $R_2 = \text{C}_2\text{H}_5$) (Scheme II) appears to occur from T_1 .³³ Thus, the triplet must survive long enough to undergo

(26) For interesting discussions of the biradical problem see (a) R. Freeman, *Can. J. Chem.*, **44**, 245 (1966); (b) L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

(27) N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, **2**, 98 (1970).

(28) D. R. Morton, Columbia University, unpublished results.

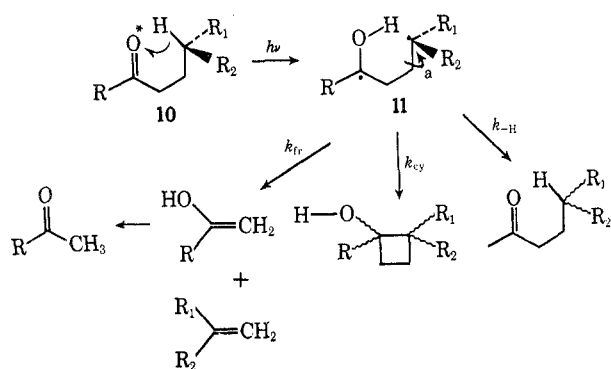
(29) (a) P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966); (b) R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 3751 (1967).

(30) N. J. Albert, *et al.*, *Chem. Ber.*, **103**, 1372 (1970).

(31) G. Farrington and R. Hautala, Columbia University, unpublished results.

(32) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

Scheme II

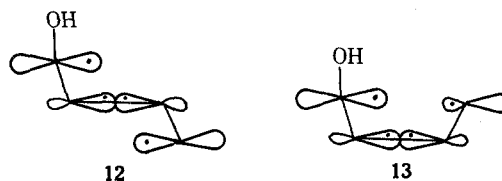


rotations about bond a and then disproportionate by hydrogen return to yield the optical enantiomer of the starting material.³³ This result is also consonant with the observation that the efficiency of the type II reaction from T_1 is enhanced as solvent polarity increases, if one assumes that the intermediate biradical **11** survives long enough to be solvated and that intermolecular hydrogen bonding interferes to a greater extent with hydrogen reversal than with the fragmentation and cyclization.

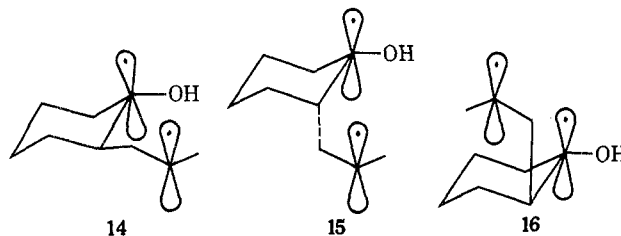
On the other hand, the S_1 state apparently does not yield a biradical which survives long enough to have its chemistry affected by solvent. In addition, the S_1 reactions of **10** do not result in racemization and are not totally efficient, thereby again demanding a "loss mechanism." Although hydrogen reversal would explain the inefficiency, *i.e.*, from a "singlet biradical," we must again impose requirements on the rates of internal molecular motions of this species, *i.e.*, rotations about bond a must be slow relative to hydrogen reversal, in order to explain the lack of racemization from S_1 . This assumption implies that an ethylene (in a properly labeled case) should be formed stereospecifically from S_1 , as has been found.^{26b}

Measurements of reactivity and efficiency can thus help reveal "invisible" radiationless paths which regenerate the starting materials. For example, quenching data suggest that type II abstraction determines the triplet lifetime of 2-*n*-propylcyclohexanone ($1/\tau_T = 7 \times 10^8 \text{ sec}^{-1}$; $1/\tau_T$ for 2-methylcyclohexanone is $3 \times 10^8 \text{ sec}^{-1}$), yet only a very small percentage of the T_1 states undergo net type II fragmentation or cyclization.^{20,34} Thus, while kinetic analyses suggest that a major deactivation path of T_1 is type II abstraction, efficiency measurements demand that hardly any net type II reaction occurs from T_1 . Kinetic and efficiency analyses of the S_1 state lead to the conclusion that the rate of type II abstraction from S_1 is $\sim 10^9 \text{ sec}^{-1}$, with an efficiency of *ca.* 10%. Interestingly then, the T_1 and S_1 states are of comparable reactivity, but S_1 is more efficient at going to products,

Scheme III



Scheme IV



in striking contrast to acyclic alkanones whose T_1 state goes to products with up to 80–100% efficiency in some cases.^{33–35}

How can we understand these results? Let us assume that (a) a biradical intermediate is produced by type II abstraction from both S_1 and T_1 and that (b) it can undergo fragmentation, cyclization, or hydrogen return. Hydrogen return to regenerate the starting ketone is apparently much faster than fragmentation or cyclization. This derives naturally from consideration of the principle of maximum overlap of developing orbitals and the shape of the lowest energy transition states for cleavage and cyclization of a 1,4-biradical. Transition states similar to **12** and **13**, in which the p orbitals at the free-radical centers can be parallel to the β bond, should be favored for cleavage (Scheme III), since they allow maximum continuing overlap of the developing π orbitals of the enol and alkene. Now, in the case of 2-*n*-propylcyclohexanone, species **14** is produced by intramolecular γ -hydrogen abstraction. Molecular models confirm what Scheme IV suggests: for **14** a transition state analogous to **15** is not attainable without severe molecular distortion, and a transition state like **16** requires either flipping the a higher energy shape, *i.e.*, one with an axial alkyl group, or a bond rotation to a twisted chair conformation. These unfavorable shapes may also be expected to resemble the best transition state for cyclization, thereby explaining the inefficiency of both cyclization and fragmentation. On the other hand, hydrogen reversal does not suffer from such orbital restrictions since only one new π system is to be developed and, indeed, the reversal becomes highly favored relative to the other two processes.

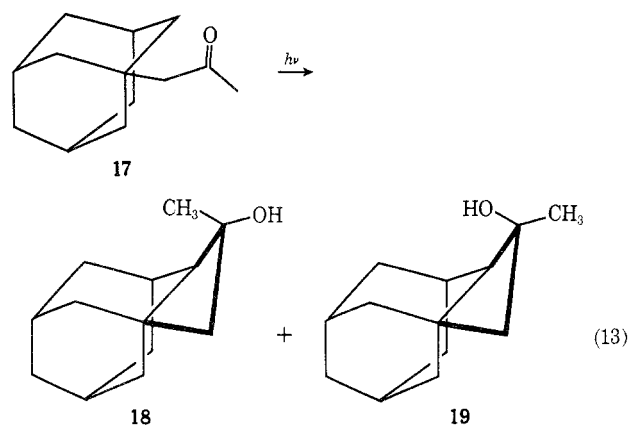
The 2-adamantyl-acetone system dramatically illustrates the effect of solvent polarity on type II reactions from S_1 and T_1 . Irradiation of **17** in benzene results in a quantitative yield³⁶ of the alcohols **18** and **19**. In

(33) (a) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **91**, 7550 (1969); (b) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

(34) D. S. Weiss and K. Dawes, Columbia University, unpublished results.

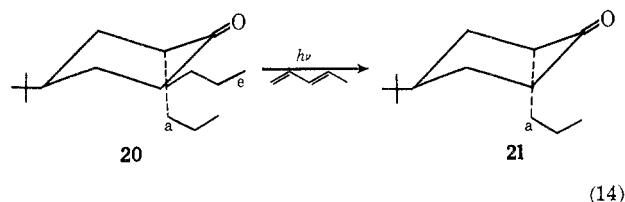
(35) P. J. Wagner, *Tetrahedron Lett.*, 5385 (1968).

(36) R. B. Gagosian, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4752 (1970).



MeOH the efficiency of formation of **18** and **19** from the S_1 state is the same as in benzene, but the efficiency of formation of **18** and **19** from T_1 is increased by a factor of 10. As expected,³⁵ the more polar solvent inhibits hydrogen back-transfer in the biradical produced from T_1 only, and allows cyclization to compete more effectively with regeneration of starting ketone.

The proposed model for the n, π^* state suggests that type II abstraction from a side chain for which cyclic interaction of a γ hydrogen with the half-vacant n orbital is geometrically feasible should be facile, relative to abstraction of a γ hydrogen which is constrained by molecular geometry to approach the carbonyl oxygen atom from one of the π faces. This conclusion derives from the electrophilic nature of hydrogen abstraction by ketone n, π^* states. A prediction, therefore, for **20** is that only the equatorial group should be cleaved photochemically, thereby forming the less stable 2-*n*-propyl epimer,³⁷ and this is indeed found to be the result. In this case, 1,3-pentadiene is a convenient solvent to quench α -cleavage reactions originating from T_1 .



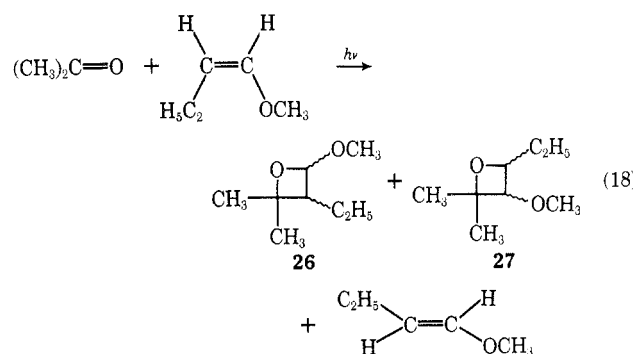
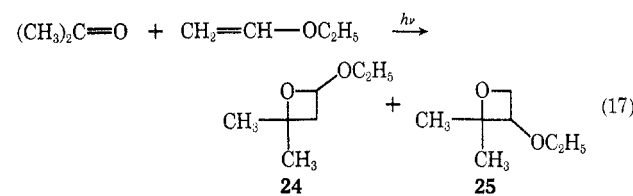
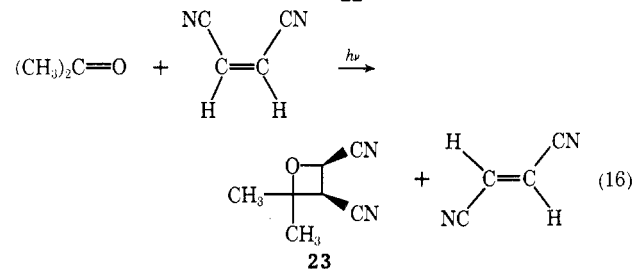
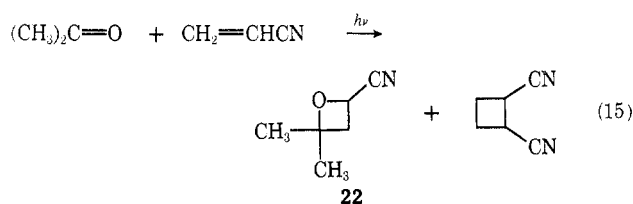
Photocycloaddition of Alkanones to Ethylenes and Photosensitized Reactions of Ethylenes

Let us now consider the interaction of the S_1 and T_1 states of alkanones with the following classes of ethylenes: (a) α, β -unsaturated nitriles³⁸ and (b) enol ethers.³⁹ Equations 15–18 summarize the types of reactions which are observed in such systems. Clearly, there exists a striking contrast in the behavior of these systems with respect to stereospecificity, regioselectivity,

Table I
Relative Rates for Quenching of Alkanone Fluorescence for Some α, β -Unsaturated Nitriles and Some Enol Ethers^a

Alkanone	Unsaturated Nitriles			
	$t\text{-NCCH=CHCN}$	$\text{CH}_2=\text{CHCN}$	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$	$\text{CH}_2=\text{CHCH=CHCN}$
Acetone	1.0 ^b	0.046	0.020	<0.01
Adamantanone	1.0 ^c	0.020	0.011	0.001
Alkanone	Enol Ethers			
	$c\text{-EtOCH=CHCHOEt}$	$\text{CH}_2=\text{C}(\text{OEt})_2$	$\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_3$	$\text{CH}_2=\text{CHCHOEt}$
Acetone	1.0 ^d	0.42	~ 0.11	<0.032
Adamantanone	1.0 ^e	0.13	~ 0.017	0.007

^a N. J. Turro, N. Schore, C. G. Lee, J. A. Barltrop, and H. A. J. Carless, *J. Amer. Chem. Soc.*, **93**, 3079 (1971). Acetonitrile solution. Error limits $\pm 20\%$. ^b The absolute quenching rate constant is $2.5 \times 10^9 M^{-1} \text{sec}^{-1}$. ^c The absolute quenching rate constant is $5.0 \times 10^9 M^{-1} \text{sec}^{-1}$. ^d The absolute quenching rate constant is $2.0 \times 10^9 M^{-1} \text{sec}^{-1}$. ^e The absolute quenching rate constant is $1.1 \times 10^9 M^{-1} \text{sec}^{-1}$.



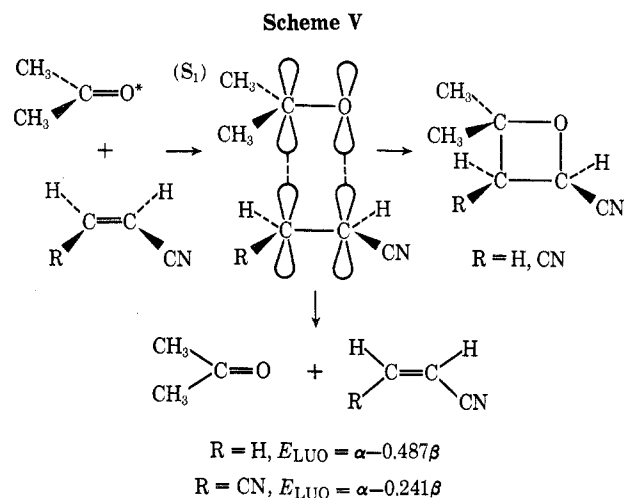
and sensitization of ethylene reactions. With such a wide variation in behavior one is faced with a challenging task to present a unifying theory, consistent with the previously discussed behavior of alkanone excited states.

Acetone fluorescence quenching by ethylenes (Table I) offers some real insight into and places severe restrictions on a unifying explanation of how the excited

(37) K. Dawes, J. C. Dalton, and N. J. Turro, *Mol. Photochem.*, **3**, 71 (1971).

(38) (a) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968); (b) J. J. Beereboom and M. von Witterman, *J. Org. Chem.*, **30**, 1231 (1965).

(39) (a) S. H. Schroeter and C. M. Orlando, *ibid.*, **34**, 1181 (1969); (b) N. J. Turro and P. A. Wriede, *ibid.*, **34**, 3562 (1969).



alkanone-ethylene interaction occurs. We see that the reactivity of S_1 toward unsaturated nitriles, which should behave as electrophilic (electron-poor) substrates, increases roughly as the "electron poorness" of the C=C bond increases. On the other hand, the reactivity of S_1 toward enol ethers, which should behave as nucleophilic (electron-rich) substrates, increases roughly as the "electron richness" of the C=C bond increases. Remember that S_1 is an amphoteric reagent (in the sense of Lewis acids and bases). In fact, the simple model of an n, π^* state has precisely the properties desired to explain the amphoteric nature of the S_1 state of alkanones: (a) an electrophilic region, due to a half-vacant n orbital, about the "edges" of the carbonyl oxygen, and (b) a nucleophilic region of space, due to the presence of a π^* electron, above and below the carbonyl "faces" (see Figure 2). The precise geometry of the S_1 state is deduced to be somewhat puckered on the basis of spectroscopic analyses,⁴⁰ although rapid inversion of one puckered shape into another is also expected. Thus, we anticipate that the interaction between the S_1 state and the nucleophilic cyanoethylenes will be most favorable when the reagent and substrate approach each other so that the π^* electron of S_1 overlaps most effectively with the lowest unoccupied orbital (LUO) of the cyanoethylenes. Such an expectation allows us to write down an interaction which nicely rationalizes the stereospecificity, regioselectivity, and reactivity of S_1 of alkanones and cyanoethylenes: the geometry for the most favored interaction transforms smoothly into the geometry of the product, and, therefore, stereospecificity is a natural consequence of the π^* -LUO interaction (Scheme V).

Indeed, the regioselectivity also nicely derives from such an interaction since the π^* orbital of the S_1 state is expected to have a coulombic negative character near the carbonyl carbon and a coulombic positive character near the carbonyl oxygen. Therefore, the sole formation of **22** is easily understandable on the basis of stabilization of plus-minus forces. Finally, the energy of the LUO of $\text{CH}_2=\text{CHCN}$ is much higher than that

Table II
Quenching of the Fluorescence of Norcamphors^{a, b}

Alkanone	k_q^f (t-DCE)	k_q^f (o-DEE)
	5.3	1.3
	2.1	0.16
	1.0	1.5
	5.7	1.4

^a Reference 43a and unpublished results. ^b 0.1 M solutions of ketones in acetonitrile. k_q^f values $\times 10^{-9} M^{-1} \text{sec}^{-1}$.

of $\text{NCCH}=\text{CHCN}$; therefore, the rate constant for quenching by the latter should be faster, and is indeed found to be, in spite of increased steric hindrance to the approach of the interacting centers.

The maximum efficiency of oxetane formation from S_1 is only about 10%. Thus, 90% of the photon energy is lost and does not result in isomerization or dimerization (at least in the case of *trans*-1,2-dicyanoethylene, DCE).⁴¹ This result leads us to propose that the interaction between S_1 and DCE yields an exciplex,⁴² *i.e.*, an aggregate of S_1 and DCE which possesses some measure of stability and for which electronic excitation is a property of the aggregate rather than being essentially localized on either component. The exciplex can then (a) stereospecifically dissociate into S_0 of the alkanone and S_0 of DCE with the electronic energy being dissipated as increased translational or vibrational energy of the fragments and solvent, or (b) stereospecifically collapse into oxetane (Scheme V).

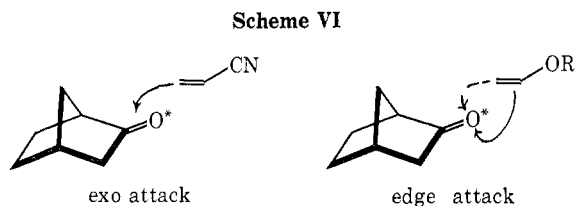
A compelling confirmation of the strong directional specificity of quenching of S_1 by DCE was obtained by a study of fluorescence quenching⁴³ of norcamphor and some of its alkyl derivatives (bicyclo[2.2.1]-2-heptanones) by DCE (Table II). The results convincingly demonstrate a preference for quenching by DCE above and below the carbonyl faces, *i.e.*, the region of space expected to be nucleophilic according to the n, π^* state model. Furthermore, 7-methyl groups have the strongest effect on inhibiting the rate of quenching by DCE. It should be noted that the response of k_q^f (eq 7, fluorescence quenching) to ketone structure shows a strong resemblance to the reactivity for attack of nucleophiles on the ground states of bicyclo[2.2.1]-2-

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

(42) T. Forster, *Angew. Chem., Int. Ed., Engl.*, **8**, 333 (1969); exciplexes are molecular aggregates defined as being stable in an electronically excited state but not in their ground states.

(43) (a) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Amer. Chem. Soc.*, **92**, 6978 (1970); for related studies see (b) J. C. Dalton, D. M. Pond, and N. J. Turro, *ibid.*, **92**, 2173 (1970); (c) N. J. Turro, M. Niemczyk, and D. M. Pond, *Mol. Photochem.*, **2**, 345 (1970).

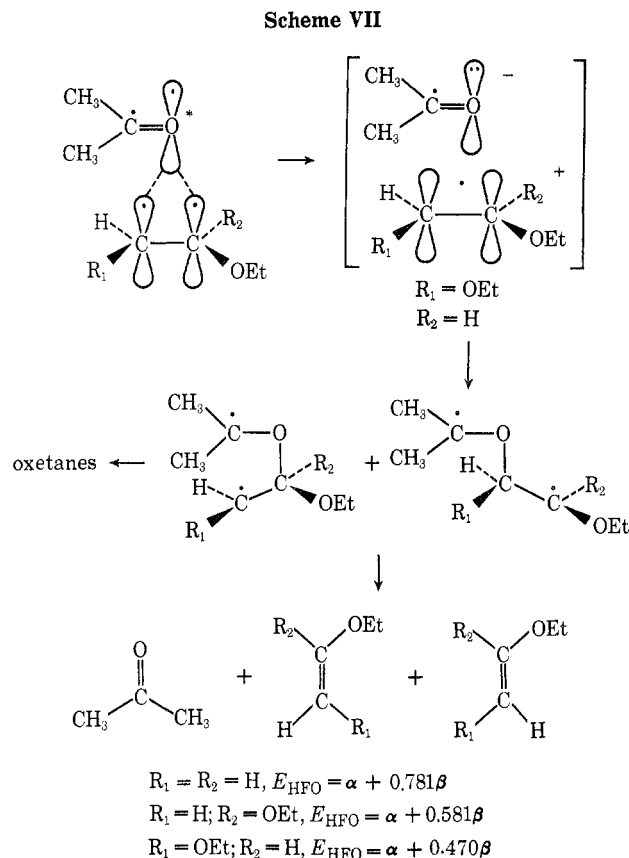
(40) H. E. Howard-Lock and G. W. King, *J. Mol. Spectrosc.*, **36**, 53 (1970).



heptanones; *i.e.*, attack on the *exo* face of the carbonyl group is favored (Scheme VI).

In striking contrast to the situation for unsaturated nitriles, the formation of oxetanes from enol ethers is neither stereospecific nor regioselective. Furthermore, the reactivity pattern resembles that expected for attack by an electrophilic reagent on the nucleophilic enol ethers. Our model for the n, π^* state suggests that the edges of the carbonyl oxygen atom attack the highest filled orbital (HFO) of the enol ethers, *i.e.*, the reactivity increase indicated in Table I parallels the increase in energy of the electrons in the enol ether's HFO. This, in turn, suggests a transition state for quenching which possesses considerable charge-transfer (CT) character. In fact, if the transition states for product formation also are assumed to possess CT character, then the lack of stereospecificity and regioselectivity can be explained in the following way. Suppose the interaction of, *e.g.*, S_1 with an enol ether is dominated by the overlap of the half-filled n orbital with the HFO of the enol ether to form either a radical anion-radical cation pair or to lead to a transition state for quenching very similar to such a pair, *i.e.*, as shown in Scheme VII. The charge densities of C_1 and C_2 of a radical cation of an enol ether turn out to be very similar, so that the collapse of a transition state possessing considerable CT character (or an actual radical cation-radical anion pair) might well be very unselective with respect to the regioselectivity of C-O bond formation. The loss of stereospecificity could come about in one of two ways: the radical cation may have a sufficiently low bond order that it may isomerize prior to oxetane formation or capture of an electron to regenerate an enol ether; the second possibility is that collapse of the radical cation-radical anion pair leads to biradicals which themselves lose stereochemistry and collapse to oxetanes or ground-state alkanone and enol ether. Calculations⁴⁴ indicate that the bond order in the radical cations of enol ethers is too high to permit facile bond rotation.

Another interesting aspect of oxetane formation and olefin isomerization is revealed by quenching studies with 1,3-pentadiene. At a fixed concentration of 1-methoxybutene (0.05 *M*), linear Stern-Volmer kinetics for quenching of T_1 of acetone are observed at low concentrations of diene (<0.05 *M*), while at higher concentrations of diene (>0.1 *M*) the Stern-Volmer plot shows clear-cut curvature downwards, until at ~ 0.4 *M* a residual unquenchable reaction remains.⁴⁵



Thus, we conclude that at higher concentrations of diene S_1 is reacting with methoxybutene to yield oxetane and to isomerize the enol ether, while at lower concentrations of diene both S_1 and T_1 attack the enol ether. Importantly, (a) there is greater oxetane-forming stereospecificity in the S_1 reaction relative to T_1 reaction, (b) the efficiency of isomerization by S_1 appears to be less than that of T_1 , (c) the rate constants for attack by S_1 and T_1 are comparable, and (d) the regioselectivity for oxetane formation is essentially the same for attack of S_1 or T_1 on 1-methoxybutene.⁴⁵

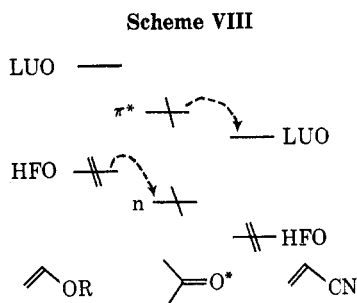
Points a and b relate, we believe, to the spin state immediately preceding the intermediates (charge radical pairs or 1,4-biradicals) which lose stereochemistry, *i.e.*, the singlet intermediates tend to cyclize to oxetanes or fragment to starting alkanone and enol ether favorably relative to loss of stereochemistry. However, the triplet intermediates may only rotate about single bonds, thereby losing initial stereochemical memory, until a spin flip occurs. At that point the newly formed singlet biradical can collapse to stable products. Indeed, as measured by stereochemical loss in oxetane formation, the triplet intermediate(s) undergo many bond rotations before cyclization occurs.

Now let us consider the alkanone photosensitization⁴⁶ of ethylene dimerization and isomerization and ask whether dimerizations and *cis-trans* isomerizations are mechanistically connected to photocycloaddition,

(44) N. Schore, Columbia University, unpublished results. For parameters see: B. Pullman and A. Pullman, *Rev. Mod. Phys.*, **32**, 428 (1960).

(45) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970); **90**, 6863 (1968).

(46) N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969).



or are they unrelated side reactions?¹¹ The isomerization and dimerization of the unsaturated nitriles probably result solely as a result of triplet energy transfer from T_1 to the ethylene. The triplet energy (E_3) of $\text{CH}_2=\text{CHCN}$ is estimated to be ~ 60 kcal/mole above its ground state.⁴⁷ Thus, T_1 of alkanones ($E_3 \sim 78$ kcal/mole) should transfer excitation to α,β -unsat-

urated nitriles at close to the diffusion-controlled rate. Whether dimerization occurs or not is probably a function of unsaturated nitrile structure, with 2-substituents reducing the efficiency of triplet ethylene coupling to form dimers, relative to simple deactivation of triplet ethylene by rotation about the excited $\text{C}=\text{C}$ bond.

Scheme VIII summarizes our view of the leading interactions between the n,π^* states of alkanones and ethylenes. This formulation emphasizes donor-acceptor interactions in the transition state for quenching. Thus, a charge transfer from the HFO of an enol ether to the electrophilic n orbital in the one case, and a charge transfer from the π^* orbital to the LUO of the unsaturated nitrile, appear to be the most important electronic factors in the quenching step.

The authors wish to thank Mr. C. Lee for measuring some of the Stern-Volmer data reported herein. Preprints of important contributions of Professors N. C. Yang and P. J. Wagner are also gratefully acknowledged. The splendid research efforts of Drs. P. Wriede, D. S. Weiss, and R. B. Gagosian provided the basis for much of the work discussed in this manuscript.

(47) (a) D. M. Gale, *J. Org. Chem.*, **35**, 970 (1970); (b) R. S. H. Liu and D. M. Gale, *J. Amer. Chem. Soc.*, **90**, 1897 (1968); (c) M. Herberhold and G. S. Hammond, *Ber. Bunsenges. Phys. Chem.*, **72**, 309 (1968).