The results lead one to treat compounds containing four-membered rings in a different fashion than other cycloalkanes. A more detailed treatment for these compounds must separate local effects of bond angle deformation from the 1-3 repulsive part and must address the problem of torsional interactions.

References and Notes

(1) Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-72-2239. The calculations were performed using POLYATOM-II and GAUSSIAN-70 and the CDC 6600 and 7600 computers at the Brookhaven National Laboratory. The programs were obtained from the Quantum Chemistry Program Exchange.

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(12) Similar results would be expected for other AH_4 species. However, with NH_3 and other compounds having a lone pair and missing an atomic center at one vertex of the tetrahedron, the results will be quite different.

(13) The figures were drawn using the computer program developed by W. L. Jorgensen (cf. W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973). We thank Dr. Jorgensen for making the program available to us. It was modified by J. W. to accept STO-3G and 4-31G wave functions and to run on a PDP-11/45 minicomputer.

(14) The C–H overlap population decreases from 0.381 at 109.5° to 0.352 at 160° and 0.312 at 180°. Similarly, the hydrogen charge drops from 0.848 to 109.5° to 0.777 at 160° and 0.638 at 180° (r = 1.0936 Å, 4-31G).

(15) A similar observation has been made by J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969), in their study of the relative energies of pyramidal and planar ammonia.

(16) This molecule will, of course, not be planar. In one reasonable conformation, a plane could be passed through the central carbon and the four methylene groups. Two of the CH groups would lie above this plane and two would lie below it. An angle $\alpha \approx 140°$ would appear reasonable for such a conformation.

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(18) Cyclobutane and polycyclic compounds containing cyclobutane rings are unique in that there are fewer 1-3 interactions than C-C-C bond angles. Thus, cyclobutane has four C-C-C angles but only two 1-3 interactions, whereas cyclopentane has five C-C-C angles and five 1-3 interactions. It is not unreasonable to relate 1-3 hydrogen interactions and 1-3 carbon interactions despite the obviously larger nuclear charge of carbon. Much of the nuclear charge is shielded by the electrons and so the effective charge is only slightly greater than that of hydrogen. This is compensated by the greater C-C bond length. The similarity of 1-3 interactions for a given angle is shown by the observation that the C-C-C angle in propane is only slightly larger than tetrahedral.

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Mechanisms of Photochemical Reactions in Solution. LXXVII.[1] Energy Wastage and Exciplex Formation in the Quenching of a Ketone Triplet by Sterically Hindered Alkenes

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Abstract: The interactions of acetophenone, a familiar triplet photosensitizer, with the cis and trans isomers of 2,2-dimethyl-3-hexene (**1**), 4,4-dimethyl-2-pentene (**2**), and 3,4-dimethyl-2-pentene (**3**) have been studied. All the alkenes are reactive quenchers of the excited sensitizer molecules. However, the quantum yields for isomerization of *trans*-**1**, *trans*-**2**, and both isomers of **3** are very low. Since little or no oxetane formation is observed in any case, we conclude that quenching results mostly in energy wastage by nonradiative decay with the four alkenes which do not isomerize efficiently. *cis*-Piperylene was allowed to compete with *cis*-**1** for sensitizer triplets. The results indicate that the alkene and acetophenone triplets form an exciplex which can be quenched by piperylene. Competition between *trans*-**3** and *cis*-piperylene at high concentration of the alkene indicates that there is a quenching reaction which is kinetically second order with respect to the alkene.

The interaction of the triplet states of ketones with alkenes leads to energy transfer and energy wasting steps in which both molecules revert to their single ground states.[2-4] Such bimolecular reactions are often discussed by reference to mechanistic models involving the intermediate formation of triplet exciplexes.

Singlet exciplexes are obviously formed when fluorescence quenching is accompanied by new, red-shifted emission[6] so extension to many fast fluorescence-quenching interactions even when no new emitting species is formed seems reasonable.[7-12] This kind of speculation is fortified by the fact that seemingly modest variation of structure of quencher and quenchee produces new classes of fluorescent exciplexes.[13-15] In fact, Caldwell and Smith present kinetic evidence that quenchable precursors to [2 + 2] cycloaddition are the fluorescent exciplexes formed from 9-cyanophenanthrene and various electron rich olefins.

Further extension of the exciplex model to molecular reactions of triplet states is often made,[2,3,16-26] albeit with less confidence. Although the binding energy of triplet exci-

Table I. Data from Stern–Volmer Studies of Alkenes in Benzene

Alkene	$(k_q\ \tau)^{-1\,a}$	$\Phi^{\infty\,b}$	$k_t{}^c$ or $k_c{}^c$
trans-2,2-Dimethyl-3-hexene (*trans*-1)	6.2	0.044	5.4×10^6
cis-2,2-Dimethyl-3-hexene (*cis*-1)	0.05	0.51	5.8×10^7
trans-4,4-Dimethyl-2-pentene (*trans*-**2**)	1.96	0.053	1.4×10^7
cis-4,4-Dimethyl-2-pentene (*cis*-**2**)	0.083	0.77	2.3×10^7
trans-3,4-Dimethyl-2-pentene (*trans*-3)	1.0	0.004	3.7×10^8
cis-3,4-Dimethyl-2-pentene (*cis*-3)	0.95	0.007	2.2×10^8

[a] Slope in mol l.$^{-1}$. [b] Intercept^{-1}. [c] Intercept/slope × τ; units M^{-1} sec^{-1}.

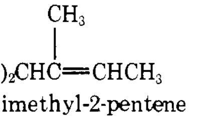
plexes is expected to be lower than that of singlet exciplexes,[27] there are well-documented examples of phosphorescence from triplet exciplexes,[28] but not many.

In this paper we will present the results of a study of the interaction of acetophenone triplets with some sterically hindered alkenes. The results show: (1) steric hindrance can divert most quenching encounters to energy-wasting, nonradiative decay; (2) quenching reactivity is not simply correlated with reactivity in energy transfer; and (3) kinetics indicate involvement of triplet exciplexes.

Results

Three pairs of cis–trans isomeric alkenes were studied.

$CH_3CH_2CH{=\!=}CHC(CH_3)$	$(CH_3)_3CCH{=\!=}CHCH_3$
2,2-dimethyl-3-hexene	4,4-dimethyl-2-pentene
cis- and *trans*-1	*cis*- and *trans*-**2**



$$\overset{\displaystyle CH_3}{\overset{|}{(CH_3)_2CHC}}{=\!=}CHCH_3$$

3,4-dimethyl-2-pentene
cis- and *trans*-**2**

Irradiation of benzene solutions containing the alkenes and acetophenone with 313-nm light led to isomerization in each case but with considerable variation in the quantum yields. Analysis for residual acetophenone after prolonged irradiation showed that quantum yields for disappearance of the sensitizer were very low (<0.002) in all cases. Vapor chromatograms showed the presence of only traces of other compounds. The amounts were so small that we made no attempt to isolate and characterize these other photoproducts. Quantum yields for oxetane formation[5] are apparently very low in these systems.

Quantum yields for isomerization were measured at different alkene concentrations and treated by the Stern-Volmer method by plotting Φ^{-1} against $[\text{alkene}]^{-1}$. The slope of such a plot should be $k_q\tau$ where k_q is the rate constant for quenching and τ the lifetime of sensitizer triplets in the absence of quencher. The intercept should be $(\Phi^\infty)^{-1}$, the reciprocal of the limiting quantum yield for isomerization at infinite alkene concentration. The lifetime of acetophenone triplets in benzene solution has been determined using flash excitation and triplet-triplet absorption as 2.6 μsec.[29] Since triplet lifetimes in solution are very sensitive to the presence of quenching impurities, we made an independent estimate of the lifetime using the induced phosphorescence of biacetyl as a monitor.[30] We assumed that the rate constant for energy transfer from acetophenone triplets to biacetyl is 6×10^9 l. mol^{-1} sec^{-1}, the quasi-experimental value of Kochevar and Wagner[20] for the diffusion-controlled limit in benzene at room temperature. The lifetime of acetophenone triplets estimated by this method was 0.67 μsec, in reasonable agreement with the flash kinetic result. Using our value for τ and the values of slopes and intercepts of the Stern-Volmer plots, we calculated rate constants for quenching by the various alkenes. The results are summarized in Table I.

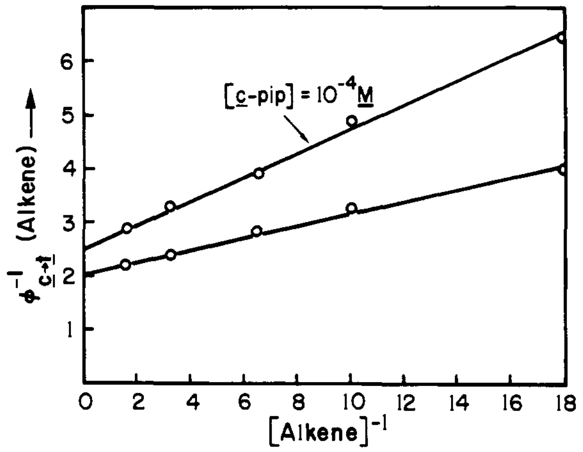


Figure 1. Variation in quantum yield for isomerization of *cis*-2,2-dimethyl-3-hexene, with and without 10^{-4} M *cis*-piperylene.

The rate constants for quenching are in the same range as those previously reported for quenching of acetophenone triplets by simple alkenes,[20,31] although the quenching rates for the trisubstituted alkenes, *trans*-**3** and *cis*-**3** are unusually high. The most remarkable feature of the data is the very low values for limiting quantum yields for isomerization with four of the alkenes, *trans*-**1**, *trans*-**2**, and both isomers of **3**. Apparently quenching of acetophenone triplets by these olefins must involve almost exclusively energy wastage, rather than energy transfer or any kind of chemical reaction.

In order to obtain an independent estimate of the reactivity of some of the alkenes, we introduced *cis*-piperylene (1,3-pentadiene) as a competitor since we expect the latter to quench acetophenone triplets by energy transfer at approximately the diffusion-controlled rate.[32] Competition involving *cis*-**1** was observed by monitoring the isomerization of the alkene at various alkene concentrations with a fixed concentration (10^{-4} M) of piperylene. The data were treated by the Stern-Volmer method and typical results are shown in Figure 1. A plot of data obtained in a parallel run with no piperylene is included for comparison. As expected, the slope is larger when piperylene is present. The intercept is also greater, indicating that the quantum yield at infinite alkene concentration is lowered by the presence of piperylene.

We also measured quantum yields for isomerization of *cis*-piperylene in the presence of varying amounts of *cis*-**1**. These experiments were unusually taxing. Because piperylene is much more reactive than *cis*-**1**, it was necessary to use a large excess of the latter in order to demonstrate competitive behavior. We were unable to find a vapor chromatographic column on which the retention time of the alkene was greater than that of the diene. Consequently we resorted to very long columns from which the alkene was eluted sufficiently earlier to keep interference with the analysis of piperylene isomers by the tail of the alkene fraction to a tolerable minimum. The results are summarized in Figure 2.

Competition between *cis*-piperylene and *trans*-**3** was also studied by monitoring piperylene isomerization. This was experimentally easier than the work described above with *cis*-**1** because *trans*-**3** is a more reactive quencher and because its higher boiling point facilitated analysis by vapor chromatography. The concentration of alkene was varied over a range of concentrations up to 0.7 M with a constant piperylene concentration of 5×10^{-3} M. The results are summarized in Figure 3.

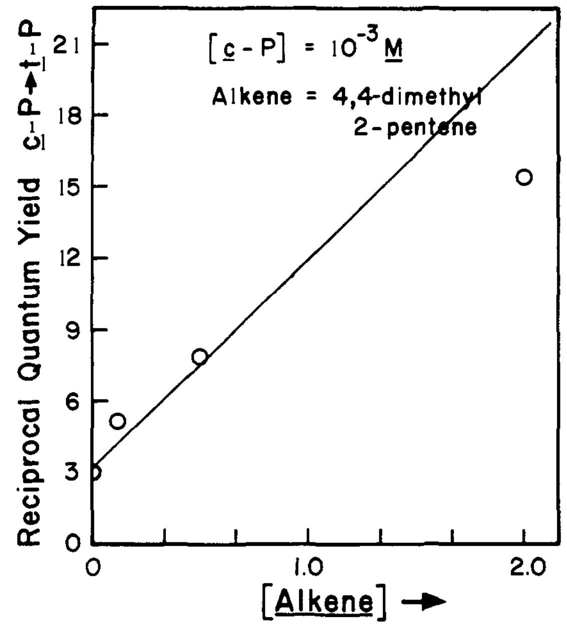


Figure 2. Variation in quantum yield for isomerization of *cis*-piperylene (10^{-3} *M*) as a function of concentration of *cis*-2,2-dimethyl-3-hexene.

Discussion

Quantum Yields and Relative Reactivity. The minimum mechanism needed to account for sensitized isomerization of olefinic compounds[32] must be expanded to even begin to account for the data which we report. Equations 1-12 are adequate to account for our data, although the mechanism is sufficiently complex to discourage any claims for uniqueness of the mechanistic model

$$^3S \xrightarrow{k_d} S \tag{1}$$

$$^3S + t \xrightarrow{k_t} t\text{-ex} \tag{2}$$

$$^3S + c \xrightarrow{k_c} c\text{-ex} \tag{3}$$

$$t\text{-ex} \xrightarrow{k_{dt}} \alpha T + (1-\alpha)\text{other} \tag{4}$$

$$c\text{-ex} \xrightarrow{k_{dc}} \beta T + (1-\beta)\text{other} \tag{5}$$

$$T \xrightarrow{k'_d} at + (1-a)c \tag{6}$$

$$^3S + c\text{-P} \xrightarrow{k_q} T \tag{7}$$

$$t\text{-ex} + c\text{-P} \xrightarrow{k_{qc}} \gamma T + (1-\gamma)\text{other} \tag{8}$$

$$c\text{-ex} + c\text{-P} \xrightarrow{k_{qt}} \delta T + (1-\delta)\text{other} \tag{9}$$

$$T \xrightarrow{k_{dP}} b(t\text{-P}) + (1-b)(c\text{-P}) \tag{10}$$

$$t\text{-ex} + t \xrightarrow{k_{t\text{-ex}}} 2t + S \tag{11}$$

$$c\text{-ex} + c \xrightarrow{k_{c\text{-ex}}} 2c + S \tag{12}$$

where S = sensitizer, t = *trans*-alkene, c = *cis*-alkene, t-ex = exciplex of *trans*-alkene, c-ex = exciplex of *cis*-alkene, other = all other interaction products, c-P = *cis*-piperylene, t-P = *trans*-piperylene, and T = piperylene triplet.

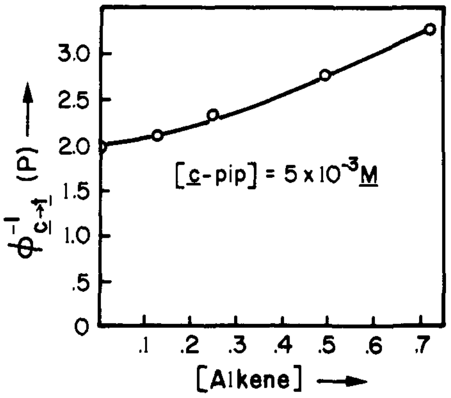


Figure 3. Variation in quantum yield for isomerization of *cis*-piperylene (5 × 10^{-3} *M*) as a function of concentration of *trans*-3,4-dimethyl-2-pentene.

Equations 11 and 12 are not needed for discussion of most of the results so they will be omitted in derivation of the kinetic laws. With this omission the mechanism leads to the following relationships

$$1/\Phi^\circ_{c\to t} = (a\beta)^{-1}\left(\frac{k_c[c] + k_q[P] + k_d}{k_c[c]}\right)\left(\frac{k_{dc} + k_{qc}[P]}{k_{dc}}\right) \tag{13}$$

$$1/\Phi^\circ_{t\to c} = [(1-a)\alpha]^{-1}\left(\frac{k_t[t] + k_q[P] + k_d}{k_t[t]}\right) \times \left(\frac{k_{dt} + k_{qt}[P]}{k_{dt}}\right) \tag{14}$$

$$1/\Phi^\circ_{P(t)} = b^{-1}\left(\frac{k_q[P] + k_t[t] + k_d}{k_q[P] + \gamma Z k_t[t]}\right) \tag{15}$$

where $\Phi^\circ_{c\to t}$ = initial quantum yield for conversion of *cis*- to *trans*-alkene, $\Phi^\circ_{t\to c}$ = initial quantum yield for conversion *trans*- to *cis*-alkene, $\Phi^\circ_{P(t)}$ = initial quantum yield for isomerization of *cis*-piperylene in presence of *trans*-alkene, and $Z = k_{qt}[P]/(k_{qt}[P] + k_{dt})$.

In the absence of piperylene, eq 13 to 14 reduce to (16) and (17), the usual Stern-Volmer forms.

$$1/\Phi^\circ_{c\to t} = (a\beta)^{-1}(1 + [k_d/(k_c[c])]) \tag{16}$$

$$1/\Phi^\circ_{t\to c} = [(1-a)\beta]^{-1}(1 + [k_d/(k_t[t])]) \tag{17}$$

Equations 16 and 17 and our experimental value of k_d were used to evaluate the rate parameters listed in Table I. When energy transfer is the only significant process, α and β are unity and the sum of the limiting quantum yields for any pair of isomeric alkenes is also unity. This condition is not approached closely by any of the isomeric pairs included in this work. In many "well-behaved" sensitized isomerizations, the values of a have turned out to be in the range of 0.5 ± 0.2; i.e., alkene triplets appear to partition with little discrimination between cis and trans ground state molecules when they decay. By this criterion it appears that the limiting quantum yields from *cis*-**1** ($\Phi^\infty_{c\to t}$ = 0.51) and *cis*-**2** ($\Phi^\infty_{c\to t}$ = 0.77) are in a "normal" range. Unless the values of a are very unusual, the results indicate that the values of α for the trans isomers must be very small. Since the limiting quantum yields are very low with both *cis*- and *trans*-**3** ($\Phi^\infty_{t\to c}$ = 0.004 and $\Phi^\infty_{c\to t}$ = 0.007), it seems probable that in this system both α and β are small.

Capture of Exciplexes. The principal evidence for formation of an exciplex, or at least some long-lived intermediate, between acetophenone triplets and an alkene (*cis*-**1**) is presented in Figure 1. Many additional measurements were carried out with this system but the results presented are derived from a single run using two series of samples in which concentrations of the alkene were matched exactly. *cis*-Piperylene at fixed concentration was included in one series but not in the other. The intercepts are clearly different and indicate that quenching by piperylene would still occur at infinite concentration of the alkene. The result excludes a simple competitive mechanism but is compatible with the idea that an exciplex formed from acetophenone triplets and the alkene can be quenched by piperylene. From the slope and intercept of a plot of the data obtained in the presence of piperylene, one can extract a simple combination of rate constants, just as was done in the Stern-Volmer treatment of data collected with no piperylene present.

$$I^P/S^P = k_c/(k_d + k_q[P]) \tag{18}$$

The value of I^P/S^P with 10^{-4} *M* piperylene is 14.4 M^{-1}. Using the value of 1.5×10^6 sec^{-1} for k_d and 6×10^9 M^{-1} sec^{-1} for k_q, we calculate that k_c is 3.0×10^7 M^{-1} sec^{-1}, in reasonable agreement with the value derived from study of the alkene alone. This merely showed that the relative reactivities of piperylene and *cis*-**2** toward acetophenone triplets are approximately as expected. By comparison of the intercepts with and without piperylene, we can obtain a comparison of the values of the rate constants for unimolecular decay of the exciplex and its quenching by piperylene.

$$I^P/I = (k_{dc} + k_{qc}[P])/k_{dc} \tag{19}$$

The ratio of intercepts is 1.33 so $k_{dc} = 3.0k_{qc}[P]$. Since the excitation energy of the exciplex is unlikely to be a great deal less than that of acetophenone triplets (E_T = 73.6 kcal mol^{-1}) excitation transfer to piperylene (E_T = 57 kcal mol^{-1}) probably would be diffusion controlled. If k_{qc} is 6×10^9 M^{-1} sec^{-1}, k_{dc} is 1.8×10^7 sec^{-1}, i.e., almost a factor of ten faster than that of the sensitizer triplets ($k_d \simeq 1.5 \times 10^6$ sec^{-1}).

Piperylene Isomerization. The discussion in the preceding paragraph implies that quenching of an alkene-acetophenone exciplex by piperylene should involve energy transfer and lead to isomerization of piperylene. The initial quantum yield for isomerization is predicted by eq 15 or the analogous equation for the *cis*-alkene. At high alkene concentration, the quantum yield should become constant and equal to $b\gamma Z$. The limiting quantum yield might in principle be either higher or lower than in the absence of the alkene. The prediction was tested again using *cis*-**1** as the quencher. Figure 2 shows that the quantum yield decreases as the alkene concentration is increased and then seems to level off at high alkene concentration as predicted. The slope of the plot of $(\Phi_{P(t)})^{-1}$ against *t* at low [*t*] should approximate $k_t/k_q[P]$. The straight line drawn in the figure has the calculated slope assuming that k_t has the value from Table I and that k_q is 6×10^9 M^{-1} sec^{-1}. The data are not sufficiently accurate to justify detailed analytical treatment, but the large discrepancy between the observed values of $(\Phi^\circ{}_{P(t)})^{-1}$ at high alkene concentration and those predicted supports the presumption that, at high concentration of the alkene, an exciplex is formed and sensitizes the isomerization of piperylene. The limited data suggest that the slope may actually be greater than the calculated value. This is quite possible because of error in our determination of k_t or because of uncertainty in the value of k_q. Assignment of a higher value to the slope would only increase the discrepancy at high concentration.

Study of the isomerization of piperylene in the presence of *trans*-**3** was initiated because it was anticipated that the measurements could be made with greater accuracy than with *cis*-**1**. Since the reactivity of piperylene toward acetophenone triplets is about three orders of magnitude greater than that of *cis*-**1**; the data for Figure 3 were taken using very high [alkene]/[piperylene] ratios, necessitating measurement of the piperylene isomerization rate at very low piperylene concentrations. The greater reactivity of *trans*-**3** permits use of much more nearly equivalent concentrations of the two competitors. The experimental advantage is real, but the results do not take the form anticipated as is shown in Figure 3. The quantum yield appears to decrease monotonously as the alkene concentration is increased. This could occur if the value of γZ were very small. The value of γ would be small if quenching of the exciplex led predominantly to internal conversion rather than energy transfer, a situation which we would have difficulty in rationalizing. A low value of *Z* could be attributed to a very fast decay rate (large k_{dt}) for the exciplex, a question about which we have no strong bias. If $\gamma Z k_t[t]$ is much smaller than $k_q[P]$, eq 15 reduces to eq 20, a simple Stern-Volmer relationship.

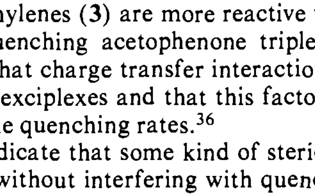
$$\frac{1}{\Phi^\circ{}_{P(t)}} \simeq b^{-1}\left(\frac{k_q[P] + k_d}{k_q[P]} + \frac{k_t[t]}{k_q[P]}\right) \tag{20}$$

Equation 20 predicts a linear relationship between $1/\Phi^\circ{}_{P(t)}$ and [*t*] and that the quotient, *I/S* will be equal to $(k_q[P] + k_d)/k_t$. If we ignore the nonlinear appearance of the experimental points in Figure 2 and force fit the data to eq 20, we obtain a value of 1.1 *M* for that quotient. Using the measured value of k_d and again using 6×10^9 M^{-1} sec^{-1} for k_q, we calculate a value of 3.0×10^7 M^{-1} sec^{-1} for k_t. This is in poor agreement with the estimate (3.7×10^8 M^{-1} sec^{-1}) obtained by analysis of alkene isomerization alone. This, coupled with the fact that the curvature of the plot in Figure 2 occurs in the wrong sense,[33] indicates that the mechanism as formulated is inadequate.

If the value of k_t listed in Table I is reasonably accurate, the quantity $k_t[t]$ with $[t] = 0.5$ *M* should be much larger (1.8×10^8 sec^{-1}) than $(k_d + k_q[P])$ (3.1×10^7 sec^{-1}), and the quantum yield (0.35) should be close to the limiting value Since the quantum yield continues to fall smoothly ($\Phi^P = 0.31$ at $[t] = 0.75$ *M*), it appears that, at high concentration of alkene, a new quenching reaction becomes important. Reaction 11, quenching of the exciplex by the alkene, is a likely candidate. This process would be hard to detect by study of alkene isomerization alone because the quantum yields for isomerization of *trans*-**3** are very small under all conditions. The fact that data obtained with *trans*-**3** alone gave an excellent fit to the Stern-Volmer relationship (eq 14) is easily understood since the concentrations of alkene were much lower and the range barely overlaps that used in the work with piperylene as a competitor. In order to obtain reasonable precision in measurements of $\Phi^\circ{}_{P(t)}$, it was necessary to use piperylene concentrations as high as that chosen (5×10^{-3} *M*). This in turn required increase of alkene concentrations to higher values and apparently led to uncovering of an additional quenching process. Qualitatively Figure 3 suggests that the curve begins being relatively flat, suggesting that γZ is not much smaller than $k_q[P]/(k_q[P] + k_d)$ and that the new quenching process begins to become important in the region of $[t] \simeq 0.5$ *M*. A great deal of additional data would be required to justify an attempt at a quantitative dissection of the rate factors.

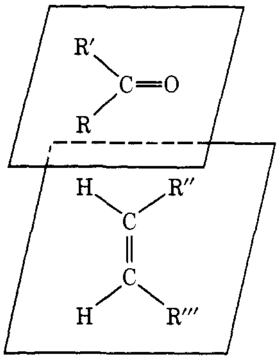
Structure of Intermediates. Saltiel and co-workers[31] have carefully documented a much less egregious, but still clearly significant, example of a case in which a single decay ratio does not serve to characterize a sensitized isomerization (of the 2-pentenes) by acetophenone. In terms of the mechanism presented above, their data indicated significant energy wastage in the interaction of ketone triplets with *trans*-2-pentene. With acetone and benzene as sensitizers, more nearly "normal" behavior is observed and we can probably assume that the data gathered with benzene sensitizer in the vapor phase establish the true value of the decay ratio (the *a* factor) of 2-pentene triplets. Saltiel pointed out the mandatory requirement that interaction of acetophenone triplets with the isomeric alkenes involve at least some significant, nonidentical intermediates. The results were explained by invoking the Schenck mechanism[34] in which the ketone triplet adds to the alkene forming a biradical which either undergoes ring closure to an oxetane or falls apart regenerating the isomeric alkenes and the sensitizer in their ground states. Isomerization in this mechanism results from rotation about the erstwhile double bond in the biradical. Yang and co-workers[5] reached an essentially identical position in their study of the interaction of benzophenone triplets with 3-methyl-2-pentene.

Out data and all of those previously reported can be interpreted in terms of any mechanism in which sensitizer triplets interact with alkenes to form intermediates which decay, at least in part, to ground states without alteration of the geometric configuration of the alkene. The Schenck mechanism seems hard to fit to our data. Consider the case of *cis*- and *trans*-**3**. Since both isomers give very low limiting quantum yields, it would be necessary to postulate that biradicals formed by addition of ketone triplets do not undergo significant rotation about the newly made single bond in the intermediate. However, the data of Figures 1, 2, and 3 show that intermediates formed from *trans*-**3** and *cis*-**1** live long enough to be intercepted by piperylene and quenched with preferential, perhaps exclusive, return of the alkenes to their original ground states. As was discussed above, it is clear the intermediate of *trans*-**3** is causing isomerization of *cis*-piperylene when the latter is present at a concentration level of 5×10^{-3} *M*. If we assume that the quenching rate is 6×10^{9} M^{-1} sec^{-1}, we must conclude that the lifetime of the intermediate is 10^{-8} sec or greater, a time that should be long enough to allow rotation about the central bond in a biradical such as **4** with any reasonable assumptions concerning barriers.[35] In view of these considerations, we are strongly inclined toward the view that the interceptable intermediates are complexes which retain the double bonded character of the parent alkenes. The fact that trialkylethylenes (**3**) are more reactive than dialkyl derivatives in quenching acetophenone triplets is consistent with the idea that charge transfer interactions contribute to binding in the exciplexes and that this factor contributes to variations in the quenching rates.[36]



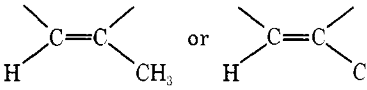
4

Our data indicate that some kind of steric effects inhibit isomerization without interfering with quenching. Probably some relative orientations of substrate and sensitizer which permit efficient decay to ground states are not effective in energy transfer or addition. Apparently two trans substituents with at least one being bulky makes access to orientations favorable for energy transfer (or biradical formation) difficult. It is hard to see how this is compatible with an arrangement in which sensitizer and substrate lie in parallel planes with the C-O axis parallel to the C=C axis since steric interactions should be similar with cis and trans isomers. There are two kinds of exciplex geometry which would account for the high reactivity of *cis*-**1** and -**2** in isomerization compared with *trans*-**1** and -**2** and both *cis*- and *trans*-**3**. A parallel planar arrangement with the C-O axis perpendicular to the C=C axis might be favored by having one unhindered side in the alkene as indicated in the following schematic drawing.



Any approach of the carbonyl triplet to a side of an alkene molecule would be favored by having small substituents on at least one side of the alkene.

The above rationalization has a weakness in that it does not assign a special role to the attachment of a single, very bulky *tert*-butyl group attached to the olefinic unit. This must be of significance because the less hindered side of the unreactive alkenes present atomic environments, i.e.:



which are also found on both sides of simple alkenes which are more "normal" in accepting energy from ketone triplets. For example, the sum of quantum yields ($\Phi_{c \rightarrow t} + \Phi_{t \rightarrow c} + \Phi_{\text{oxetane}}$) in the interaction of benzophenone with the 3-methyl-2-pentenes is 0.76.[5] Similarly, the sum of quantum yields for interaction of the 2-butenes is 0.54.[26] In both cases some energy wastage occurs but is not nearly as extensive as that with some of the compounds involved in our study.

The possibility that the results are spurious and attributable to quenching by very reactive impurities in the alkenes must be considered. This seems unlikely because the alkenes were carefully purified and vapor chromatograms showed no extra peaks. Consideration of the data for *trans*-**3**, the most reactive quencher, is instructive. The estimated quenching rate constant is 3.7×10^{8} M^{-1} sec^{-1}, only 20-fold smaller than the value assumed for piperylene. The results obtained would require the presence of 5% of an impurity as reactive as piperylene. There is no realistic possibility that there is any impurity present anywhere near this concentration level unless that impurity has a retention time the same as that of *trans*-**3** on all VPC columns used. An isomeric alkene could conceivably show such behavior but would not be expected to have the requisite high quenching reactivity.

Quenching reactivity does not parallel reactivity in sensitized isomerization. Both isomers of **3** are fourfold or more times more reactive than any of the compounds **1** and **2** in quenching but show the lowest efficiencies of isomerization. In quenching reactivity, the two trisubstituted ethylenes fall together, three of the disubstituted ethylenes fall in another group, and *trans*-**1** stands by itself as notably unreactive. We have tried setting up models to analyze the data assuming: (1) that *a* factors lie within the range 0.2-0.8; and (2) quenching consists of two independent processes, one leading to energy transfer and the other leading to decay to ground states. The analysis leads to no interpretable structure-reactivity pattern.[37]

Experimental Section

Materials. The alkenes were obtained from Chemical Samples in 1-ml ampules, packed under N_2. They were bulb-to-bulb distilled from $LiAlH_4$ and kept under vacuum until just prior to use.

Acetophenone (reagent grade) was obtained from M C and B and was distilled under reduced pressure. *cis*-Piperylene was obtained from Chemical Samples and was bulb-to-bulb distilled from $LiAlH_4$ just before use.

Benzene (spectrograde) from Mallinckrodt was purified by the photochlorination method.[38] *n*-Hexane was purchased from Phillips (pure grade) and was passed through an alumina column. Gas chromatographic analysis showed that it contained isomeric hexanes, heptane, and isopentane as impurities. Acetonitrile (spectrograde) was obtained from M C and B and was distilled from K_2CO_3 under nitrogen.

Diethyl ether (reagent grade) was obtained from Mallinckrodt and was distilled before use. Anisole (spectrograde) was obtained from M C and B and was used as received.

Quantum Yields. Solutions were degassed in 13-mm o.d. Pyrex tubes (three freeze-thaw cycles; maximum pressure $<10^{-4}$ mmHg) and irradiated simultaneously in a "merry-go-round" apparatus[39] equipped with appropriate filter combination to isolate the 3130 Å Hg line (band pass 18 nm).

The olefins were analyzed on a Hewlett-Packard ns 5750 research gas chromatograph equipped with a flame ionization detector using the following columns: (i) all olefins 26 ft × ⅛ in. aluminum column containing 22% *β,β'*-oxydipropionitrile on Chrom P (60-80), henceforth referred to as A; (ii) olefins, piperylene, and benzene, column A and one 12 ft × ⅛ in. stainless steel column containing two 1/% SE-30 on Chrom W (60-80) in tandem for 3,4-dimethyl-2-pentenes and piperylene; one 45 ft × ⅛ in. aluminum column containing 25% *β,β'*-oxydipropionitrile on Chrom P (60-80) for 4,4-dimethylpentenes and piperylenes.

Actinometry was done by the ferrioxalate method and benzophenone sensitized isomerization of piperylene with concordant results.

Lifetimes of Acetophenone Triplets. Lifetimes were measured by monitoring the intensity of sensitized phosphorescence of biacetyl as a function of biacetyl concentration. Biacetyl was obtained from Aldrich (reagent grade) and was bulb-to-bulb distilled twice before use. All solutions were prepared under safe light to minimize photodegradation of biacetyl.

They were degassed (five freeze-thaw cycles; maximum pressure $<10^{-6}$ mmHg). The phosphorescence spectra were recorded with a Hitachi MPF 3-A spectrofluorimeter. Use of ratio recording helped stabilize baselines. In some cases, the excitation spectrum rather than the emission spectrum was recorded. The concentrations of the sensitizer and biacetyl were such that biacetyl absorbed less than 1% of the light. However a broad weak band was sometimes seen at 420-460 nm that could be acetophenone phosphorescence, biacetyl fluorescence, or both. We think it is the latter, since the intensity of this band varied rather erratically with concentration.

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(37) For example, an attempt to dissect the rate constants for *cis*- and *trans*-**1** assuming that $a = 0.5$ gives rate constants for energy transfer as 0.5×10^5 and 5.8×10^7 sec^{-1} for *trans*-**1** and *cis*-**1**, respectively, and rate constants for quenching without energy transfer as 4.9×10^6 sec^{-1} and zero. The same assumptions applied to the isomers of **3** give both the value of 3×10^{-6} sec^{-1} for the energy transfer rate constant and values of 3.6×10^8 and 2.2×10^8 sec^{-1} for the nontransfer quenching rate constants for *trans*-**3** and *cis*-**3**, respectively.

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