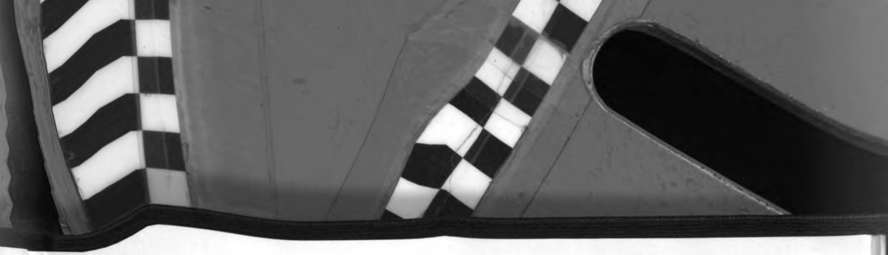

ABSTRACT

A KINETIC STUDY OF THE QUENCHING OF TRIPLET BUTYROPHENONE BY MONOOLEFINS: A MODEL FOR KETONE TRIPLET-MONOOLEFIN INTERACTIONS

by

Irene Emily Kochevar

This research was undertaken to determine the nature of the interaction between ketone triplets and ground state monoolefins in solution which leads to quenching of the ketone triplet.

Norrish Type II photoelimination which occurs from the triplet state of butyrophenone was partially quenched by various amounts of monoolefins. The rate constants for quenching, k_q, were determined using Stern-Volmer kinetics. The values of k_q for the monoolefins were determined relative to that for 2,5-dimethyl-2,4-hexadiene. The diene was assumed to quench with the maximum rate constant in benzene solution.

The quenching efficiencies of the chloroolefins increased with the number of chlorosubstituents on the double bond. Cis-1,2-dichloroethylene quenched triplet butyrophenone ∿30 times less efficiently than the diene whereas tetrachloroethylene was only ∿3 times less efficient than the diene. Product formation was not detected between trichloro- or tetrachloroethylene and butyrophenone.

These results along with others in the literature indicate that energy transfer is responsible for the quenching of ketone triplets by chloroolefins.

Values of k_q were determined for a series of eleven acyclic alkenes. Alkyl substitution on the double bond generally increased k_q. For example, k_q for cis-2-pentene was 5.07×10^7 M^{-1} sec^{-1} but increased to $46. \times 10^7$ M^{-1} sec^{-1} for 2,3-dimethyl-2-butene. The cis isomer of a cis-trans olefin pair was always a 2-3 times better quencher than the trans isomer. Less than 15 percent of the quenching resulted in product formation between the ketone and olefin in the two cases studied.

Quenching by the cyclic olefins was more efficient than quenching by most of the acyclic cis-1,2-disubstituted ethylenes. The values for k_q decreased in the order $C_8 > C_7 \simeq C_4 > C_5 > C_6 >$ norbornene. About 45 percent of the quenching by cyclohexene yielded product which was postulated to result from allylic hydrogen abstraction. Olefin dimers resulted from the quenching of butyrophenone by cyclopentene and norbornene.

These results were most consistent with predominant quenching by the hydrocarbon olefins through formation of a complex in which the olefin acted as an electron donor and the ketone as an electron acceptor. Radical addition of the carbonyl oxygen to the olefin was eliminated as a quenching mechanism because the k_q values were too large for this process and the relative rates expected for addition to cyclic olefins were almost opposite to those observed. Quenching by energy transfer to the olefins was ruled out except for the small cyclic olefins which probably have lower triplet energies than their acyclic analogues.

A general scheme for triplet ketone-olefin interactions is proposed. The scheme points out how the mechanism and rate constant for interaction depend upon the relative triplet energies of the ketone-olefin pair and upon the electron donor and acceptor ability of the olefin and triplet ketone, respectively.

A KINETIC STUDY OF THE QUENCHING OF TRIPLET BUTYROPHENONE BY MONOOLEFINS: A MODEL FOR KETONE TRIPLET-MONOOLEFIN INTERACTIONS

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I. INTRODUCTION

The research reported in this dissertation lies within the general area concerning the interaction between atoms or molecules in their first excited triplet states and ground state nonconjugated olefins. This interaction quenches the triplet state molecule or atom and may result in a variety of products. When quenching yields triplet state olefin, the process is called triplet-triplet energy transfer (Equation 1). The triplet state olefin may subsequently isomerize, dimerize or undergo a variety of other inter- and intramolecular reactions (Equation 2). ${}^3S^*$ and ${}^1S_0$ represent sensitizer molecules in their excited triplet

$$ {}^3S^* + {}^1\text{olefin}_0 \xrightarrow{k_{et}} {}^1S_0 + {}^3\text{olefin}^* \qquad (1) $$

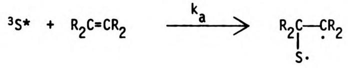
$$ {}^3\text{olefin}^* \longrightarrow \text{Products} \qquad (2) $$

state and ground state, respectively. The olefin triplet and ground state are shown as ^{3}olefin* and ^{1}olefin$_0$.

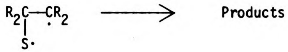
In other cases, chemical quenching occurs. The predominant chemical quenching reactions are allylic hydrogen abstraction (Equation 3) and addition to the olefin double bond (Equation 5). Both pathways can lead to products involving the sensitizer (Equations 4 and 6).

$$ {}^3S^* + R_2CHC{=}CR_2 \xrightarrow{k_h} \cdot SH + R_2\dot{C}CR{=}CR_2 \qquad (3)$$

$$\cdot SH \longrightarrow \text{Products} \qquad (4)$$



$$ {}^3S^* + R_2C{=}CR_2 \xrightarrow{k_a} R_2\underset{\underset{S\cdot}{|}}{C}-\underset{\cdot}{C}R_2 \qquad (5)$$



$$ R_2\underset{\underset{S\cdot}{|}}{C}-\underset{\cdot}{C}R_2 \longrightarrow \text{Products} \qquad (6)$$

The relative triplet state energies of the triplet state molecule or atom (sensitizer) and of the olefin (quencher) are a major factor in determining the type of quenching and the rate constant for quenching. Consequently, research pertaining to the triplet state energy of ethylene is reviewed first. Quenching of various types of sensitizers is then discussed in order of decreasing sensitizer triplet energy (metal atoms, benzene and substituted benzenes, dialkyl ketones, phenyl alkyl ketones and diphenyl ketones).

A. Triplet Energy of Ethylene and Substituted Ethylenes

The zeroth vibrational level of the first excited triplet state of ethylene is predicted[1,2] to have a 90° angle between the planes of the $-CH_2$ groups whereas the lowest vibrational level of the ground state is planar. Walsh[3] predicted that rehybridization of the $-CH_2$ groups from sp^2 to sp^3 stabilizes the perpendicular triplet. His prediction has been subjected to calculations[4,5,6] but the results have been inconclusive.

The energy levels of ethylene can be best discussed in terms of the following diagrams.

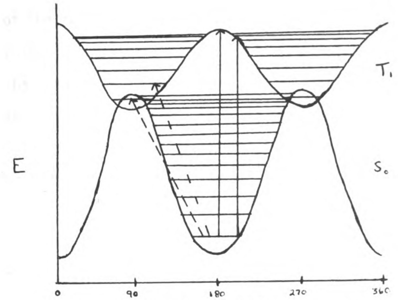


Figure 1. Energy level diagram for ethylene showing twisting vibrational levels

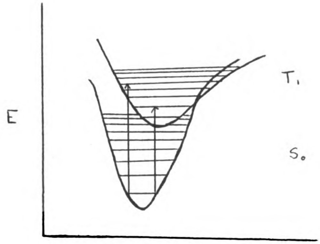


Figure 2. Energy level diagram for ethylene showing C-C stretching vibrational levels

In Figure 1 the vibrational levels drawn represent the quantization of the twisting vibration about the carbon-carbon bond whereas in Figure 2 the quantization of the carbon-carbon stretching vibration is shown. The actual vibrational levels result mainly from combinations of these two vibrational modes. Examples of Franck-Condon allowed (vertical) S → T transitions are represented by solid arrows and nonvertical transitions by broken arrows.

Although the singlet-triplet absorption spectrum of ethylene has been published[7,8] and numerous triplet energy calculations have been reported[4,9] there is still disagreement among researchers over the energies of these transitions. Reid[7] in 1955 and Evans[8] in 1960 reported the singlet-triplet spectrum of ethylene. The absorption maximum was observed at 2700 Å (106 $\frac{\text{kcal}}{\text{mole}}$) and the longest wavelength absorption occurred at 3484 Å (82 $\frac{\text{kcal}}{\text{mole}}$). These researchers concluded that the nonvertical transition from the zeroth vibrational level of ground state ethylene to the zeroth vibrational level of twisted triplet ethylene required about 82 $\frac{\text{kcal}}{\text{mole}}$. This value for the 0-0 transition has been accepted by many researchers.

Calculations by Baird[9], Lodquet[4] and others predict energies of 54-70 $\frac{\text{kcal}}{\text{mole}}$ for the lowest vibrational level of twisted triplet ethylene. Merer and Mulliken[10] in a review article concluded that the lowest triplet level of ethylene may be as low as 60 $\frac{\text{kcal}}{\text{mole}}$ based mainly on the ability of low energy sensitizers to isomerize olefins.

The singlet-triplet absorption spectra for five alkyl substituted ethylenes have been determined by Itoh and Mulliken[11]. The results are given in Table I.

TABLE I. Singlet-triplet Absorption Spectra of Substituted Ethylenes.

Olefin	λ_{onset}, cm^{-1}	$E_{onset}, \frac{kcal}{mole}$	λ_{max}, cm^{-1}	$E_{max}, \frac{kcal}{mole}$
propene	28,200	80.5	33,900	97.0
2-methylpropene	28,200	80.5	33,000	94.5
trans-2-butene	28,200	80.5	32,800	93.8
trimethylethylene	27,000	77.	29,850	85.5
tetramethylethylene	26,400	75.5	29,400	84.1

The O_2-induced singlet-triplet spectra of cis and trans-1,2-dichloroethylene reported by Grabowski and Bylina[12] appear to begin at 3850 Å and 4000 Å respectively. If the onset of singlet-triplet absorption results from nonvertical transition to a twisted molecule, the energy of the 0-0 transition can be estimated to $\leq E_{onset}$.

Dimerization of cyclic olefins sensitized by molecules with known triplet energies can be used to estimate olefinic triplet energies also. Sensitized dimerization is thought to involve triplet-triplet energy transfer and subsequent attack of triplet olefin upon a ground state olefin molecule to yield dimer[13].

Arnold[14] has reported the ratios of dimer/oxetane obtained from the quenching by norbornene of a series of phenyl alkyl ketones with triplet energies in the range 71-75 $\frac{kcal}{mole}$. Oxetane results from chemical quenching. Dimer was virtually the only product when the ketone had a $E_T > 72 \frac{kcal}{mole}$ indicating that the triplet of norbornene could be produced with an energy as low as 72 $\frac{kcal}{mole}$. Because norbornene's bicyclic structure does not allow it to twist significantly, a near-planar triplet must have

been formed. Taking into account the facts that low efficiency energy transfer does occur when a donor's triplet energy is 2-3 $\frac{\text{kcal}}{\text{mole}}$ less than that of the acceptor[15] and that some twisting can occur, the planar triplet may be estimated to have an energy of 80-85 kcal/mole.

This estimate of the planar triplet energy can also be used to explain the acetone ($E_T = 80$ $\frac{\text{kcal}}{\text{mole}}$[16]) photosensitized dimerizations of cyclopentene[17], cyclobutene[18], 1-methylcyclobutene[18] and norbornene[19].

These dimerization studies indicate that the E_{onset} values measure the energy of the vertical transition to the lowest vibrational level of the planar olefin triplet.

B. Quenching of Hg and Cd Triplets

Atomic mercury has a lowest triplet energy of 113 $\frac{\text{kcal}}{\text{mole}}$[20]. A review covering mercury photosensitization[20] lists the relative quenching efficiencies of a number of unsaturated hydrocarbons. Examination of a sample of the values reported (Table II) does not reveal a relationship between olefin structure and quenching efficiency.

TABLE II. Quenching of $(^3P_1)$Hg and $(^3P_1)$Cd by Olefins.

Olefin	$Hg(^3P_1)$	$Cd(^3P_1)$
ethylene	0.90	1.03 ± .09
ethylene-d_4	—	.96 ± .01
propene	0.93	1.18 ± .04
1-butene	—	1.08 ± .09
1-pentene	1.00	—
iso-butene	.95	1.11 ± .03
cis-2-butene	1.00	1.00
cyclohexene	—	1.02 ± .07
trimethylethylene	—	1.02 ± .10
tetramethylethylene	.95	.99 ± .11
1,3-butadiene	.93	1.13 ± .04

Tsunashima and Sato[21] studied the pressure dependence of the Hg-photosensitized cis-trans isomerization of 2-butene and concluded that a transient complex was formed between Hg($^3P_1$) and the olefin (Equation 7). This complex (HgC* or HgT*) broke up to give ground state Hg and either triplet olefin (B*) (Equations 8, 9) which isomerized (Equation 11) or vibrationally excited ground state olefin ($C^\dagger$ or $T^\dagger$) which did not isomerize (Equations 10, 12).

$$^3Hg^* + C(\text{or } T) \longrightarrow HgC^* \ (\text{or } HgT^*) \tag{7}$$

$$HgC^* \ (\text{or } HgT^*) \longrightarrow Hg + B^* \tag{8}$$

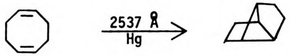
$$HgC^* \ (\text{or } HgT^*) + M \longrightarrow Hg + B^* + M \tag{9}$$

$$HgC^* \ (\text{or } HgT^*) \longrightarrow Hg + C^\dagger \ (\text{or } T^\dagger) \tag{10}$$

$$B^* \longrightarrow 1/2C + 1/2T \tag{11}$$

$$C^\dagger \ (\text{or } T^\dagger) \longrightarrow C \ (\text{or } T) \tag{12}$$

Other mercury photosensitized reactions include decomposition of ethylene[22] and cycloalkenes[23], and dimerization of ethylene[24]. Internal cycloaddition of nonconjugated dienes photosensitized by mercury has been studied by Srinivasan[25] (Equations 13, 14).



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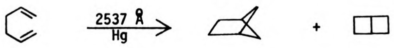

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Atomic cadmium (E_T = 87.7 kcal) has been used to photosensitize the decomposition of ethylene[26] with low efficiency and the interconversion of cis-, trans- and gem-ethylene-d_2[26,27]. Huziker[26] assumed that transfer of energy from triplet Cd must have been to a twisted ethylene. Consequently, he postulated the initial formation of a complex between $^3Cd_1$ and the olefin. The relative efficiencies of olefins in quenching triplet cadmium atoms was studied using competitive quenching by Tsunashima, Satoh and Sato[28]. Their results, summarized in Table II, are similar to those found for triplet mercury photosensitization suggesting that energy transfer is exothermic to both metal atoms.

C. Quenching of Benzene and Substituted Benzene Triplets

The triplet energy of benzene (84.4 $\frac{kcal}{mole}$[29]) is greater than the E_{onset} of ethylene and substituted ethylenes. Consequently, triplet olefins have been proposed as intermediates in all benzene photosensitized reactions. The scrambling of deuteriums[30,31], cis-trans isomerization[31], and (at low pressures) decomposition to hydrogen and acetylene[30] of 1,2-dideuteroethylene have been photosensitized by benzene, although the rate constants for these processes were lower than those obtained with Hg-photosensitization[30]. Hirokami and Sato studied the pressure dependence of the first two of these reactions when photosensitized by a number of benzene derivatives[31].

Schmidt and Lee used competitive quenching of the benzene photosensitized isomerization of cis-2-butene to determine the kinetic isotope effect on quenching by ethylene[32]. The observed isotope effect, $k_H(C_2H_4)/k_D(C_2D_4)$ = 1.7 ± .2, was attributed to the higher triplet energy of the deuterated compound as determined from the relative onsets of the

singlet-triplet absorption spectra of the two olefins. Since quenching of benzene by butadiene and butadiene-d_6 did not exhibit an isotope effect, $k_H(C_4H_6)/k_D(C_4D_6) = 1.0 \pm .2$, the authors concluded that quenching of benzene by ethylene was an endothermic process.

The benzene photosensitized cis-trans isomerization of 2-butene in the gas phase was reported by two groups in 1963[33,34]. Cundall, Milne and Fletcher observed that the isomerization occurred with a variety of other sensitizers as long as their triplet energies were greater than $65 \frac{kcal}{mole}$ and concluded that the 0-0 transition of 2-butene required an energy of about $65 \frac{kcal}{mole}$[34]. Lee, Denschlag, and Haninger used the benzene photosensitized cis-trans-isomerization of 2-butene to moniter the relative quenching efficiences of other olefins[35]. Their results are summarized along with those of Morikawa and Cvetanovic[36], who made a similar study, in Table III. The ratio of initial rates, $R_{c \to t}/R_{t \to c}$, of 2-butene isomerization was determined to be $1.03 \pm .02$[35].

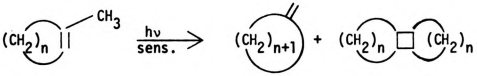
TABLE III. Quenching of Triplet Benzene by Olefins.

Olefin	relative quenching rate constants Lee, Denschlag + Haninger 23°	 Morikawa + Cvetanovic ~26°	 30°	 70°
ethylene	0.17	0.22	0.25	0.33
propene	0.52	0.47	—	—
1-butene	0.46	0.50	0.51	—
1-pentene	0.47	0.54	—	—
isobutene	—	1.27	—	—
2-methyl-1-butene	—	0.80	—	—
cis-2-butene	1.00	1.00	1.00	1.00
trans-2-butene	1.09	—	—	—
cyclopentene	0.85	—	—	—
trimethylethylene	1.65	1.61	—	—
tetramethylethylene	3.00	2.67	2.75	2.29
1,3-butadiene	11.8	16.2	15.8	13.0

The contrast between these results and those found for metal atom photosensitizations suggests that the quenching process is now endothermic.

Both groups of researchers pointed out that the relative quenching efficiencies of the olefins paralleled the order found for the addition of electrophilic reagents to olefins. In addition, Morikawa and Cvetanovic suggested that energy transfer from triplet state benzene to olefin occurred through the formation of a complex. During the lifetime of the complex, the olefin assumed a twisted conformation and accepted energy from the benzene triplet. From the observation that the relative quenching efficiencies differed less at higher temperatures, these authors concluded that an activation energy for energy transfer was indicated.

Benzene has also been used to photosensitize olefin reactions in the liquid phase. Kropp[37-40] and Marshall[41] have reported the products of benzene and substituted benzene photosensitized reactions of some cyclic monoolefins. 1-Methylcycloalkenes photosensitized by benzene or a substituted benzene in the absence of hydroxylic compounds isomerized to the exocyclic isomer and dimerized (Equation 15).



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The yield of exocyclic isomer increases in the order norbornene < n = 3 < n = 4 < n = 5[38]. Some reduction of the double bond was found when methyl substituted benzenes were used to photosensitize the reaction (Equation 16).

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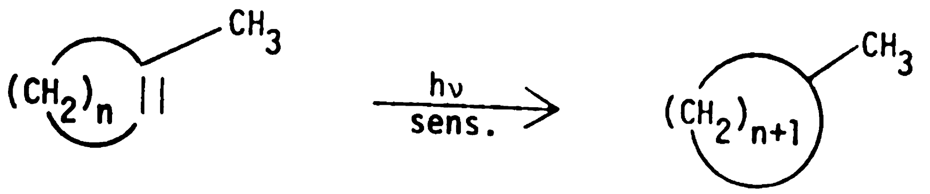

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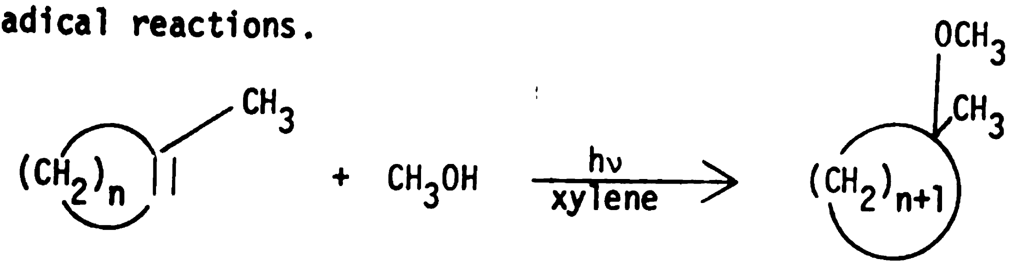
The ratio of dimer to exocyclic alkene produced from the sensitized photolysis of 1-methylcyclohexene was determined[40] (Table IV).

TABLE IV. Sensitized Photolysis of 1-Methylcyclohexene.

Sensitizer	E_T, kcal/mole	$\frac{\text{dimer}}{\text{methylenecyclohexane}}$
Benzene	84[a]	10.
Toluene	83[b]	7.2
p-Xylene	81-82[c]	1.8
Mesitylene	80[c]	0.5

[a]Ref. 29; [b]D. F. Evans, J. Chem. Soc., 2753 (1959); [c]D. R. Kearns, J. Chem. Phys., 36, 1608 (1962).

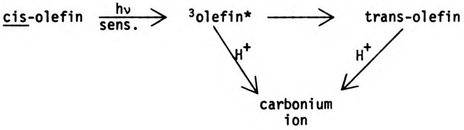
Photosensitized photolysis of cycloalkenes and 1-methylcycloalkenes in xylene-methanol solution yields mixtures of dimers, exocyclic alkenes, methanol addition products (Equation 17) and various products attributed to radical reactions.



(17)

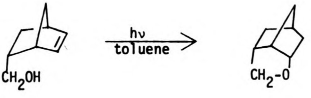
In general, the products from the photosensitized reactions of cycloalkenes indicate that the excited state of cyclopentenes and 2-norbornenes exhibited radical behavior whereas those formed from cyclohexenes and cycloheptenes undergo protonation. The radical behavior of the smaller ring compounds was attributed to the π,π^* triplet. The authors concluded

that protonation of the six- and seven-membered rings probably occurs through the formation of a trans-double bond but the possibility of protonating the triplet was not discounted (Equation 18)[40].



(18)

Intramolecular addition of alcohol has been photosensitized by toluene[39] (Equation 19).



(19)

Intramolecular quenching of benzene triplets was reported for dilute solutions of cis-1-phenyl-2-butene by Morrison[42,43]. Kinetic experiments in which the sensitized isomerization of the double bond was quenched by piperylene yielded a value of 2.0×10^8 sec^{-1} for intramolecular triplet-triplet energy transfer[43]. Nakagawa and Sigal[44] also studied the kinetics of this sensitized cis-trans isomerization but concluded that four processes were occurring: singlet-singlet inter- and intramolecular energy transfer and triplet-triplet inter- and intramolecular energy transfer.

D. Quenching of Dialkyl Ketone Triplets

Quenching of the triplet state of dialkyl ketones has been studied in both the gaseous and liquid phases. Research to determine the mechanism of quenching in the liquid phase, triplet-triplet energy transfer or chemical quenching, has been reported whereas triplet-triplet energy transfer has been assumed to account for quenching in the gas phase.

The first report of ketone photosensitized isomerization of a monoolefin was made by Hammond, Turro and Leermakers[45]. These researchers observed that in solution 2-pentene and 1,2-dichloroethylene isomerized when irradiated with wavelengths which they did not absorb in the presence of a variety of ketones from acetone ($E_T = 80 \frac{\text{kcal}}{\text{mole}}$) to fluorenone ($E_T = 53 \frac{\text{kcal}}{\text{mole}}$).

Rebbert and Ausloos carried out a systematic study in the gas phase of the relative quenching of acetone phosphorescence by a series of alkyl substituted monoolefins[46]. Their results in Table V should be compared with those in Tables II and III for metal atoms and benzene.

TABLE V. Quenching of Triplet Acetone by Olefins

Olefin	Relative Quenching x 10^4	Olefin	Relative Quenching x 10^4
ethylene	0.053	1,4-pentadiene	0.38
propene	0.11	2-pentene	0.42
1-butene	0.11	2-methyl-1-butene	0.48
1-pentene	0.13	trimethylethylene	0.64
isobutene	0.22	1-methylcyclohexene	0.67
cyclohexene	0.30	tetramethylethylene	2.90
trans-2-butene	0.31	1,3-butadiene	290
cis-2-butene	0.33	1,3-pentadiene	440
		styrene	10,000

The order of increasing quenching efficiencies parallels both that expected for decreasing triplet energies of the monoolefins and for increasing ease of attack by electrophilic ketone triplet. Consequently, no conclusion can be drawn regarding the mechanism of quenching from these data alone. In addition, these researchers reported that tetramethylethylene quenched acetone-d_6 phosphorescence 1.14 times more efficiently than acetone-h_6 phosphorescence and postulated that the longer lifetime of acetone-d_6 was responsible for this effect. But Schmidt and Lee[32] showed that when the difference in lifetimes of acetone-h_6 and acetone-d_6 (τ = .20 and .51 msec, respectively) are taken into account the isotope effect was k_H $(CH_3COCH_3)/k_D$ (CD_3COCD_3) = 2.2. The isotope effect for the quenching of acetone phosphorescence by ethylene and deuterated ethylene, $k(C_2H_4)/k(C_2D_4)$, was determined to be 1.9 ± .2[32] compared to the value of 1.7 found for quenching of benzene triplet. For quenching by propylene and propylene-d_6 the isotope effect was somewhat smaller[32].

The mechanism of acetone photosensitized <u>cis</u>-<u>trans</u> isomerization of 2-pentene has been studied in solution by Kearns[16] and by Saltiel[47]. Kearns calculated from the initial rate of isomerization of <u>cis</u>-2-pentene a rate constant for quenching of triplet acetone by <u>cis</u>-2-pentene of about 2×10^7 M^{-1} sec^{-1} at 25°C. The quenching rate constant at -78°C was about twenty times smaller. Because the rate constant for quenching was approximately 100 times smaller than the expected diffusion-controlled value and decreased as the temperature decreased, Kearns postulated that triplet-triplet energy transfer between acetone and <u>cis</u>-2-pentene required an activation energy. The following mechanism was postulated to account for these results (Equations 20, 21, 22).

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$$^3A^* + {}^1C_o \xrightarrow{k_a} [{}^3A^* \text{---} {}^1C_o] \quad (20)$$

$$[{}^3A^* \text{---} {}^1C_o] \xrightarrow{k_b} {}^3A^* + {}^1C_o \quad (21)$$

$$[{}^3A^* \text{---} {}^1C_o] \xrightarrow{k_c} {}^1A_o + {}^3C^* \quad (22)$$

where A represents acetone and ^1C_o represents cis-2-pentene. Because the collision complex, $[{}^3A^* \text{---} {}^1C_o]$, was assumed to have negligible stability, k_a and k_b would have the same temperature dependence. Therefore, the observed temperature dependence was attributed to k_c (Equation 22). In addition, the authors suggest that two mechanisms may be operating because the photostationary cis/trans ratio increases from 1.7 at 300°K to 2.5 at 200°K but decreases to 1.1 at 77°K. The two competing mechanisms suggested are a thermally activated interaction which predominates around room temperature but which gives way partially at low temperatures to a quantum-tunneling process.

Saltiel also concluded that two quenching mechanisms were operating from studies of the acetone and acetophenone photosensitized isomerization of 2-pentene[47]. He reasoned that if only one mechanism were operating (Equations 23-27), the ratio, $\alpha/1-\alpha$, for a given quencher would not change with sensitizer.

$$S_o \xrightarrow{h\nu} {}^1S^* \rightarrow {}^3S^* \quad (23)$$

$$^3S^* \xrightarrow{k_4} S_o \quad (24)$$

$$^3S^* + t_o \xrightarrow{k_5} {}^*X \quad (25)$$

$$^3S + c_o \xrightarrow{k_6} {}^*X \quad (26)$$

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$$*X \xrightarrow{k_7} \alpha t_0 + (1-\alpha)c_0 \qquad (27)$$

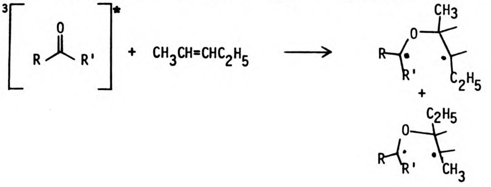
where S represents sensitizer, c_0 and t_0 are <u>cis</u> and <u>trans</u> ground state 2-pentene and X* represents an unspecified common intermediate.

Equations 28 and 29 were derived assuming steady state approximations for $^3S^*$ and X*.

$$\frac{1}{\phi_{t\to c}} = \frac{1}{1-\alpha} \left(1 + \frac{k_4}{k_5[t]}\right) \qquad (28)$$

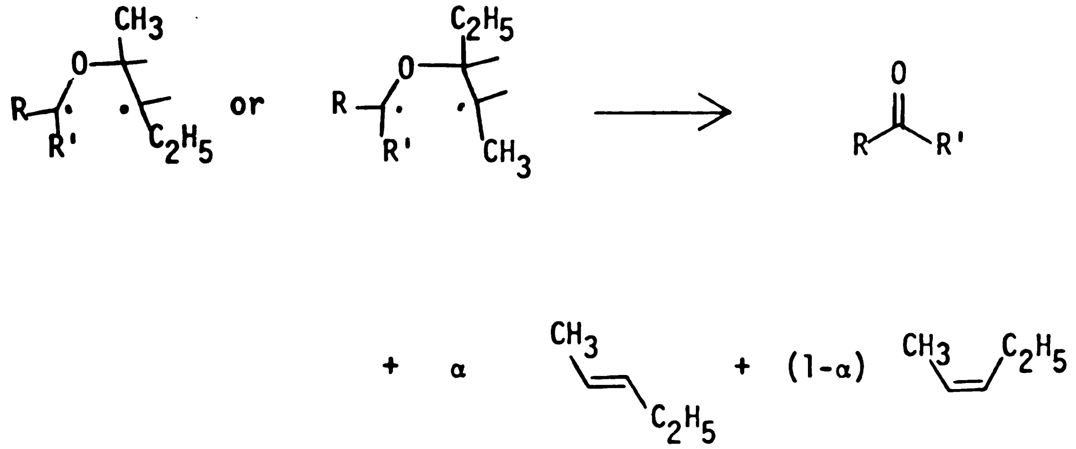
$$\frac{1}{\phi_{c\to t}} = \frac{1}{\alpha} \left(1 + \frac{k_4}{k_6[c]}\right) \qquad (29)$$

The ratio of the intercepts obtained from plotting the inverse isomerization quantum yields, $\frac{1}{\phi_{t\to c}}$ and $\frac{1}{\phi_{c\to t}}$, versus the initial concentration of 1/<u>trans</u>- and 1/<u>cis</u>-2-pentene, respectively, yield values for $\frac{\alpha}{1-\alpha}$. The values obtained for acetone and acetophenone ($E_T = 74$ kcal/mole) photosensitization (1.17 and 1.90, respectively) were compared with that obtained from benzene photosensitized isomerization of 2-butene (1.00), which was assumed to occur by triplet-triplet energy transfer. The increase in $\frac{\alpha}{1-\alpha}$ from unity was attributed to intervention of a biradical intermediate formed from attack of the ketone triplet on the olefin (Equation 30) which decayed to <u>cis</u>- and <u>trans</u>-2-pentene



(30)

(Equation 31). The decay ratio, $\frac{\alpha}{1-\alpha}$, from the biradical was expected



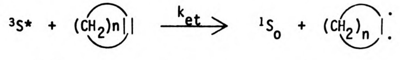
(31)

to differ from that found for olefin triplet decay. The authors concluded that acetone photosensitized isomerization proceeded predominantly via formation of olefin triplets whereas in acetophenone sensitization the biradical pathway, chemical quenching, is largely responsible for the isomerization.

Many irradiations of dialkyl ketones in the presence of mono-olefins have been reported in which some or all of the products were characterized but kinetic measurements were not made. In many of these cases, the product mixture can be accounted for by a single quenching mechanism or a combination of competing mechanisms. But in some cases, no choice between mechanisms can be made on the basis of products alone.

Some examples of the former situation are acetone photosensitized dimerizations, oxetane formation, and some reductions. Combinations of these reactions were often found. Acetone photosensitized dimerization of nonconjugated olefins occurs when the carbon-carbon double bond is in a four or five-membered ring or a strained polycyclic compound. The mechanism, which requires triplet-triplet energy

transfer, is given in Equations 32-35 (n = 2, 3, 4).



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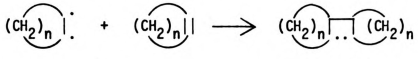

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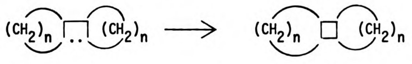

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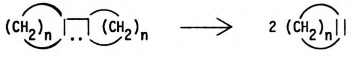

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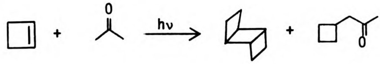
Acetone photosensitized dimerizations are often accompanied by reductions (see below). For example:



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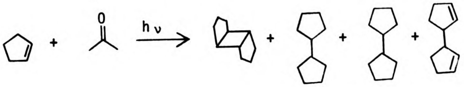

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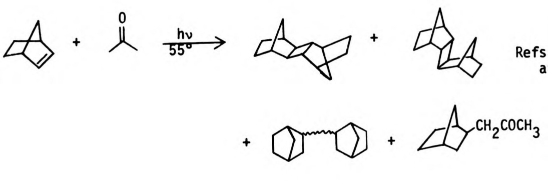

(38)
Refs. 19, and 48

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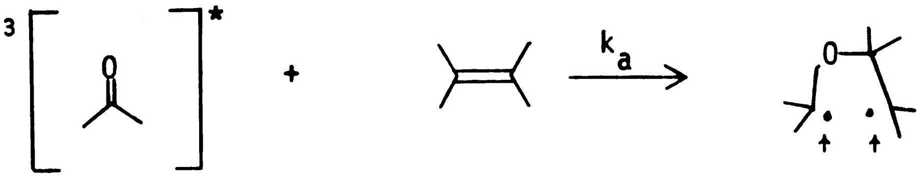
Light-initiated oxetane formation which results in quenching of ketone triplets is believed to take place through closing of the biradical formed from the attack of a ketone triplet upon a ground state olefin (Equations 39-91).



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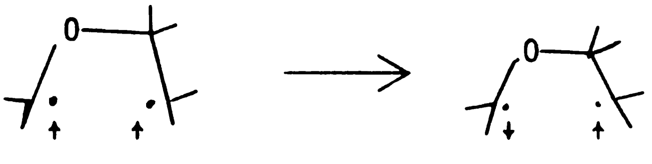

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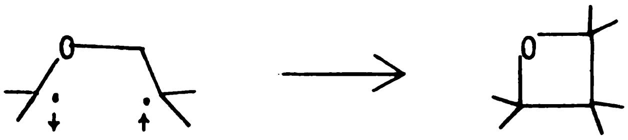
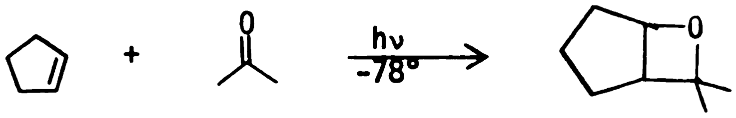


(41)

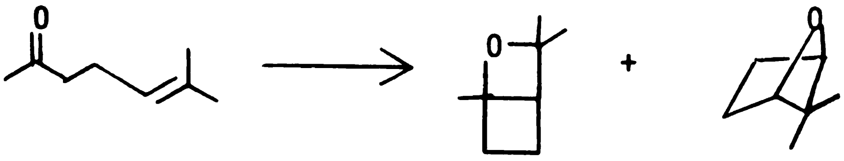
This mechanism has been invoked to explain the formation of oxetane in the following reactions.



(42)
Ref. 49

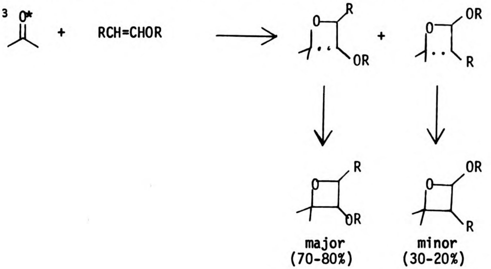
(43)
Ref. 50

(44)
Ref. 51



(45)
Ref. 52

Schroeter and Orlando[53] have studied the addition of acetone triplets to vinyl ethers and found that the major product always resulted from attack on the olefin to give the more stable biradical (Equation 46).



(46)

The authors noted that since the major product was not the exclusive product, as would have been predicted by relative rates of free radical attack[54], other factors such as cleavage/coupling ratios are important in determining product ratios.

Interesting results were found when the quenching of hexadeuteroacetone by tetramethylethylene was studied by Japar, Pomeratz and Abrahamson[55]. The products from photolysis to 1% conversion with either 3130Å or 3657Å light in solution consisted partly of non-deuterated acetone and hexadeuterotetramethylethylene (Equation 47). The authors proposed that a vibrationally excited oxetane was formed which then decomposed.

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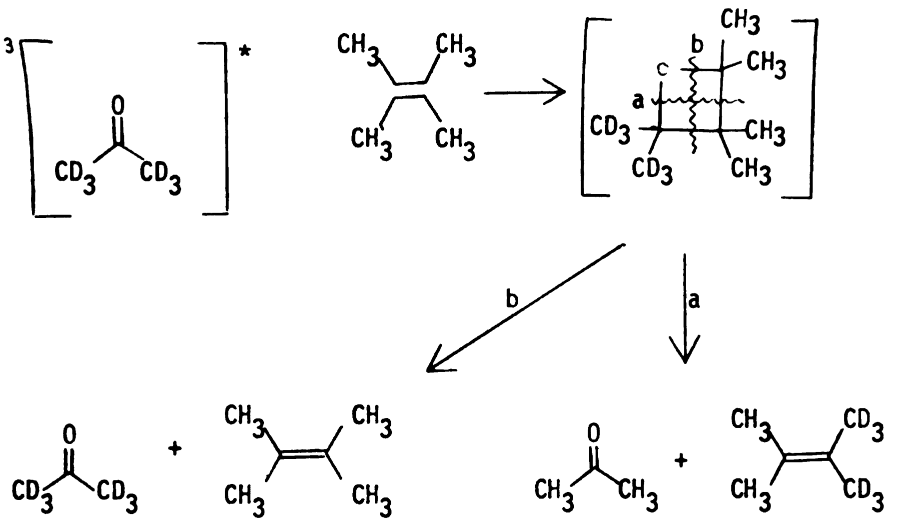

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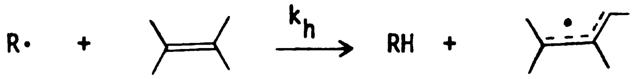
Reductions which are initiated by triplet ketones occur by combinations of hydrogen abstraction and radical coupling reactions. R· in the following equations may be the ketone triplet, the olefin triplet or other radical generated by these triplets.



(48)

$$2R\cdot \longrightarrow R\text{-}R$$

From the identity of the reduction products it is usually possible to decide if quenching of the ketone triplet occurred by energy transfer (products from triplet olefin are found) or by chemical quenching (products from hydrogen abstraction by acetone triplets are found). Equation 50 shows a case where photoreduction predominated over dimerization and oxetane formation[56].

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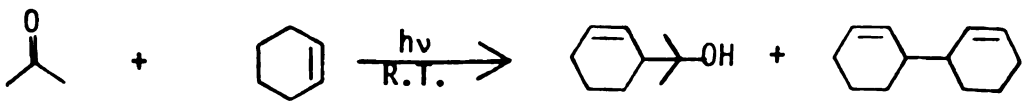
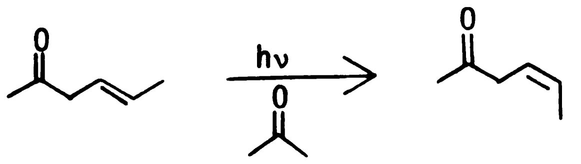


(50)

Examples of photosensitized reactions for which a choice between quenching mechanisms cannot be made are found with some cis-trans isomerizations. Morrison has studied the intramolecular photosensitized isomerization of 2-hexen-4-ones and 2-hepten-5-ones^{42}.



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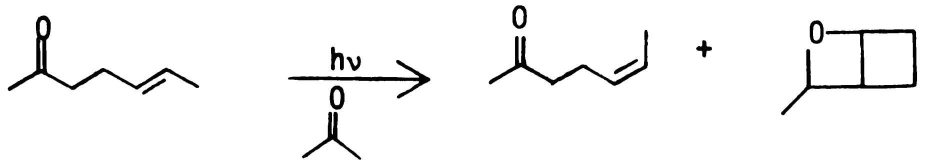

(52)

Either energy transfer or initial attack of the carbonyl oxygen upon the olefin can explain the isomerization reaction.

E. Quenching of Phenyl Alkyl Ketones and Diphenyl Ketones

The kinetic results reviewed below along with those of Saltiel cited above were published after the research presented in this dissertation was begun. The relationship of these results to the present research will be covered in the Discussion.

Photosensitized olefin dimerization, cis-trans isomerization, and oxetane formation have been reported to result from the interaction of k

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olefins with phenyl alkyl ketone triplets whereas quenching of diphenyl ketone triplets has been reported to yield only the latter two processes. Because of their low triplet energies (E_T = 75-68 $\frac{\text{kcal}}{\text{mole}}$) quenching of these ketones by triplet-triplet energy transfer is not expected to be efficient although the results of Saltiel[47] and Arnold[14] discussed above indicate that at least for acetophenone (E_T = 74.5 kcal/mole) some energy transfer quenching does occur.

The quenching rate constants have been determined for several triplet ketone olefin pairs. The first research in this area was published by Yang who studied the quenching of benzophenone and benzaldehyde triplets by 3-methyl-2-pentene[57] and by 2,3-dimethyl-2-butene[58]. The quantum yields obtained for oxetane formation and cis-trans-isomerization (for 3-methyl-2-pentene) are given in Table VI.

TABLE VI. Product Quantum Yields From Benzophenone and Benzaldehyde with Olefins.

Sensitizer	E_T	Olefin (conc.)	ϕ_{ox}	$\phi_{c\to t}$	$\phi_{t\to c}$
Benzaldehyde	71.5	2,3-dimethyl-2-butene (1M)	0.465	—	—
Benzaldehyde	71.5	2,3-dimethyl-2-butene (4M)	0.527	—	—
Benzaldehyde	71.5	2,3-dimethyl-2-butene (neat)	0.397	—	—
Benzaldehyde	71.5	cis-3-methyl-2-pentene (1M)	0.45	.18	—
Benzaldehyde	71.5	trans-3-methyl-2-pentene (1M)	0.45	—	.12
Benzophenone	68.0	cis-3-methyl-2-pentene (1M)	0.16	.36	—
Benzophenone	68.0	trans-3-methyl-2-pentene (1M)	0.16	—	.24

Oxetane formation and isomerization were quenched by varying amounts of conjugated diene at constant olefin concentration and the results were plotted according to the Stern-Volmer equation (Equation 53):

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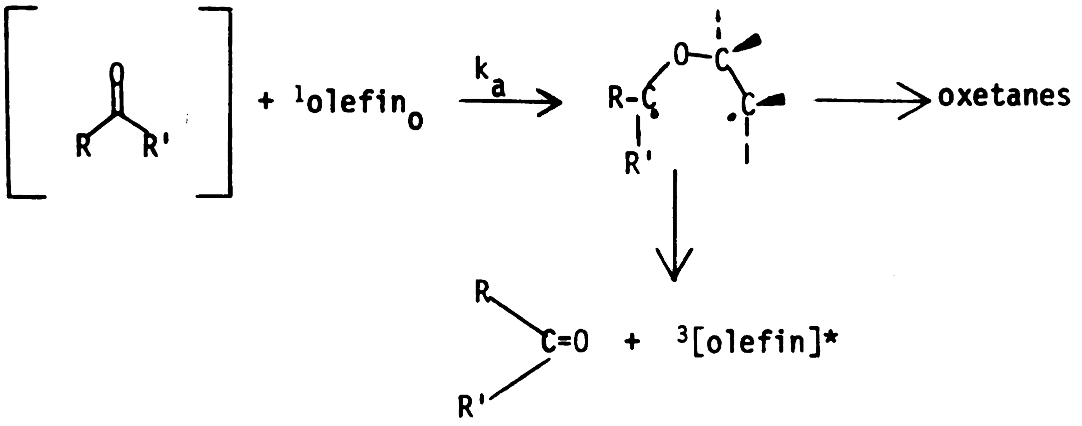
$$\frac{\phi^0}{\phi} = 1 + \frac{k_q\,[diene]}{k_d + k_r\,[olefin]} \qquad (53)$$

where ϕ^0 = quantum yield for isomerization or oxetane formation in absence of added diene, ϕ = quantum yield with added diene, k_q = rate constant for quenching of carbonyl triplet by diene (assumed to be diffusion controlled), k_d = rate constant for decay of carbonyl triplet in absence of olefin and diene, and k_r = rate constant for quenching interaction of olefin and carbonyl triplet. When k_d is assumed to be small relative to k_r [olefin], the values summarized in Table VIII are obtained.

Yang found that photosensitized isomerization of and oxetane formation from 3-methyl-2-pentene were quenched at the same rate. Such results indicate that a common excited state of the sensitizer may be responsible for both reactions. In addition, he concluded that isomerization of the olefin resulted from an olefin triplet formed upon cleavage of the initially formed biradical (Equation 54).



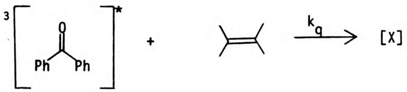
(54)

Kinetic isotope effects on the quenching of benzophenone triplets by 1,2-dichloroethylene and 2-butene have been studied by Caldwell[59,60]. His results are summarized in Table VII.

TABLE VII. Isotope Effects on the Quenching of Benzophenone Triplets.

Reaction Measured	Olefin Pair	k_H/k_D	Ref.
c→t	<u>cis</u>-CHCl=CHCl/<u>cis</u>-CDCl=CDCl	1.15 ± .02	59
t→c	<u>trans</u>-CHCl=CHCl/<u>trans</u>-CDCl=CDCl	1.18 ± .02	59
c→t	<u>cis</u>-$CH_3CH=CHCH_3$/<u>cis</u>-$CH_3CD=CDCH_3$	1.02 ± .01	59
c→t	<u>cis</u>-$CH_3CH=CHCH_3$/<u>cis</u>-$CH_3CD=CHCH_3$	0.985 ± .02	59
c→t	<u>cis</u>-$CH_3CH=CHC_2H_5$/<u>cis</u>-$CH_3CD=CHC_2H_5$	1.00 ± .01	60
t→c	<u>trans</u>-$CH_3CH=CHC_2H_5$/<u>trans</u>-$CH_3CD=CHC_2H_5$	1.01 ± .01	60
oxetane	<u>cis</u>-$CH_3CH=CHCH_3$/<u>cis</u>-$CH_3CD=CDCH_3$	1.03 ± .02	60

Caldwell pointed out that if biradical formation was the rate-determining step in quenching as was previously postulated for benzophenone an inverse isotope effect should have been found since the sp^2-hybridized carbons in the olefin would change to sp^3. The authors proposed that formation of a complex between the ketone triplet and the olefin before formation of a biradical would be consistent with the observed isotope effect (Equations 55-58).



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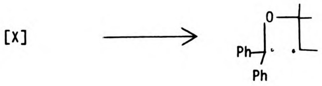

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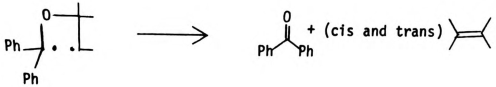

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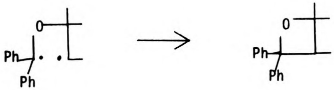


(58)

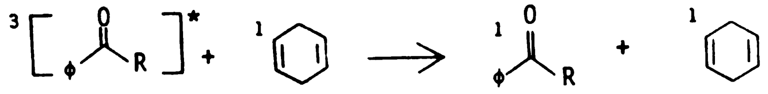
Caldwell also determined the rate constants for quenching by cis-2-butene of a series of substituted benzophenones. Because the results (Table VIII) indicate that quenching increases as electron attracting groups are introduced onto the carbonyl compound, an electron-transfer complex was proposed as the intermediate, X[60].

X

Also consistent with this intermediate was the observation that benzophenone triplet was quenched six times more rapidly by cis-2-butene than by cis-1,2-dichloroethylene even though the latter olefin probably has a lower triplet energy[59].

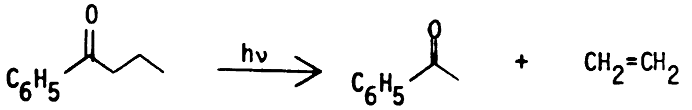
Quenching by a nonconjugated diene, 1,4-cyclohexadiene, of the acetophenone and β-chloropropiophenone photosensitized isomerization of cis-piperylene was reported by Braun, Hammond and Cassidy[61]. Based on examples of possible singlet electronic-vibrational energy transfer,

these authors proposed an analogous process for triplet quenching (Equation 59, Table VIII).



(59)

The present research consists mainly of a systematic study of the effect of changing olefin structure on the rate constant for quenching triplet state butyrophenone, a phenyl alkyl ketone. Butyrophenone undergoes Norrish Type II photoelimination exclusively from its triplet state yielding acetophenone and ethylene (Equation 60).



(60)

The quenching rate constants were determined by measuring the quantum yield of acetophenone without olefin and with various concentrations of olefin present and applying the Stern-Volmer relationship. This method has the advantage of measuring the quenching of a reaction of the excited ketone triplet rather than a reaction of the quencher as was done previously.

TABLE VIII. Quenching of Phenyl Alkyl and Diphenyl Ketones by Nonconjugated Olefins.

Sensitizer	E_T, kcal/mole		k_q, $M^{-1}sec^{-1}$[a]	Ref.
β-Chloropropiophenone	75.1	1,4-cyclohexadiene	5.5×10^7	B, H + C[61]
Acetophenone	74.	1,4-cyclohexadiene	3.0×10^7	"
Acetophenone	74.	cis-2-pentene	6.7×10^6[b]	Saltiel[47]
Acetophenone	74.	trans-2-pentene	2.9×10^6[b]	"
Benzaldehyde	71.5	2,3-dimethyl-2-butene	$1. \times 10^9$[c]	Yang[58]
Benzaldehyde	71.5	cis-3-methyl-2-pentene	8.3×10^8[d]	Yang[57]
Benzaldehyde	71.5	trans-3-methyl-2-pentene	8.0×10^8[d]	"
Benzophenone	68.5	trans-3-methyl-2-pentene	$2. \times 10^8$[d]	"
Benzophenone	68.5	cis-1,2-dichloroethylene	1.3×10^7	Caldwell[59]
Benzophenone	68.5	2,3-dimethyl-2-butene	1.3×10^9[d]	Yang[58]
Benzophenone	68.5	cis-2-butene	$7. \times 10^7$	Caldwell[59]
4,4'-Dimethoxybenzophenone	69.4	cis-2-butene	$4. \times 10^6$	Caldwell[60]
p-Trifluoromethylbenzophenone	67.6	cis-2-butene	2.2×10^8	"
4-Benzoylpyridine	67.1	cis-2-butene	3.3×10^8	"

[a] In benzene unless noted otherwise; k_q for diene assumed to be 5×10^9 M^{-1} sec^{-1}.

[b] Cyclohexane.

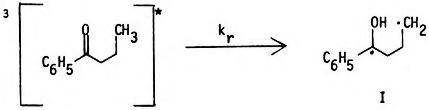
[c] Taken from graph in reference.

[d] Concentration of olefin assumed to be 1M.

II. RESULTS

A. Quenching of Butyrophenone Triplets by Olefins

The triplet state of butyrophenone was obtained by irradiating benzene solutions of the ketone through Pyrex and a filter solution which allowed wavelengths 3000 to 3200 Å to pass. The excited singlet state initially obtained, S_1, intersystem crosses with unit quantum efficiency[62] to the first excited triplet state, T_1. In the absence of quencher molecules, triplet butyrophenone abstracts a hydrogen from the methyl group to form a biradical, I[63] (Equation 61).



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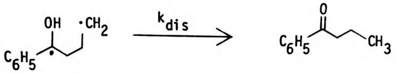
Radiative and unimolecular radiationless decay of triplet butyrophenone to the ground state are both much slower than the hydrogen abstraction process and can be ignored[64]. The hydrogen abstraction process, therefore, occurs with unit efficiency unless a quencher is present. The biradicals formed by hydrogen abstraction undergo disproportionation, cleavage and coupling in proportion to the rate constants for these processes: k_{dis}, k_{cl} and k_{cp}, respectively. Disproportionation yields ground state ketone (Equation 62), whereas cleavage and coupling yield new products, acetophenone enol and a



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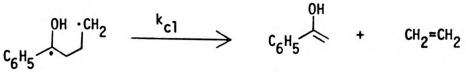

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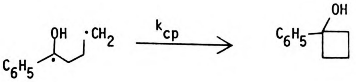


(64)

cyclobutanol, respectively, (Equations 63, 64). The processes from light absorption to product formation can be summarized in the following diagram.

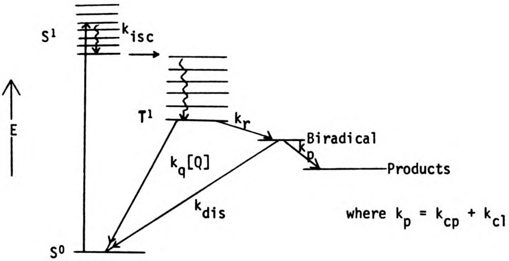


Figure 3. Jablonski Diagram for Butyrophenone.

The quantum yield for production of acetophenone, ϕ_A^0, in the absence of added quenchers can be expressed as:

$$\Phi_A^0 = \phi_{isc} \; \phi_{BR} \; \beta \tag{65}$$

where ϕ_{isc} = quantum yield for intersystem crossing

ϕ_{BR} = quantum yield for biradical formation

β = $k_{cl}/(k_{cl} + k_{cp} + k_{dis})$.

The quantum yield for intersystem crossing is unity for butyrophenone[62]. The quantum yield for biradical formation, ϕ_{BR}, equals $k_r/(k_r + k'_q\,[Q'])$ where the primed variables refer to quencher not intentionally added to the solutions. In the presence of added triplet quencher, Q, the following expression is appropriate for the quantum yield of acetophenone production (Equation 66).

$$\phi_A = \phi_{isc} \cdot \frac{k_r}{k_r + k'_q[Q'] + k_q\,[Q]} \cdot \beta \tag{66}$$

Dividing Equation 65 by Equation 66 yields the Stern-Volmer expression (Equation 67).

$$\frac{\Phi_A^0}{\Phi_A} = 1 + \frac{k_q[Q]}{k_r + k_q'[Q']} \tag{67}$$

The lifetime of the butyrophenone triplet in the absence of added quencher, τ, is equal to $1/(k_r + k'_q\,[Q'])$. Therefore, the Stern-Volmer relationship can be written as:

$$\frac{\Phi_A^0}{\Phi_A} = 1 + k_q\tau\,[Q] \tag{68}$$

In order to determine τ, 2,5-*dimethyl*-2,4-*hexadiene* was choosen as a quencher since this diene appeared to quench triplet butyrophenone at the maximum rate in benzene solution, $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$[71]. Because the value of k_q was known, the slopes of plots of Φ_A^0/Φ_A versus [Q] were used to calculate τ. The values found for τ for the four samples of butyrophenone used in these studies are summarized in Table IX.

TABLE IX. Lifetime of Butyrophenone.

Sample	$\tau \times 10^7$, sec
I	1.14
II	0.99
III	0.80
IV	1.13

A series of non-conjugated olefins were used to quench the triplet state reaction of butyrophenone. Plots of Φ_A^0/Φ_A versus [olefin] were drawn for each olefin and the slopes of these plots were determined. Tables X and XI list the olefins used as quenchers, the slopes of the Stern-Volmer plots and the sample of butyrophenone used.

3

1
t

B

N

Cy

Cy

Cy
Cy
1,4

TABLE X. Quenching of Triplet Butyrophenone by Hydrocarbon Olefins.

Olefin	Slope, M^{-1}	Ketone Sample
2,3-Dimethyl-2-butene	52.5	I
"	33.7	III
"	38.6	III
"	37.4	III
2-Methyl-2-butene	14.7	I
"	13.1	III
"	13.5	III
cis-3-Hexene	3.8	II
"	3.76	IV
trans-3-Hexene	1.25	IV
cis-4-Methyl-2-pentene	.85	I
trans-4-Methyl-2-pentene	.44	I
"	.465	II
cis-2-Pentene	3.30	III
"	4.06	III
"	4.78	III
"	5.75	IV
trans-2-Pentene	1.50	III
"	1.74	III
"	1.83	IV
2-Methyl-1-butene	3.45	I
"	2.90	I
1-Pentene	.90	I
trans-2,2,5,5-Tetramethyl-3-hexene	1.90	III
Bicyclo[4.2.0]oct-7-ene	8.8	I
"	8.3	I
Norbornene	3.84	III
"	3.05	III
Cyclopentene	6.02	I
"	5.93	I
Cyclohexene	3.05	I
"	4.4	II
"	3.85	II
"	4.48	III
Cycloheptene	8.6	I
Cyclooctene	9.4	I
1,4-Cyclohexadiene	11.6	III

TABLE XI. Quenching of Triplet Butyrophenone by Chloroolefins.

Olefin	Slope, M^{-1}	Ketone Sample
Tetrachloroethylene	165	I
"	165	I
Trichloroethylene	88	II
"	76	II
cis-1,2-dichloroethylene	18.5[a]	I
"	38.1[a]	I
"	18.4[a]	IV
trans-1,2-dichloroethylene	48[a]	I
"	43.3[a]	IV
"	46[a]	I

[a] Intercept not equal to unity.

The actual quenching rate constants for the non-conjugated olefins were calculated from the values of the slopes given in Tables X and XI and the ketone lifetimes given in Table IX. A summary of the quenching constants for nonconjugated olefins along with the relative quenching efficiencies, based on cis-2-pentene = 1, are given in Table XII.

TABLE XII. Quenching of Triplet Butyrophenone by Olefins.

Olefin	$k_q \times 10^{-7}$, M^{-1} sec^{-1}	relative quenching efficiency
2,5-Dimethyl-2,4-hexadiene	500	98.5
2,3-Dimethyl-2-butene	46. ± 3.	9.08
2-Methyl-2-butene	14.3 ± 1.5	2.82
<u>cis</u>-3-Hexene	3.58 ± .25	.71
<u>trans</u>-3-Hexene	1.11	.22
<u>cis</u>-4-Methyl-2-pentene	.745	.15
<u>trans</u>-4-Methyl-2-pentene	.414 ± .030	.08
<u>cis</u>-2-pentene	5.07 ±1.00	1.00
<u>trans</u>-2-pentene	1.89 ± .30	.37
2-Methyl-1-butene	2.76 ± .25	.54
1-Pentene	.79	.16
<u>trans</u>-2,2,5,5-Tetramethyl-3-hexene	2.39	.47
Bicyclo[4.2.0]oct-7-ene	7.5 ± .25	1.48
Norbornene	3.70 ± .10	.73
Cyclopentene	5.24 ± .04	1.03
Cyclohexene	4.2 ± 1.5	.83
Cycloheptene	7.55	1.49
Cyclooctene	8.25	1.63
1,4-Cyclohexadiene	14.6	2.88
Tetrachloroethylene	145 ± 0.	28.6
Trichloroethylene	71.8 ± 5.	14.1
<u>cis</u>-1,2-Dichloroethylene[a]	16.2 ± .1	3.20
<u>trans</u>-1,2-Dichloroethylene[a]	40. ± 2.	7.90

[a] Intercept not equal to unity.

Error represents mean deviation from average value for two or more runs.

Error on single runs estimated to be ± 5%.

B. Quenching Which Results in Product Formation Involving Butyrophenone.

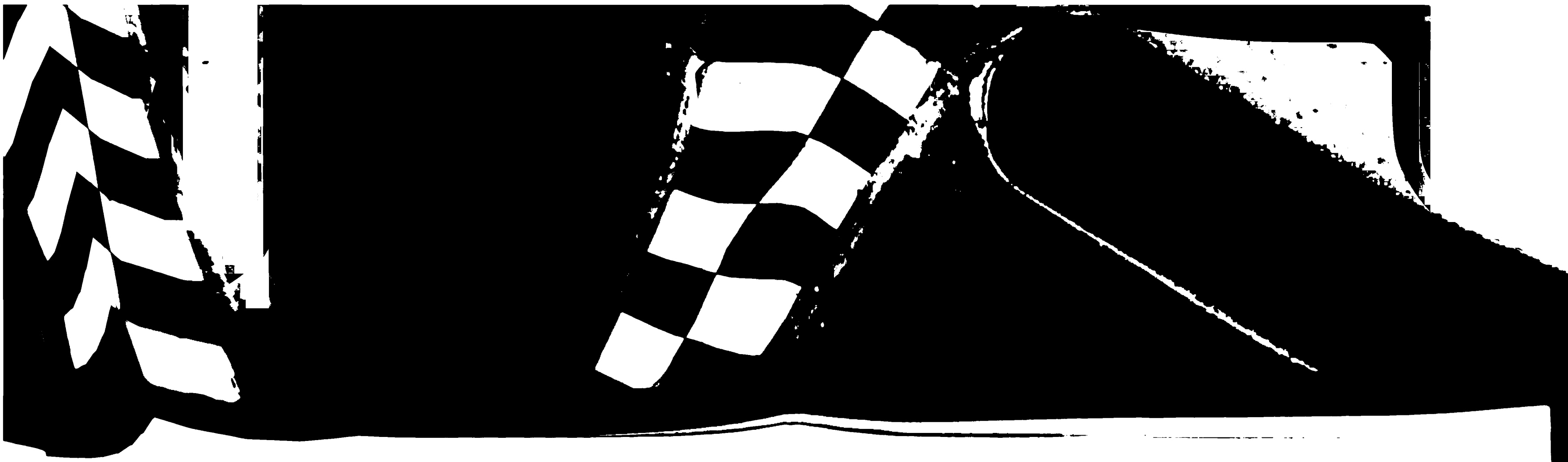
A series of irradiations were carried out with several olefins in order to get a minimum value for the fraction of quenching which occurred by a chemical quenching mechanism. The fraction of quenching due to chemical quenching was calculated by dividing the moles of butyrophenone which disappeared during the irradiation but could not be accounted for by acetophenone and cyclobutanol formation by the moles of butyrophenone triplets quenched.

The data for these calculations are in the Experimental Section and the results are summarized in Table XIII.

TABLE XIII. Chemical Quenching of Butyrophenone Triplet

Olefin	Minimum Percent of Chemical Quenching
Tetrachloroethylene	2
Trichloroethylene	2
cis-4-Methyl-2-pentene	12
2-Methyl-2-butene	5
Cyclohexene	44

These values represent the minimum percent of chemical quenching because chemical quenching which does not consume butyrophenone, i.e., that which involves revertible biradical formation, is not included. The fact that appreciable acetophenone was formed during the irradiations did not appear to affect the results.



C. Quenching of p-Trifluoromethylbutyrophenone Triplets.

In order to obtain further indications of the type of quenching interaction taking place between phenyl alkyl ketones and nonconjugated olefins, the quenching of p-trifluoromethylbutyrophenone was studied. The carbonyl group of the triplet state of this compound should be more electron deficient than that of butyrophenone. Its triplet energy was determined to 72 kcal/mole, 2.5 kcal/mole lower than that of butyrophenone. The triplet state lifetime of p-trifluoromethylbutyrophenone was determined to be .6 x 10^{-7} sec by quenching with 2,5-dimethyl-2,4-hexadiene. Therefore, the p-trifluoromethyl substituent increases the reactivity of the carbonyl oxygen toward γ-hydrogen abstraction by a factor of about 2. Rate constants for quenching of p-trifluoromethylbutyrophenone and butyrophenone by three monoolefins are compared in Table XIV.

TABLE XIV. Quenching of Butyrophenone and p-Trifluoromethylbutyrophenone by Monoolefins.

Olefin	Butyrophenone $k_q \times 10^{-7}$, M^{-1} sec^{-1}	p-Trifluoromethylbutyrophenone $k_q \times 10^{-7}$, M^{-1} sec^{-1}
cis-2-Pentene	5.07 ± 1	10.6
2-Methyl-2-butene	14.3 ± 2	25.
Norbornene	3.70 ± .1	4.68

D. Sensitized Dimerization of Norbornene and Cyclopentene

As predicted by the results of Arnold's study of the dependence of sensitized dimerization on ketone triplet energy[14], butyrophenone sensitized the dimerization of norbornene as well as that of cyclopentene. According to the mechanism for sensitized dimerization (Equations 32-35), the olefin concentration influences the dimer yield in two separate steps. Higher olefin concentration should increase the efficiency of the energy transfer process (Equation 32) and the attack of triplet olefin upon ground state olefin (Equation 33) at the expense of the competetive processes not involving a ground state olefin molecule. An 1.13-fold increase in the *exo*-*trans*-*exo* dimer yield was found as the norbornene concentration was increased from 0.999 to 2.812 M and a 2.3-fold increase in dimer yield was found as the cyclopentene concentration changed from 0.156 to 0.782 M.

p-Trifluorobutyrophenone sensitized the dimerization of norbornene about 20 times less efficiently than butyrophenone at the same olefin concentration. Since the efficiency of Equation 33 should remain the same, the efficiency of the energy transfer process appears to have decreased by a factor of 20. The shorter lifetime of *p*-trifluoromethylbutyrophenone alone only accounts for half of the decreased efficiency. Consequently, it appears that other quenching processes are able to compete more effectively with energy transfer from *p*-trifluoromethylbutyrophenone than from butyrophenone.

III. DISCUSSION

The decrease in Type II photoelimination quantum yield from butyrophenone in the presence of monoolefins is attributed to quenching of the ketone triplet by the monoolefins. The possibility of singlet-singlet energy transfer can be eliminated since the singlet energies of the monoolefins are > 50 kcal/mole greater than the singlet energy of butyrophenone. Chemical quenching of the ketone singlet can also be eliminated because of the ketone's short singlet lifetime.

The commonly proposed mechanisms for quenching of ketone triplets by nonconjugated olefins are triplet-triplet energy transfer and radical addition of the carbonyl oxygen to the carbon-carbon double bond.

Triplet-triplet energy transfer only occurs with a rate constant approaching the diffusion rate constant in solution under certain conditions. The triplet energy of the donor must be equal to or greater than that of the acceptor. Lower rates of energy transfer have been observed when this condition is not met[15,65]. Also, the triplet state lifetime must be long enough to allow for a number of collisions to take place because energy transfer does not appear to take place on every collision[66,67].

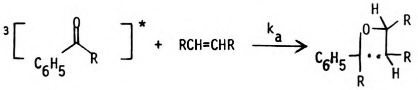
$$^3S^* + {}^1\text{olefin}_0 \xrightarrow{k_{et}} {}^1S_0 + {}^3\text{olefin}^* \qquad (1)$$

$$^{3}\text{olefin}^{*} \longrightarrow \alpha\ \textit{cis}\text{-olefin} + (1-\alpha)\textit{trans}\text{-olefin} \qquad (69)$$

$$^{3}\text{olefin}^{*} + {}^{1}\text{olefin}_{0} \longrightarrow \text{olefin dimer} \qquad (70)$$

When the acceptor is an olefin, it has been shown that energy transfer causes both isomerization and dimerization.

Radical attack by the oxygen of the triplet ketone upon the carbon-carbon double bond yields a biradical which either cleaves or couples. Allylic hydrogen abstraction, another means of chemical quenching, has not been an important interaction except in one case discussed below.



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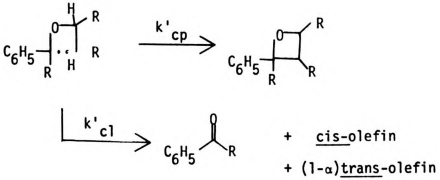

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Comparison of triplet state benzophenone with t-butoxy radical has shown that $n\pi^*$ ketone triplets act as electrophilic radicals[68]. Consequently, the rate of radical addition should increase as the ketone triplet becomes more electrophilic and as the olefin becomes more nucleophilic.

A. Chloroolefins.

The chloroolefins were the most efficient of quenchers of the monoolefins studied. The rate constants for quenching increased as chlorines were substituted for hydrogens on ethylene. Tetrachloroethylene quenched triplet butyrophenone with a rate constant only ∿3 times less than the maximum rate in benzene solution and cis-1,2-dichloroethylene was about 10 times less efficient than tetrachloroethylene.

Chloro substituents should decrease the rate of electrophilic addition to the double bond[69]. Consequently, the trend in k_q predicted for quenching by radical addition is opposite to that observed.

The lack of oxetane formation between butyrophenone and tri- or tetrachloroethylene or between benzophenone and the dichloroethylenes[59] also argues against quenching by radical addition since the biradical formed would be expected to couple part of the time.

If the triplet energies decrease as the number of chlorines on the double bond increases as has been found for the singlet energies[70], k_{et} should increase in the order dichloro- < trichloro- < tetrachloroethylene. The vertical triplet energies of the chloroolefins[12] may be approximately equal to E_T for butyrophenone. The magnitude of the k_q's is consistent with slightly endothermic energy transfer[15].

Since the trend predicted for k_q with respect to chloro substituents by an energy transfer mechanism is observed and the magnitude of the rate constants is consistent with inefficient energy transfer, triplet-triplet energy transfer is proposed as the mechanism of quenching by the chloroolefins.

This conclusion is consistent with Caldwell's results which indicate that triplet benzophenone (E_T = 69 kcal/mole) transfers energy to cis- and trans-1,2-dichloroethylene[59]. The rate constant reported for quenching of benzophenone by trans-1,2-dichloroethylene was 1.3×10^7 M^{-1} sec^{-1} whereas k_q for quenching of butyrophenone was $40. \times 10^7$ M^{-1} sec^{-1}. Caldwell based his conclusion mainly on the fact that he found a normal isotope effect on quenching (k_q(ClHC=CHCl)/k_q(ClDC=CHCl) > 1). An inverse isotope effect is expected for quenching by radical addition to the double bond.

B. Acyclic olefins.

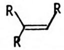
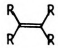
The rate constants for quenching by eleven acyclic olefins[11] varied from being ∿10 to ∿1000 times less than that of the diene. In general, k_q increased with the number of alkyl substituents on the double bond and the cis isomer of a cis-trans olefin pair was always a 2-3 times better quencher than the trans isomer.

The vertical triplet energies of these olefins are greater than E_T for butyrophenone. As seen from the following rough calculation, endothermic energy transfer would occur with lower rates constants that those determined. The decrease in energy transfer efficiency as a function of the triplet energy of the quencher is given by Equation 73, assuming that ΔE_T represents an activation energy for energy transfer.

$$\frac{\Delta \log k_{et}}{\Delta E_T} = -\frac{1}{2.303RT} \qquad (73)$$

If the vertical triplet energy of cis-2-pentene is about 80 kcal/mole (calculated by subtracting 1 kcal/mole for each alkyl substituent from the value of 82 kcal/mole for ethylene), energy transfer from butyrophenone is about 5.5 kcal/mole endothermic. Since exothermic energy transfer in benzene proceeds with a rate constant[71] equal to 5×10^9 M^{-1} sec^{-1}, k_{et} for cis-2-pentene should be less than 1×10^6 M^{-1} sec^{-1}. Since the measured k_q is over an order of magnitude greater than this value, endothermic vertical energy transfer does not appear to responsible for the quenching by monoolefins. In addition, a comparison of the relative quenching rates for four representative olefins with benzene, acetone and butyrophenone (Table XV) shows that the range between the least and the most efficient varies only by a factor of 10 from benzene to butyrophenone. If energy transfer quenching alone was determining these rate constants the variation should be much greater because quenching by energy transfer of butyrophenone is about 9 kcal/mole more endothermic than quenching of benzene.

TABLE XV. Quenching of Triplets by Alkyl Substituted Ethylenes.

Sensitizer	E_T, kcal/mole				
Benzene	84.4[a]	.54	1.00	1.6	2.7
Acetone	80[b]	.32	1.00	1.5	7.0
Butyrophenone	74.7[c]	.16	1.00	2.8	9.1

[a] Ref. 29; [b] R. F. Borkman and D. R. Kearns, J. Chem. Phys., 44, 945 (1966); [c] J. N. Pitts, Jr., D. R. Burley, J. C. Mani and A. D. Broadbent, J. Am. Chem. Soc., 90, 5902 (1968).

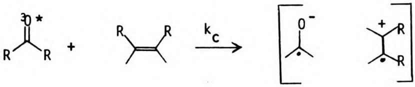
Energy transfer to a twisted olefin (non-vertical energy transfer) has been proposed to account for endothermic energy transfer to conjugated olefins[65]. This proposal was based on the observation that the rate constants for quenching of a series of sensitizers did not decrease as rapidly as Equation 73 predicted as the sensitizer triplet energy decreased.

Two factors indicate that non-vertical energy transfer is not occurring to the nonconjugated olefins in this study. First of all, the rate constants for non-vertical energy transfer to cis-olefins are always less than those for the trans isomer whereas the opposite result was consistently found in the present study. Secondly, the k_q values for cyclic olefins are larger than k_q for cis-2-pentene. If twisting was involved in the quenching process, restraining the double bond in a ring should decrease k_q.

The observed rate constants are also larger than expected for quenching by initial radical addition. Other electrophilic radicals, such as t-butoxy, abstract allylic hydrogens from olefins more rapidly than they add to them[72]. Since the rate constant for abstraction is less than 10^5 M^{-1} sec^{-1}, k_a is expected to be even lower. In addition, the lack of isotope effect reported by Caldwell[60] for the quenching of benzophenone by 2-butene cannot be reconciled with a radical addition mechanism which would predict an inverse isotope effect on k_q.

In total, the results obtained from studies of the quenching of ketones by acyclic olefins appear to rule out both energy transfer and initial radical addition as the predominant quenching process for triplet butyrophenone.

Quenching by formation of a complex which has charge-transfer character appears to be consistent with all of the kinetic results. This complex could lead to the biradical from which the observed products are formed or to ground state molecules (Equations 74-77).



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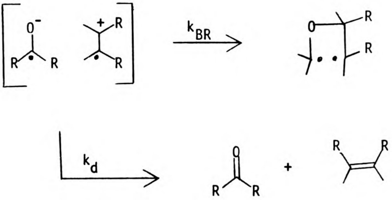

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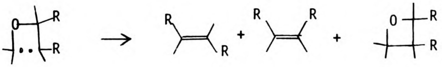

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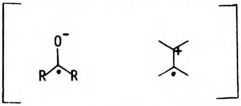
If the olefin is the donor and the ketone the acceptor, the rate constant for this process, k_c, should increase as the olefin becomes electron rich and as the ketone becomes electron deficient. Increasing the number of (electron-donating) alkyl substituents on the double bond, was found to increase k_q as predicted. Data from the present research combined with Yang's and Caldwell's results (Table XVI) further support quenching by charge-transfer complex formation.

TABLE XVI. Quenching of Some Carbonyl Compounds with Alkyl Substituted Olefins.

Ketone		$k_q \times 10^{-7}$ M^{-1} sec^{-1}		
	E_T,kcal/mole	$CR_2=CR_2$[a]	$CRR'=CHR$[b]	*cis*-$CHR=CHR'$[b]
Butyrophenone	74.7	46[c]	14.3[c]	5.07[c]
p-Trifluoromethyl-butyrophenone	72.	—	25[c]	10.6[c]
Benzaldehyde	71.5	100[d]	83[e]	—
Benzophenone	68.5	130[d]	20[e]	8[f]

[a] R = methyl; [b] R = methyl, R' = methyl or ethyl; [c] Present work; [d] ref. 55; [e] ref. 56; [f] ref. 58.

The ketones are listed in the order in which their triplet states increase in electrophilicity. The order which k_q increases is seen to be roughly the same. Consequently, formation of a complex of the form



could be responsible for the quenching. The rate of formation of this complex should be sensitive to the electron accepting ability of the ketone rather than its E_T.

Similar results obtained by Caldwell for substituted benzophenones[58] were pointed out in the Introduction. Caldwell also proposed quenching by complex formation to explain his results. The possibility that the complex collapses to ground state molecules in addition to yielding a biradical, can be tested for by summing the quantum yields of isomerization and oxetane formation when the ketone is completely quenched.

If the sum is unity this energy wasting step (Equation 76) is not important. Pertinent data are presented in Table XVII.

TABLE XVII. Sums of Quantum Yields for Sensitized Olefin Reactions.

Sensitizer	Olefin	$\phi_{c\to t}$	$\phi_{t\to c}$	ϕ_{ox}	ϕ_{-K}	ϕ_{Total}
Benzaldehyde[a]	3-Methyl-2-pentene	.18	.12	.45	.60	.75-.90
Benzophenone[a]	3-Methyl-2-pentene	.36	.24	.16	.20	.76-.80
Acetophenone[b]	2-Pentene	.50	.26	[c]	—	.76

[a] Ref. 52; [b] Ref. 46; [c] Oxetane formation was not reported.

The sum is not unity in the cases studied indicating that an energy wasting step does occur. This result is additional evidence against either an energy transfer or a radical addition mechanism since neither of these mechanisms can account for total quantum yields less than unity.

The rate constants for quenching are not unreasonable if the quenching is occuring by complex formation since this process does not involve bond formation.

C. Cyclic olefins

The cyclic olefins quench triplet butyrophenone with rate constants ~2 orders of magnitude lower than the maximum rate constant in benzene solution. The quenching rate constants for the cyclic olefins were larger than for most of the cis-1,2-dialkylsubstituted acyclic olefins.

Radical addition can be discarded as a probable quenching mechanism based on two factors. First of all, the order of radical addition is predicted[73] to be $C_4 > C_6 > C_5 > C_7 > C_8$ whereas almost the opposite

order was found for k_q. Secondly, as for the acyclic olefins, the rate constants were too large for radical addition to a carbon-carbon double bond. Also, Arnold found that benzophenone triplet abstracted hydrogens from rather than adding to cyclohexene[74]. The relative rates of k_a to k_h should be the same for butyrophenone triplet.

Chemical quenching did appear to account for a large fraction (0.44) of the quenching by cyclohexene (Table XIII). The large number of products appearing in the vpc traces of photolyzed samples containing cyclohexene and the lability of its allylic hydrogens[75] indicated that quenching by allylic hydrogen abstraction was occurring with cyclohexene. The vpc traces from other cyclic olefins did not indicate significant photoreduction.

Although the k_q values for the cyclic olefins appear to be too large for vertical energy transfer, sensitized dimerization of cyclopentene and norbornene is observed. This conflict may be resolved by proposing that energy transfer and complex formation are competing quenching processes for the cyclic olefins. The seven and eight membered rings should have the same triplet energies as the cis-1,2-dialkyl-substituted olefins. Consequently, energy transfer is slow and most of the quenching is occurring by complex formation. The larger rates for the ring systems must reflect greater ability to form a complex with charge-transfer character.

The smaller ring cycloalkenes may have lower triplet energies than their acyclic analogues. This effect could be due to rehybridization of the olefinic carbons from sp^2 in the ground state to sp^3 in the triplet. Such rehybridization would be expected to lower the triplet

energy by relieving some of the strain in the molecule. From absorption spectra, the five and six-membered cyclic olefins appear to have lower singlet energies than the cis-1,2-dialkylsubstituted olefins[76]. The observed k_q values for the small cycloalkenes therefore are a combination of k_c and k_{et}.

A rough estimate of the fraction of energy transfer occurring with norbornene can be made. The data in Table XIV show that k_q doubled for cis-2-pentene when the ketone changed from butyrophenone to p-trifluoromethylbutyrophenone but only increased by a factor of 1.25 for norbornene. Assuming that quenching of p-trifluoromethylbutyrophenone by cis-2-pentene is almost entirely by complex formation and that energy transfer to norbornene decreases by an order of magnitude because of the 2.5 kcal/mole decrease in the sensitizer triplet energy, the fraction of quenching of butyrophenone by energy transfer comes out to be 0.35. Therefore, complex formation is still the predominant quenching mechanism.

The following scheme summarizes the conclusions from the above discussion.

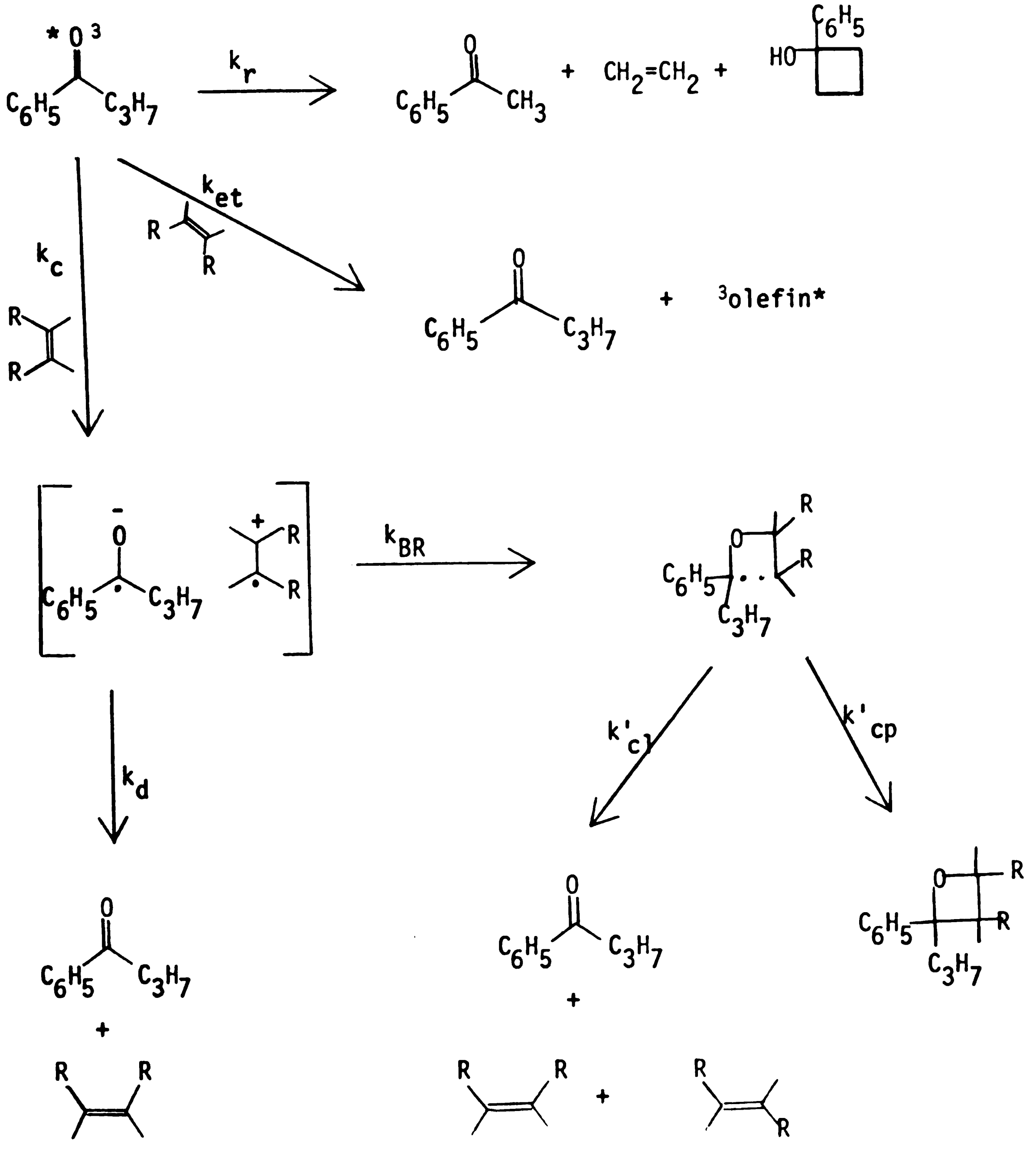


Figure 4. Quenching of Butyrophenone Triplet by Monoolefins.

D. Summary

In summary, the mechanism and rate constant for quenching butyrophenone triplet depend upon the olefin triplet energy and upon the electron density of the double bond. The chloroolefins, which have triplet energies near that of butyrophenone but do not have electron rich double bonds, quench triplet butyrophenone by energy transfer. Both the acyclic and the cyclic hydrocarbon olefins quench by formation of a complex in which the ketone acts as an electron acceptor and the olefin as a donor. The quenching rate constant increases as the olefin becomes a better donor. The smaller ring cycloalkenes also quench partially by energy transfer due to their lower triplet energies.

E. Further Experiments

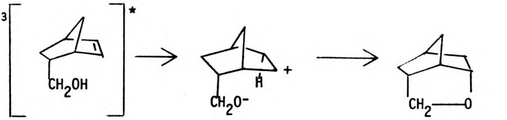
Some experiments which either test parts of the proposed scheme or are designed to yield further data about the steps in the scheme can now be described.

1. To determine if the values of k_q for cycloheptene and cyclooctene represent only k_c, these olefins should be used to quench _p_-trifluoromethylbutyrophenone. If the high rate constant for quenching of butyrophenone reflects greater complex formation ability of these cyclic olefins exclusively, k_q should double for _p_-trifluoromethylbutyrophenone as was found for _cis_-2-pentene and 2-methyl-2-butene.

2. To confirm that quenching of butyrophenone by 2-methyl-2-butene and _cis_-2-pentene is occurring by complex formation, the product(s) detected (see Table XIII) should be identified. If the product is oxetane, the proposed mechanism is confirmed. Since radical addition does not compete effectively against hydrogen abstraction, the oxetane

must arise through initial complex formation.

3. To determine the fraction of norbornene quenching due to energy transfer, butyrophenone should be used to sensitize the internal addition of methanol to norbornene triplet (Equation 78). Kropp has proposed that this reaction occurs through the norbornene triplet[40].



(78)

The moles of adduct formed over the moles of butyrophenone triplets quenched yields the fraction of norbornene quenching which occurs by energy transfer.

4. A study to determine the relative rates of k_{BR} to k_d and of k'_{cl} to k'_{cp} and the dependence of these ratios on olefin structure could be undertaken. The ratio k_{BR}/k_d can be determined by measuring the ratio $\phi_{BR}/(\phi_q-\phi_{BR})$ where $\phi_{BR} = \phi_{c\to t} + \phi_{t\to c} + \phi_{ox}$ and ϕ_q = quantum yield of triplets quenched. The ratio k'_{cl}/k'_{cp} can be determined by measuring the relative quantum yields of isomerized olefin and oxetane. The following olefins appear to be appropriate for these measurements: cis- and trans-3,4-dimethyl-3-heptene; cis- and trans-3-methyl-2-pentene; and, cis- and trans-3-heptene. The measurements on the trisubstituted olefin will probably be complicated by the formation of two biradicals in unequal amounts.

F. Model for Ketone Triplet-Monoolefin Interaction

In view of the systematic kinetic study made in this research and the abundance of both kinetic and product identification data in the literature, it seemed appropriate to propose a model for ketone triplet-monoolefin interactions which was consistent with these data. Such a model would be valuable for its ability to predict quenching rates and products. Also, this model should set up a framework for future research.

The model proposed in Figure 5 is based on competition between two processes, energy transfer and charge-transfer complex formation. The relative values of k_{et} and k_c determine which process is responsible for quenching. The rate constant for energy transfer approaches the diffusion controlled rate constant when the triplet energy of the ketone is greater than that of the olefin but drops off rapidly as the process becomes endothermic (Equation 73).

In the proposed complex the ketone triplet acts as an electron acceptor and the olefin as an electron donor. Consequently, k_c increases as electron withdrawing substituents are substituted onto the ketone and as electron donating substituents are substituted onto the olefin.

The results obtained in the present study have already been explained in terms of this scheme as it applied to butyrophenone (E_T = 74.5 kcal/mole) specifically. Quenching of acetone (E_T = 80 kcal/mole) appears to occur by energy transfer. Acetone-sensitized dimerization of olefins has been found[17,18,19]. In addition the relative rate constants[46] decrease about as expected for endothermic energy transfer if the olefin vertical triplet energies are calculated by substracting 1 kcal/mole from the value of 82 kcal/mole for ethylene for each alkyl substituent on the double bond.

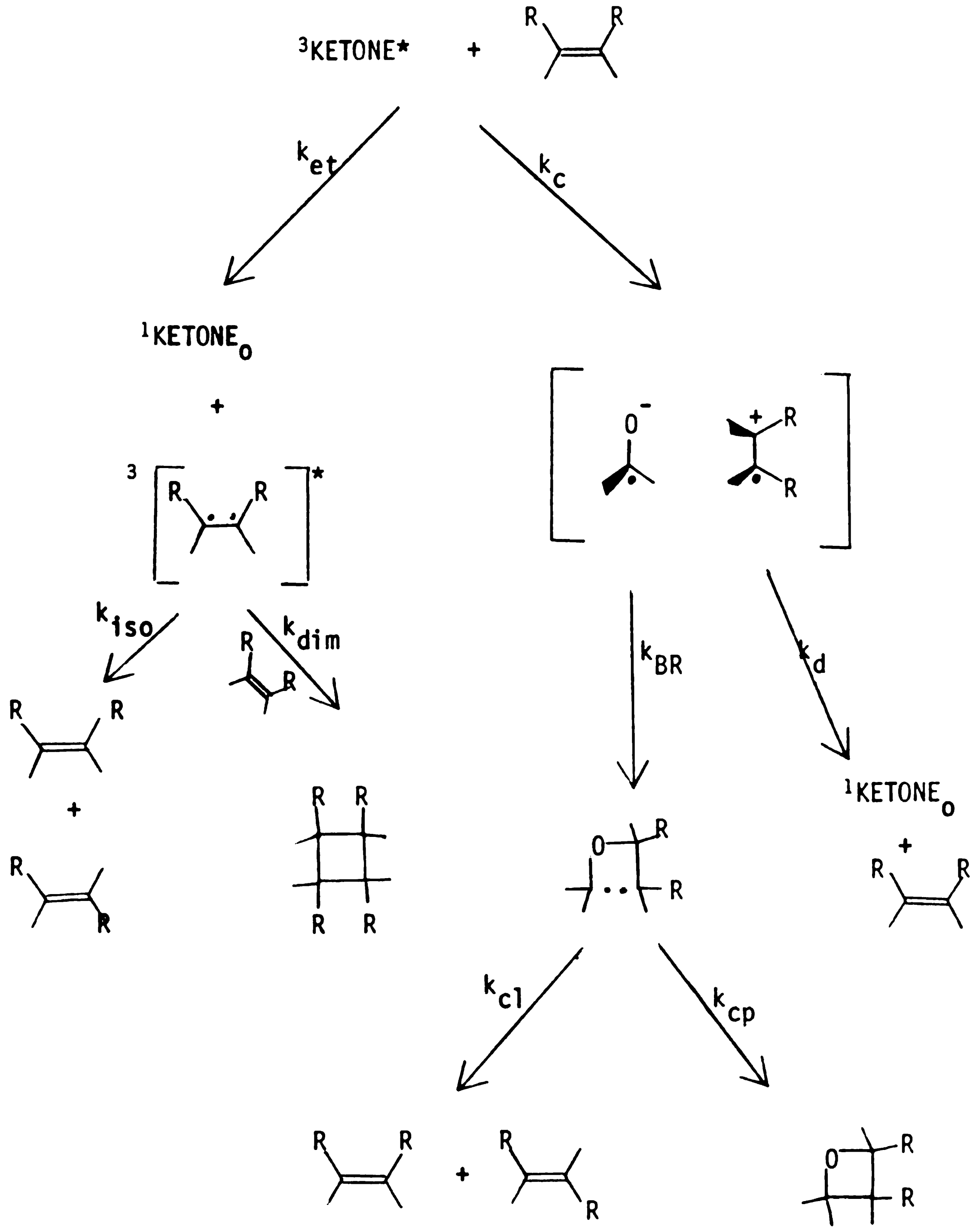


Figure 5. Scheme for Ketone Triplet-Monoolefin Interaction.

Saltiel also reached this conclusion through kinetic studies.

Caldwell's results on the quenching of benzophenone (E_T = 69 kcal/mole) indicate that complex formation is determining the quenching rate constant[60]. This is reasonable according to the proposed scheme since benzophenone's triplet energy is much lower than that of the olefins and the phenyl groups should make the carbonyl group fairly electron deficient.

The results summarized in Table XVI and already discussed are also consistent with this scheme.

Some interesting ketone-olefin pairs could be studied to determine the predictive value of this scheme. For instance, an electron deficient olefin such as 1,1,1,4,4,4-hexafluoro-2-butene should be a poor quencher for butyrophenone and worse for p-trifluoromethylbutyrophenone. The value of k_c should be low and if the trifluoromethyl groups do not decrease the olefin triplet energy greatly, k_{et} should also be low. The difference between k_q for the cis and trans isomers of this olefin could be used to determine the mechanism of quenching. The cis isomer quenches more efficiently than the trans by complex formation and k_{et} for trans is usually greater than that for cis.

IV. EXPERIMENTAL

Chemicals

Butyrophenone: Four samples of butyrophenone were used in the course of these experiments. Their characteristics can be summarized as follows:

Sample I: Obtained from Aldrich Chemical Company. Purified by distillation (B.P. = 73°/6 mm Hg) and recrystallization from pentane three times at Dry-Ice/isopropanol bath temperature. Initially the slope of a Stern-Volmer quenching plot with 2,5-dimethyl-2,4-hexadiene equalled 568 M^{-1} ($\tau = 1.14 \times 10^{-7}$ sec assuming $k_q = 5 \times 10^9$ M^{-1} sec^{-1} for quenching by diene in benzene[71]). After a four month lapse in the experiments the quenching slope was again determined. A value for $k_q\tau$ of 465 ($\tau = .93 \times 10^{-7}$ sec) was obtained.

Sample II: Re-distillation of Sample I yielded butyrophenone which had a lifetime of 0.99×10^{-7} sec as determined by quenching with diene.

Sample III: Obtained from Aldrich Chemical Company. Purified by distillation (B.P. = 71°/6 mm Hg), recrystallization from pentane at Dry-Ice/isopropanol bath temperature two times (first crystals formed and mother liquor discarded), and passed through a 5 cm x 1 cm column of neutral alumina. The quenching

slopes, 398 and 400 M^{-1}, indicated a value of 0.80 x 10^{-7} sec for τ and the quantum yield was determined to be 0.278, and 0.268 (relative to .33 for valerophenone) in separate experiments. Sample IV: Obtained from Matheson, Colman and Bell. Purified by distillation only (B.P. = 75°/7 mm Hg). Stern-Volmer quenching plots with 2,5-dimethyl-2,4-hexadiene as quencher yielded lifetimes of 1.05 and 1.13 x 10^{-7} sec. The higher value was taken to be the lifetime of sample IV. Quantum yield measurements gave values of 0.41 and 0.36 relative to valerophenone.

Methods used to determine quantum yields and quenching constants are described in the Methods section of the Experimental.

TABLE XVIII. Quantum Yield of Butyrophenone

Sample	Ketone	$[C_{14}H_{30}]$	$\frac{\text{Counts Acetophenone}}{\text{Counts Tetradecane}}$	[Acetophenone]	ϕ_A
III	Butyrophenone	.00252	1.23	.00624	.276
	"	.00252	1.24	.00626	
	Valerophenone	.00156	2.39	.00746	.33[a]
III	Butyrophenone	.00260	.687	.00357	.268
	"	.00260	.689	.00358	
	Valerophenone	.00156	1.37	.00428	.33[a]
	"	.00156	1.46	.00455	
IV	Butyrophenone	.00196	1.71	.00671	.41
	"	.00196	1.72	.00675	
	Valerophenone	.00196	1.38	.00541	.33[a]
	"	.00196	1.39	.00545	
IV	Butyrophenone	.00232	.866	.00402	.36
	"	.00232	.987	.00416	
	Valerophenone	.00296	.604	.00358	.33[a]
	"	.00296	.650	.00385	

[a] Value determined in ref. 61

Simple reduced pressure distillation of butyrophenone appeared to afford the highest purity ketone. A brief study of purification techniques showed that further purification only decreased the quantum yield. The relative yields of acetophenone were determined on samples taken at various stages of the purification procedure and irradiated in benzene solution with equal concentrations of tetradecane present (Table XIX).

TABLE XIX. Purification of Butyrophenone

Sample	Purification	relative acetophenone yield
1	Reduced pressure distillation	1.00
2	From 1, recrystallized 3x from pentane	.71
3	From 2, crystals formed in mother liquor	1.00
4	From 2, passed through 1 cm x 6 cm alumina column	.57
5	From 3, passed through 1 cm x 3 cm alumina column	.76
6	From 4, distilled	.58
7	From 5, distilled	.66

Valerophenone: The quantum yield measurements for butyrophenone (sample III) were made relative to a sample of valerophenone from Aldrich Chemical Company and purified by A. E. Kemppainen. The slope of a Stern-Volmer plot with 2,5-dimethyl-2,4-hexadiene as quencher was 39 M^{-1}. The quantum yield for acetophenone production was assumed to be 0.33 as measured previously[63]. The quantum yield for butyrophenone, sample IV, was determined relative to valerophenone which was obtained

from Aldrich Chemical Company and purified by R. Zepp. The quenching constant, $k_q\tau$, was the same as obtained for the previous sample of valerophenone (Table XVIII). Therefore, the quantum yield was assumed to be 0.33 again.

p-Trifluoromethylbutyrophenone was prepared on 0.075 mole scale from propylmagnesium bromide and p-trifluoromethylbenzonitrile (Columbia Chemical Company). The propylmagnesium bromide was prepared by adding from an addition funnel 10.4 g of n-propyl bromide in 20 ml anhydrous ether to 2.06 g of magnesium turnings and 10 ml anhydrous ether at room temperature in a 50 ml 3-necked round bottomed flask equipped with a condenser and a mechanical stirrer. The nitrile mixed with 10 ml anhydrous ether was added to the Grignard mixture which had been cooled in an ice-water bath. After stirring overnight the mixture was poured into about 50 ml of 2N HCl and ice mixture. Hydrolysis on a steam bath, separation of layers, extraction of the aqueous layer with ether and reduced pressure distillation yielded 8.3 g (51% yield) of the pure ketone (B.P. = 57°/ mm Hg).

Tetradecane (Columbia Chemical Company) and thiophen-free benzene (Fischer Chemical Company) were stirred with portions of sulfuric acid until the acid remained clear, washed with sodium hydroxide solution and water and dried with calcium chloride. Tetradecane distilled at 92.5°/4 mm Hg. Benzene was distilled from phosphorous pentoxide through a 4 foot glass helix packed column.

2,5-Dimethyl-2,4-hexadiene (Aldrich Chemical Company) was recrystallized from melt three times at Dry-Ice/isopropanol bath temperature.

Monoolefins: Cyclohexene, cycloheptene, cyclooctene, 1,4-cyclohexadiene, norbornene and *cis*- and *trans*-1,2-dichloroethylene were purchased from Aldrich Chemical Company. The following olefins were obtained from Chemical Samples Company: 1,4-dichloro-2-butene, *cis*-3-hexene (96% pure), trans-3-hexene (99% pure), *cis*-2-pentene (95% pure), *trans*-2-pentene (99% pure), *trans*-2,2,5,5-tetramethyl-3-hexene (99% pure) and cyclopentene (99% pure). Trichloroethylene and tetrachloroethylene were Matheson, Coleman and Bell products and 2,3-dimethyl-2-butene was purchased from Columbia Chemical Company. The remainder of the monoolefins, 2-methyl-2-butene, *cis*- and *trans*-4-methyl-2-pentene, 1-pentene and 2-methyl-1-butene were Phillips Petroleum Company Pure Grade.

All of these olefins except the chloroolefins and norbornene were purified by preparative gas-liquid phase chromatography. In addition, some were distilled on a spinning band column before chromatographic purification. Initially the olefins were used directly after preparative glpc but in later experiments the olefin purified by glpc was distilled. The olefin purification procedure is noted in the tables which contain the kinetic data for each experiment.

The chloroolefins were dried and distilled before use and norbornene was sublimed at room temperature and atmospheric pressure.

Bicyclo[4.2.0]oct-7-ene was prepared by photoisomerizing *cis*, *cis*-1,3-cyclooctadiene (Aldrich Chemical Company) to the *cis*, *trans* isomer and thermally converting this isomer to the bicyclo compound. The procedure described by Liu[77] was used. This olefin was also purified by preparative glpc.

When storage was necessary, purified olefins were refrigerated.

Vapor phase Chromatography

Analyses for acetophenone, tetradecane and butyrophenone were performed on Varian Aerograph gas-liquid partition chromatographs. Two models were used: HiFi III Series 1200; and HiFi Model 600C. Ten foot x 1/8" aluminum columns packed with a mixture of 4% QF-1 and 1% Carbowax 20M on Chromosorb G at 110-120°C effectively separated the above three compounds. A 20' x 1/8" aluminum column packed with 25% 1,2,3-tris(2-cyanoethoxy) propane on 60/80 Chromosorb P in an Aerograph HiFi Model 600-D was used to analyze olefin purity. The recorders used with these chromatographs were equipped with disc intigraters and the signal was produced by flame ionization detectors.

Acetophenone concentration was analyzed relative to a known concentration of tetradecane. A 0.2 - 0.6 μl sample of solution containing both acetophenone and tetradecane was injected onto the column and the area under each peak recorded. To correct for the difference in response of the detector to each compound the following equation was used.

$$[\text{acetophenone}] = [\text{tetradecane}] \times \text{C.F.} \times \frac{\text{Counts Acetophenone}}{\text{Counts Tetradecane}}$$

The correction factor, C.F., was determined to be 2.0 by measuring the number of counts for each compound when mixtures of known concentration in acetophenone and tetradecane were injected. Butyrophenone was analyzed relative to tetradecane in a similar manner. The correction factor was 1.42.

Preparative vapor phase chromatography of olefins was carried out with a Hewlett Packard Model 776, Prepmaster Jr. A 20' x 1/2" aluminum column packed with 25% 1,2,3-tris(2-cyanoethoxy) propane on 60/80 Chromasorb P was used.

Irradiation

All samples in a given run were placed a merry-go-round photolysis apparatus[78], which insured equal incident light intensity, and irradiated for the same length of time. A Hanovia 450-watt medium pressure mercury lamp was used as a light source. The region from 3000 Å to 3200 Å was isolated with a 1 cm path of a filter solution containing 0.002 M potassium chromate in 1% aqueous solution of potassium carbonate.

Methods

A. Quenching experiments. Two stock solutions were prepared for each run, one containing butyrophenone or p-trifluoromethylbutyrophenone and the internal standard, tetradecane, and the other containing the olefin quencher. Both of the stock solutions were prepared by weighing the appropriate amount of compound into a volumetric flask and diluting to the line with benzene. The concentration and volume of the ketone stock solution prepared for each run depended upon the number of samples to be made from the stock solution. Equal aliquots of the ketone-standard stock solutions were pipetted into 10 ml volumetric flasks along with varying aliquots of the quencher stock solution. Benzene was added to fill the flasks to volume. The concentrations of ketone and tetradecane were about 0.10 M and 0.0025 M, respectively, in the photolyzed samples. The concentration and volume of the

quencher stock solution also varied depending on the quenching rate constant and the amount of olefin purified. Quenching of two-thirds of the reaction in the sample containing the highest quencher concentration was considered optimal. Conversions were less than 5 percent.

A typical run can now be described. Stock solution I: 0.9934 g of butyrophenone and 0.0321 g of tetradecane were weighed into a 25 ml volumetric flask. The flask was filled to volume with purified benzene and inverted several times to mix the contents.

[Butyrophenone] = 0.268M

[Tetradecane] = 0.00625M

Stock solution II: 1.1079 g of cyclooctene was weighed into a 25 ml volumetric flask. The flask was filled to the line with benzene and inverted several times.

[Cyclooctene] = 0.404M

Four ml aliquots of stock solution I were pipetted into 6 10 ml volumetric flasks. Aliquots of stock solution II between 1 and 5 ml were pipetted into 5 of the flasks containing stock solution I and all flasks were filled to volume with benzene. The resulting solutions are summarized below.

TABLE XX. Solutions in a Typical Run

Sample	[Butyrophenone]	[Tetradecane]	[Cyclooctene]
blank	0.107	0.0025	0
1	0.107	0.0025	.0404
2	0.107	0.0025	.0808
3	0.107	0.0025	.1212
4	0.107	0.0025	.1616
5	0.107	0.0025	.2020

Using a 5 ml syringe, 2.8 ml aliquots of these solutions were placed in 13 x 100 mm Pyrex tubes which had been constricted about 1 cm from the mouth of the tube. Two tubes were filled from the "blank" sample and one from each of the samples containing cyclooctene. The samples were degassed by four freeze-thaw cycles ($P < .005$ cm Hg), using liquid nitrogen to freeze, and sealed. After attaining room temperature the samples were photolyzed to 4.1% conversion. Vpc analysis of the photolyzed samples yielded ratios of (counts acetophenone/counts tetradecane) which represent the relative quantum yields (Φ_0 and Φ) of acetophenone in the samples.

$$\Phi_0 = \frac{\text{counts acetophenone}}{\text{counts tetradecane}} \qquad \text{(Blank sample)}$$

$$\Phi = \frac{\text{counts acetophenone}}{\text{counts tetradecane}} \qquad \text{(Samples containing quencher)}$$

The results are summarized in Table LXXXIII.

The Stern-Volmer equation was plotted using the relative quantum yields as explained in the Results Section.

B. Quantum yield determinations. Sample tubes containing 0.1 M butyrophenone and a known concentration of tetradecane were photolyzed together with sample tubes containing 0.1 M valerophenone and a known concentration of tetradecane in a merry-go-round assembly which insures equal incident light on sample tubes. Because 0.1 M solutions of these ketones have absorbances greater than 2, essentially all of the incident light was absorbed. A comparison of the amounts of acetophenone formed gave the relative quantum yields of the two ketones. Since the quantum yield for acetophenone formation from valerophenone is 0.33[63], the quantum yield from butyrophenone could be calculated.

C. Ketone disappearance studies. Chemical quenching was expected to lead to products involving butyrophenone at least some of the time. Consequently, measurement of the ketone which disappears but cannot be accounted for by acetophenone or cyclobutanol appearance gives a minimum value for the amount of chemical quenching occuring.

Sample tube preparation was the same as for the quenching runs except that higher concentrations of tetradecane and olefin were used. Higher tetradecane concentration was used so that the ratios of ketone/tetradecane obtained from vpc analysis would be kept as near unity as possible in order to reduce error. High olefin concentrations were used to maximize the ketone-olefin interaction. Olefin concentrations estimated to be sufficient to quench 50-90 percent of the triplet reaction were used.

The tubes were photolyzed long enough to ensure significant ketone disappearnace.

The composition of the samples and the results from the vpc analysis are given in Tables XXI - XXV. Additional peaks appeared in the vpc traces, especially for cyclohexene, but these products were not identified.

In order to determine the minimum fraction of quenching due to chemical quenching (CQ), butyrophenone disappearance (-B) not accounted for by acetophenone (A) and cyclobutanol (CB) appearance divided by the butyrophenone triplets quenched (T_q) was calculated.

$$\text{fraction CQ} = \frac{-B - (A + CB)}{T_q} \qquad (79)$$

Butyrophenone disappearance was calculated from the ratios of counts of butyrophenone/tetradecane from vpc analysis. The acetophenone yield was calculated similarly and the total yield of acetophenone plus cyclobutanol was calculated by dividing the acetophenone yield by 0.85[63].

T_q was calculated by first finding the triplets produced, T_o, and subtracting the triplets reacted, T_R.

$$T_q = T_o - T_R \qquad (80)$$

T_R was calculated by dividing the yield of acetophenone and cyclobutanol by 0.38 since it was known that only 0.38 of the biradicals formed from triplet butyrophenone yield these products[64].

$$T_R = \frac{A}{(.85)(.38)} \qquad (81)$$

T_o was then calculated by using the Stern-Volmer relationship with the value of $k_q\tau$ determined from quenching experiments.

TABLE XXI. Samples for Tetrachloroethylene/butyrophenone Product Study.

TABLE XXI. Samples for Tetrachloroethylene/butyrophenone Product Study.

[Butyrophenone]	[Tetradecane]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts Tetradecane}}$	$\frac{\text{Counts Butyrophenone}}{\text{Counts Tetradecane}}$
.100	.040	.00530	.316	1.21
.100	.040	.0106	.199	1.38
.100	.040	.0159	.147	1.47
.100	.040	.0212	.122	1.51

TABLE XXII. Samples for Trichloroethylene/butyrophenone Product Study.

[Butyrophenone]	[Tetradecane]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts Tetradecane}}$	$\frac{\text{Counts Butyrophenone}}{\text{Counts Tetradecane}}$
.101	.040	.0113	.385	1.09
.101	.040	.0226	.250	1.29
.101	.040	.0339	.180	1.40
.101	.040	.0452	.146	1.45

TABLE XXIII. Samples for <u>cis</u>-4-Methyl-2-pentene/butyrophenone Product Study

[Butyrophenone]	[Tetradecane]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts Tetradecane}}$	$\frac{\text{Counts Butyrophenone}}{\text{Counts Tetradecane}}$
.098	.00955	.545	1.00	5.25
.098	.00955	.817	.862	5.43
.098	.00955	1.09	.745	5.68
.098	.00955	1.361	.675	5.74

TABLE XXIV. Samples for 2-Methyl-2-butene/butyrophenone Product Study

[Butyrophenone]	[Tetradecane]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts Tetradecane}}$	$\frac{\text{Counts Butyrophenone}}{\text{Counts Tetradecane}}$
.100	.0248	.110	.244	2.31
.100	.0248	.165	.163	2.40
.100	.0248	.220	.147	2.44
.100	.0248	.275	.139	2.52

TABLE XXV. Samples for Cyclohexene/butyrophenone Product Study

[Butyrophenone]	[Tetradecane]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts Tetradecane}}$	$\frac{\text{Counts Butyrophenone}}{\text{Counts Tetradecane}}$
.202	.0234	.214	.500	4.29
.202	.0234	.428	.340	3.86
.202	.0234	.624	.256	3.99
.202	.0234	.856	.196	4.37
.202	.0234	1.07	.149	4.20

$$\frac{T_o}{T_R} = 1 + k_q\tau\,[\text{olefin}] \tag{82}$$

The results are given in Tables XXVI - XXX and the average CQ values for each olefin are shown in Table XIII.

TABLE XXVI. Product Formation from Quenching of Butyrophenone by Tetrachloroethylene

[Olefin]	I [Acetophenone]	II [Butyrophenone] Consumed	III [Triplets] Quenched	$\frac{II-I/.85}{III}$ x 100
.00530	.0253	.0300	.0614	0
.0106	.0159	.0200	.0931	2
.0159	.0118	.0150	.1068	1
.0212	.0098	.0127	.1136	1

[Triplets] produced = .147M.

TABLE XXVII. Product Formation from Quenching of Butyrophenone by Trichloroethylene

[Olefin]	I [Acetophenone]	II [Butyrophenone] Consumed	III [Triplets] Quenched	$\frac{II-I/.85}{III}$ x 100
.0113	.0308	.0370	.071	1
.0226	.0200	.0260	.108	2
.0339	.0144	.0185	.127	1
.0452	.0117	.0156	.136	1

[Triplets] produced = .175M.

TABLE XXVIII. Product Formation from Quenching of Butyrophenone by cis-4-Methyl-2-pentene

[Olefin]	I [Acetophenone]	II [Butyrophenone] Consumed	III [Triplets] Quenched	$\frac{II-I/.85}{III}$ x 100
.545	.0191	.0268	.0283	15
.817	.0165	.0244	.0373	13
1.09	.0142	.0209	.0451	9
1.36	.0129	.0202	.0494	10

[Triplets] produced = 0.0929M.

TABLE XXIX. Product Formation from Quenching of Butyrophenone by 2-Methyl-2-butene

[Olefin]	I [Acetophenone]	II [Butyrophenone] Consumed	III [Triplets] Quenched	$\frac{II-I/.85}{III}$ x 100
.110	.0121	.0187	.073	6
.165	.0082	.0155	.074	8
.220	.0073	.0141	.088	6
.275	.0069	.0112	.106	3

[Triplets] produced = 0.114M

TABLE XXX. Product Formation from Quenching of Butyrophenone by Cyclohexene

[Olefin]	I [Acetophenone]	II [Butyrophenone] Consumed	III [Triplets] Quenched	$\frac{II-I/.85}{III}$ x 100
.214	.0234	.055	.067	40
.428	.0159	.070	.092	55
.642	.0120	.065	.106	48
.856	.00920	.052	.115	36
1.07	.00697	.058	.123	41

[Triplets] produced = 0.146M.

D. Olefin dimerization studies. Samples were prepared containing the concentrations listed in Table XXXI in the same manner as for the quenching runs. The tubes were degassed, sealed and photolyzed 8.5 hrs.

TABLE XXXI. Sensitized Dimerization of Cyclopentene

[Butyrophenone]	[Tetradecane]	[Cyclopentene]	$\frac{\text{Counts dimer}}{\text{Counts tetradecane}}$
.10	.005	.156	.079
.10	.005	.312	.106
.10	.005	.312	.149
.10	.005	.468	.117
.10	.005	.468	.170
.10	.005	.624	.153
.10	.005	.624	.182
.10	.005	.782	.270
.10	.005	.782	.180

Vpc analysis was performed ∿90°C on the same column used for the quenching experiments. The photolyzed samples showed peaks in the vpc traces which were attributed to dimers. The area of the dimer relative to tetradecane in each sample is listed in Table XXXI.

The sensitized dimerization of norbornene was studied similarly. The samples were irradiated for 24 hrs. The pertinent data are shown in Table XXXIa. The dimer measured was identified as <u>exo</u>-<u>trans</u>-<u>exo</u> by

TABLE XXXIa. Sensitized Dimerization of Norbornene

[Butyrophenone]	[Tetradecane]	[Norbornene]	$\frac{\text{Counts dimer}}{\text{Counts tetradecane}}$
.10	.00546	.999	2.12
.10	.00546	1.882	2.24
.10	.00546	2.812	2.39

comparison of vpc retention times with samples of the *exo*-*trans*-*exo* and *endo*-*trans*-*exo* dimers received from Dr. D. Arnold.

Norbornene dimerization was sensitized by *p*-trifluoromethylbutyrophenone also. Sample tubes containing 1.72 M norbornene, 0.00259 M tetradecane and either 0.10 M butyrophenone or 0.10 M trifluoromethylbutyrophenone were photolyzed 10.5 hrs. The dimer yield was at least 20 x greater in the tube containing butyrophenone than in that containing *p*-trifluoromethylbutyrophenone.

Phosphorescence Spectrum of *p*-Trifluoromethylbutyrophenone.

The phosphorescence spectrum of *p*-trifluoromethylbutyrophenone was obtained by Mrs. Mary May. A $\sim 10^{-3}$ M sample of the ketone in methylcyclohexane was irradiated through quartz and water with a 1KW UV lamp. The cylindrical phosphorescope was operated at 40 msec/rev. The first emission band appeared at 3950 Å (72.5 kcal/mole). The spectrum was measured at 77°K.

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VI. APPENDIX

TABLE XXXII. Quenching of Triplet Butyrophenone[a] by 2,5-Dimethyl-2,4-hexadiene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.0955	.00259	0	2.47	
.0955	.00259	.512	1.83	1.35
.0955	.00259	1.024	1.55	1.59
.0955	.00259	1.536	1.35	1.83
.0955	.00259	2.048	1.12	2.20
.0955	.00259	2.560	1.04	2.37

[a] Sample I; [b] $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$.

TABLE XXXIII. Quenching of Triplet Butyrophenone[a] by 2,5-Dimethyl-2,4-hexadiene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.101	.0025	0	.660	
.101	.0025	.816	.485	1.36
.101	.0025	1.63	.391	1.69
.101	.0025	2.45	.337	1.96
.101	.0025	3.26	.297	2.22

[a] Sample III; [b] $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$.

TABLE XXXIV. Quenching of Triplet Butyrophenone[a] by 2,5-Dimethyl-2,4-hexadiene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00232	0	.866	
.100	.00232	0	.897	
.100	.00232	1.04	.587	1.52
.100	.00232	2.08	.415	2.15
.100	.00232	3.12	.326	2.73
.100	.00232	4.16	.261	3.41
.100	.00232	5.20	.211	4.22

[a] Sample III; [b] $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$.

TABLE XXXV. Quenching of Triplet Butyrophenone[a] by 2,5-Dimethyl-2,4-hexadiene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.099	.0032	0	.710	
.099	.0032	0	.722	
.099	.0032	2.16	.334	2.16
.099	.0032	3.24	.259	2.79
.099	.0032	4.32	.245	2.95
.099	.0032	5.40	.206	3.51

[a] Sample II; [b] $k_q = 5 \times 10^9$ M^{-1} sec^{-1}.

TABLE XXXVI. Quenching of Triplet Butyrophenone[a] by 2,5-Dimethyl-2,4-hexadiene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.109	.00190	0	2.22	
.109	.00190	1.50	1.16	1.91
.109	.00190	3.00	.953	2.33
.109	.00190	4.50	.673	3.30
.109	.00190	6.00	.610	3.64
.109	.00190	7.50	.500	4.44

[a] Sample II; [b] $k_q = 5 \times 10^9$ M^{-1} sec^{-1}.

TABLE XXXVII. Quenching of Triplet Butyrophenone[a] by 2,5-Dimethyl-2,4-hexadiene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.086	.00256	0	.630	
.086	.00256	0	.616	
.086	.00256	.001	.466	1.35
.086	.00256	.002	.348	1.81
.086	.00256	.003	.289	2.16
.086	.00256	.004	.269	2.34

[a] Sample III; [b] $k_q = 5 \times 10^9$ M^{-1} sec^{-1}.

TABLE XXXVIII. Quenching of p-Trifluoromethylbutyrophenone by 2,5-Dimethyl-2,4-hexadiene[a]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.082	.0025	0	.859	
.082	.0025	3.52	.506	1.70
.082	.0025	7.04	.385	2.23
.082	.0025	10.6	.292	2.94

[a] $k_q = 5 \times 10^9$ M^{-1} sec^{-1}.

TABLE XXXIX. Quenching of p-Trifluoromethylbutyrophenone by 2,5-Dimethyl-2,4-hexadiene[a]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin] x 10^3	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.096	.00202	0	1.73	
.096	.00202	0	1.74	
.096	.00202	2.04	1.24	1.40
.096	.00202	4.08	.853	2.04
.096	.00202	6.12	.808	2.15
.096	.00202	8.16	.668	2.61
.096	.00202	10.2	.566	3.08

[a] $k_q = 5 \times 10^9$ M^{-1} sec^{-1}.

TABLE XL. Quenching of Triplet Butyrophenone[a] by Tetrachloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00259	0	1.53	
.100	.00259	.00533	.865	1.77
.100	.00259	.01066	.571	2.68
.100	.00259	.01599	.459	3.34
.100	.00259	.02132	.357	4.29
.100	.00259	.02665	.291	5.26

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLI. Quenching of Triplet Butyrophenone[a] by Tetrachloroethylene

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.095	.00272	0	.953	
.095	.00272	0	.966	
.095	.00272	.0101	.373	2.59
.095	.00272	.0202	.230	4.20
.095	.00272	.0303	.156	6.18
.095	.00272	.0404	.121	7.99

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLII. Quenching of Triplet Butyrophenone[a] by Trichloroethylene

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00259	0	1.39	
.100	.00259	0	1.41	
.100	.00259	.010	.821	1.71
.100	.00259	.020	.568	2.47
.100	.00259	.030	.420	3.32
.100	.00259	.040	.339	4.13
.100	.00259	.050	.278	5.03

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLIII. Quenching of Triplet Butyrophenone[a] by Trichloroethylene

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetephenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.101	.00295	0	2.20	
.101	.00295	0	2.23	
.101	.00295	.0101	1.25	1.78
.101	.00295	.0202	.850	2.61
.101	.00295	.0303	.628	3.54
.101	.00295	.0404	.478	4.65
.101	.00295	.0505	.402	5.53

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLIV. Quenching of Triplet Butyrophenone[a] by _cis_- and _trans_-1,2-Dichloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00185	0	1.85	
.100	.00185	0	1.82	
	trans-1,2-dichloroethylene			
.100	.00185	.0086	1.53	1.20
.100	.00185	.0171	1.16	1.59
.100	.00185	.0513	.582	3.16
.100	.00185	.0513	.600	3.07
.100	.00185	.0855	.392	4.70
	cis-1,2-dichloroethylene			
.100	.00185	.0158	1.57	1.17
.100	.00185	.0158	1.52	1.21
.100	.00185	.0474	.972	1.89
.100	.00185	.0474	.977	1.88
.100	.00185	.0316	.720	2.56

[a] $\tau = 1.13 \times 10^{-7}$ sec.

TABLE XLV. Quenching of Triplet Butyrophenone[a] by _trans_-1,2-Dichloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.0945	.00265	0	1.04	
.0945	.00265	0	1.02	
.0945	.00265	.01005	.861	1.21
.0945	.00265	.02010	.648	1.60
.0945	.00265	.03015	.494	2.10
.0945	.00265	.04020	.420	2.48
.0945	.00265	.05025	.346	3.01

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLVI. Quenching of Triplet Butyrophenone[a] by *trans*-1,2-Dichloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
0.0948	.00259	0	2.08	
0.0948	.00259	0	2.22	
0.0948	.00259	.010	1.90	1.07
0.0948	.00259	.020	1.38	1.61
0.0948	.00259	.030	1.10	2.02
0.0948	.00259	.040	.891	2.49
0.0948	.00259	.050	.733	3.03

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLVII. Quenching of Triplet Butyrophenone[a] by *cis*-1,2-Dichloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
0.100	.00282	0	1.69	
0.100	.00282	0	1.71	
0.100	.00282	.010	1.63	1.04
0.100	.00282	.020	1.36	1.25
0.100	.00282	.030	1.16	1.46
0.100	.00282	.040	.994	1.71
0.100	.00282	.050	.895	1.90

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLVIII. Quenching of Triplet Butyrophenone[a] by *cis*-1,2-Dichloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.126	.00250	0	1.29	
.126	.00250	0	1.31	
.126	.00250	.05	.574	2.27
.126	.00250	.10	.324	4.02
.126	.00250	.15	.219	5.94
.126	.00250	.20	.176	7.38

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE XLIX. Quenching of Triplet Butyrophenone[a] by *trans*-1,2-Dichloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.0945	.00265	0	1.04	
.0945	.00265	0	1.02	
.0945	.00265	.01005	.961	1.21
.0945	.00265	.02010	.648	1.60
.0945	.00265	.03015	.494	2.10
.0945	.00265	.04020	.420	2.48
.0945	.00265	.05025	.346	3.01

[a] $\tau = 1.14 \times 10^{-7}$ sec

TABLE L. Quenching of Triplet Butyrophenone[a] by *trans*-1,2-Dichloroethylene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.0948	.00259	0	2.08	
.0948	.00259	0	2.22	
.0948	.00259	.010	1.90	1.07
.0948	.00259	.020	1.38	1.61
.0948	.00259	.030	1.10	2.02
.0948	.00259	.040	.891	2.49
.0948	.00259	.050	.733	3.03

[a] $\tau = 1.14 \times 10^{-7}$ sec

TABLE LI. Quenching of Triplet Butyrophenone[a] by 2,3-Dimethyl-2-butene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00238	0	1.02	
.100	.00238	0	1.06	
.100	.00238	.00875	.768	1.37
.100	.00238	.0175	.635	1.66
.100	.00238	.0263	.545	1.93
.100	.00238	.0350	.465	2.26
.100	.00238	.0438	.387	2.71

[a] $\tau = 0.80 \times 10^{-7}$ sec; [b] Purified by prep vpc, then distilled.

TABLE LII. Quenching of Triplet Butyrophenone[a] by 2,3-Dimethyl-2-butene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
.100	.00252	0	.711	
.100	.00252	0	.712	
.100	.00252	.00916	.503	1.41
.100	.00252	.0183	.408	1.74
.100	.00252	.0275	.352	2.02
.100	.00252	.0366	.303	2.35
.100	.00252	.0458	.258	2.76

[a] τ = 0.80 x 10^{-7} sec; [b] Purified by prep vpc, then distilled.

TABLE LIII. Quenching of Triplet Butyrophenone[a] by 2,3-Dimethyl-2-butene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
0.100	.00264	0	1.14	
0.100	.00264	.0127	.626	1.82
0.100	.00264	.0254	.483	2.36
0.100	.00264	.0381	.378	3.02
0.100	.00264	.0635	.270	4.22

[a] τ = 1.14 x 10^{-7} sec; [b] Purified by prep vpc.

TABLE LIV. Quenching of Triplet Butyrophenone[a] by 2,3-Dimethyl-2-butene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
.100	.00252	0	1.23	
.100	.00252	0	1.24	
.100	.00252	.00742	.912	1.36
.100	.00252	.0223	.697	1.78
.100	.00252	.0223	.697	1.78
.100	.00252	.0371	.567	2.19
.100	.00252	.0371	.583	2.13

[a] τ = 0.80 x 10^{-7} sec; [b] Purified by prep vpc, then distilled.

TABLE LV. Quenching of Triplet Butyrophenone[a] by 2-Methyl-2-butene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.0995	.00280	0	.905	
.0995	.00280	0	.841	
.0995	.00280	.0112	.695	1.30
.0995	.00280	.0224	.648	1.39
.0995	.00280	.0336	.598	1.51
.0995	.00280	.0560	.498	1.82

[a] τ = 1.14 x 10^{-7} sec; [b] Purified by prep vpc.

TABLE LVI. Quenching of Triplet Butyrophenone[a] by 2-Methyl-2-butene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00252	0	.651	
.100	.00252	0	.630	
.100	.00 52	.00752	.424	1.51
.100	.00252	.02256	.331	1.94
.100	.00252	.0376	.271	2.34
.100	.00252	.0337	.430	1.49
.100	.00252	.1011	.280	2.29
.100	.00252	.1685	.226	2.83

[a] τ = 0.80 x 10^{-7} sec; [b] Purified by prep vpc.

TABLE LVII. Quenching of Triplet Butyrophenone[a] by 2-Methyl-2-butene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00238	0	1.02	
.100	.00238	0	1.06	
.100	.00238	.0225	.800	1.31
.100	.00238	.0450	.718	1.46
.100	.00238	.0675	.604	1.74
.100	.00238	.0900	.543	1.93
.100	.00238	.1125	.464	2.26

[a] τ = 0.80 x 10^{-7} sec; [b] Purified by prep vpc, then distilled.

TABLE LVIII. Quenching of Triplet Butyrophenone[a] by *cis*-3-Hexene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.099	.00326	0	1.30	
.099	.00326	0	1.44	
.099	.00326	.0942	1.07	1.34
.099	.00326	.283	.661	2.18
.099	.00326	.471	.531	2.71

[a] $\tau = 0.99 \times 10^{-7}$ sec; [b] Distilled from sodium under N_2.

TABLE LIX. Quenching of Triplet Butyrophenone[a] by *cis*- and *trans*-3-Hexene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.0950	.00213	0	1.36	—
.0950	.00213	0	1.35	—
cis-3-Hexene				
.0950	.00213	.097	.965	1.40
.0950	.00213	.194	.762	1.77
.0950	.00213	.582	.419	3.22
.0950	.00213	.582	.422	3.20
.0950	.00213	.970	.290	4.65
trans-3-Hexene				
.0950	.00213	.0756	1.18	1.14
.0950	.00213	.151	.988	1.37
.0950	.00213	.454	.920	1.47
.0950	.00213	.454	.852	1.58
.0950	.00213	.756	.732	1.84

[a] $\tau = 1.13 \times 10^{-7}$ sec; [b] Purified by prep vpc, then distilled.

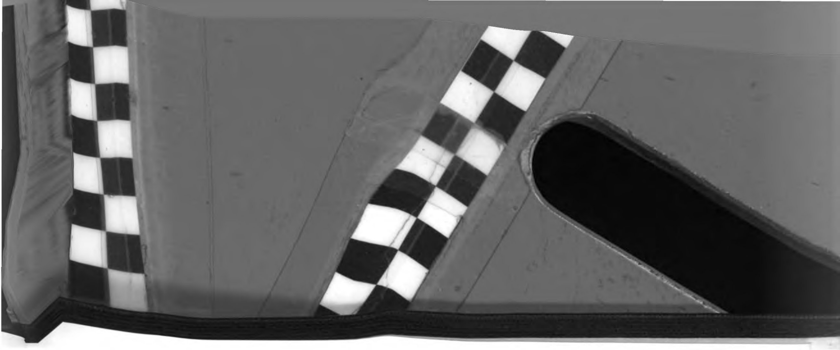

TABLE LX. Quenching of Triplet Butyrophenone[a] by *trans*-4-octene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.101	.00242	0	1.15	
.101	.00242	.150	.620	1.86
.101	.00242	.300	.568	2.02
.101	.00242	.450	.577	1.99
.101	.00242	.600	.517	2.22
.101	.00242	.750	.460	2.50

[a] $\tau = 1.14 \times 10^{-7}$ sec; [b] Purified by prep vpc.

TABLE LXI. Quenching of Triplet Butyrophenone[a] by *cis*-4-Methyl-2-pentene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.104	.00278	0	1.18	
.104	.00278	0	1.23	
.104	.00278	.275	1.00	1.23
.104	.00278	.550	.809	1.52
.104	.00278	.825	.725	1.70
.104	.00278	1.10	.635	1.94

[a] $\tau = 1.14 \times 10^{-7}$ sec; [b] Purified by prep vpc.

TABLE LXII. Quenching of Triplet Butyrophenone[a] by *trans*-4-Methyl-2-pentene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.102	.00287	0	.870	
.102	.00287	0	.987	
.102	.00287	.574	.790	1.25
.102	.00287	.861	.678	1.46
.102	.00287	1.435	.629	1.57

[a] $\tau = 0.99 \times 10^{-7}$ sec; [b] Purified by prep vpc.

TABLE LXIII. Quenching of Triplet Butyrophenone[a] by trans-4-Methyl-2-pentene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
.106	.00164	0	1.83	
.106	.00164	0	1.85	
.106	.00164	.387	1.38	1.34
.106	.00164	.387	1.60	1.16
.106	.00164	1.16	1.22	1.52
.106	.00164	1.93	.961	1.92

[a] τ = 0.99 x 10^{-7} sec; [b] Distilled on spinning band column.

TABLE LXIV. Quenching of Triplet Butyrophenone[a] by cis-2-Pentene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
.104	.0025	0	.502	
.104	.0025	0	.502	
.104	.0025	.100	.311	1.61
.104	.0025	.200	.236	2.13
.104	.0025	.600	.114	4.40

[a] τ = 0.80 x 10^{-7} sec; [b] Purified by prep vpc.

TABLE LXV. Quenching of Triplet Butyrophenone[a] by cis- and trans-2-Pentene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
.100	.00252	0	.879	
.100	.00252	0	.910	
		cis-2-pentene		
.100	.00252	.065	.830	1.10
.100	.00252	.130	.600	1.52
.100	.00252	.390	.342	2.68
.100	.00252	.650	.250	3.64
		trans-2-pentene		
.100	.00252	.078	.751	1.21
.100	.00252	.155	.712	1.28
.100	.00252	.465	.633	1.71
.100	.00252	.775	.445	2.05

[a] τ = 0.80 x 10^{-7} sec; [b] Purified by prep vpc, then distilled.

TABLE LXVI. Quenching of Triplet Butyrophenone[a] by *cis*- and *trans*-2-Pentene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
.100	.00238	0	.585	
.100	.00238	0	.552	
		cis-2-pentene		
.100	.00238	.115	.353	1.66
.100	.00238	.230	.281	2.08
.100	.00238	.345	.218	2.68
.100	.00238	.460	.176	3.33
.100	.00238	.575	.158	3.64
		trans-2-pentene		
.100	.00238	.103	.462	1.27
.100	.00238	.206	.429	1.36
.100	.00238	.309	.384	1.52
.100	.00238	.412	.343	1.71
.100	.00238	.515	.304	1.93

[a] $\tau = 0.80 \times 10^{-7}$ sec; [b] Purified by prep vpc, then distilled.

TABLE LXVII. Quenching of Triplet Butyrophenone[a] by *cis*- and *trans*-2-Pentene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	Counts Acetophenone / Counts $C_{14}H_{30}$	Φ^0/Φ
.0950	.00213	0	1.40	
.0950	.00213	0	1.33	
		cis-2-pentene		
.0950	.00213	.184	.695	2.01
.0950	.00213	.553	.344	4.07
.0950	.00213	.921	.208	6.73
		trans-2-pentene		
.0950	.00213	.116	1.14	1.23
.0950	.00213	.231	.990	1.41
.0950	.00213	.693	.589	2.38
.0950	.00213	.693	.638	2.19
.0950	.00213	1.16	.450	3.11

[a] $\tau = 1.13 \times 10^{-7}$ sec; [b] Purified by prep vpc, then distilled.

TABLE LXVIII. Quenching of Triplet Butyrophenone[a] by trans-2,3,5,5-Tetramethyl-3-hexene

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00238	0	.600	
.100	.00238	0	.640	
.100	.00238	.0825	.563	1.14
.100	.00238	.165	.490	1.31
.100	.00238	.495	.364	1.76
.100	.00238	.495	.329	1.95
.100	.00238	.825	.370	1.73

[a] $\tau = 0.80 \times 10^{-7}$ sec.

TABLE LXIX. Quenching of Triplet Butyrophenone[a] by 2-Methyl-1-butene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.104	.00229	0	1.97	
.104	.00229	.196	1.07	1.84
.104	.00229	.246	1.18	1.67
.104	.00229	.295	.968	2.04

[a] $\tau = 1.14 \times 10^{-7}$ sec; [b] Purified by prep vpc.

TABLE LXX. Quenching of Triplet Butyrophenone[a] by 2-Methyl-1-butene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.101	.00270	0	.899	
.101	.00270	0	.915	
.101	.00270	.090	.672	1.36
.101	.00270	.180	.625	1.46
.101	.00270	.270	.515	1.71
.101	.00270	.360	.390	2.34
.101	.00270	.450	.407	2.25

[a] $\tau = 1.14 \times 10^{-7}$ sec; [b] Purified by prep vpc.

TABLE LXXI. Quenching of Triplet Butyrophenone[a] by 1-Pentene[b]

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.101	.00278	0	1.34	
.101	.00278	0	1.35	
.101	.00278	.505	.826	1.63
.101	.00278	1.515	.550	2.46
.101	.00278	2.525	.410	3.29
.101	.00278	2.525	.384	3.52

[a] $\tau = 1.14 \times 10^{-7}$ sec; [b] Purified by prep vpc.

TABLE LXXII. Quenching of Triplet Butyrophenone[a] by Bicyclo[4.2.0]oct-7-ene

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.0025	0	.847	
.100	.0025	.180	.340	2.49

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE LXXIII. Quenching of Triplet Butyrophenone[a] by Bicyclo[4.2.0]oct-7-ene

[Butyrophenone]	$[C_{14}H_{30}]$	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00292	0	.502	
.100	.00292	0	.494	
.100	.00292	.334	.127	3.96

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE LXXIV. Quenching of Triplet Butyrophenone[a] by Norbornene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00252	0	1.23	
.100	.00252	0	1.24	
.100	.00252	.275	.729	1.70
.100	.00252	.275	.732	1.69
.100	.00252	.459	.524	2.37
.100	.00252	.459	.492	2.52

[a] $\tau = 0.80 \times 10^{-7}$ sec.

TABLE LXXV. Quenching of Triplet Butyrophenone[a] by Norbornene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00252	0	.651	
.100	.00252	0	.630	
.100	.00252	.0846	.613	1.04
.100	.00252	.254	.384	1.67
.100	.00252	.423	.266	2.41

[a] $\tau = .80 \times 10^{-7}$ sec.

TABLE LXXVI. Quenching of Triplet Butyrophenone[a] by Cyclopentene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.116	.00232	0	1.16	
.116	.00232	0	1.20	
.116	.00232	.1915	.552	2.18
.116	.00232	.1915	.553	2.18
.116	.00232	.5745	2.71	4.43
.116	.00232	.5745	2.78	4.32

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE LXXVII. Quenching of Triplet Butyrophenone[a] by Cyclopentene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00358	0	.641	
.100	.00358	0	.635	
.100	.00358	.0965	.391	1.65
.100	.00358	.1930	.296	2.15
.100	.00358	.2895	.227	2.81
.100	.00358	.3860	.186	3.43

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE LXXVIII. Quenching of Triplet Butyrophenone[a] by Cyclohexene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.103	.00242	0	2.41	
.103	.00242	0	2.40	
.103	.00242	.555	.875	2.76
.103	.00242	.925	.639	3.77
.103	.00242	1.11	.550	4.38

[a] $\tau = 1.14 \times 10^{-7}$ sec; [b] Purified by spinning bond distillation, then prep vpc.

TABLE LXXIX. Quenching of Triplet Butyrophenone[a] by Cyclohexene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.101	.00202	0	1.63	
.101	.00202	0	1.60	
.101	.00202	.148	1.05	1.55
.101	.00202	.444	.551	2.96
.101	.00202	.740	.382	4.27

[a] τ = .99 x 10^{-7} sec; [b] Purified by prep vpc.

TABLE LXXX. Quenching of Triplet Butyrophenone[a] by Cyclohexene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.100	.00166	0	1.29	
.100	.00166	0	1.25	
.100	.00166	.181	.827	1.56
.100	.00166	.181	.755	1.71
.100	.00166	.543	.451	2.86
.100	.00166	.543	.391	3.30
.100	.00166	.907	.271	4.76
.100	.00166	.907	.285	4.53

[a] τ = 0.99 x 10^{-7} sec; [b] Refluxed with maleic anhydride, distilled on spinning band column.

TABLE LXXXI. Quenching of Triplet Butyrophenone[a] by Cyclohexene[b]

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.104	.0025	0	.529	
.104	.0025	0	.522	
.104	.0025	0.100	.321	1.65
.104	.0025	0.200	.274	1.93
.104	.0025	0.600	.155	3.41
.104	.0025	1.00	.100	5.29

[a] τ = 0.80 x 10^{-7} sec; [b] Distilled on spinning band column, then purified by prep vpc.

TABLE LXXXII. Quenching of Triplet Butyrophenone[a] by Cycloheptene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.102	.00288	0	.950	
.102	.00288	0	1.01	
.102	.00288	.080	.608	1.66
.102	.00288	.120	.500	2.02
.102	.00288	.160	.423	2.38
.102	.00288	.240	.326	3.10

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE LXXXIII. Quenching of Triplet Butyrophenone[a] by Cyclooctene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.107	.00259	0	.823	
.107	.00259	0	.841	
.107	.00259	.0404	.633	1.33
.107	.00259	.0808	.474	1.77
.107	.00259	.1212	.404	2.08
.107	.00259	.1616	.327	2.57
.107	.00259	.2020	.290	2.90

[a] $\tau = 1.14 \times 10^{-7}$ sec.

TABLE LXXXIV. Quenching of Triplet Butyrophenone[a] by 1,4-Cyclohexadiene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.099	.0026	0	.687	
.099	.0026	0	.689	
.099	.0026	.0395	.445	1.54
.099	.0026	.0790	.369	1.87
.099	.0026	.0790	.378	1.82

[a] $\tau = 0.80 \times 10^{-7}$ sec.

TABLE LXXXV. Quenching of p-Trifluoromethylbutyrophenone[a] by *cis*-2-pentene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.082	.0025	0	.975	
.082	.0025	0	.968	
.082	.0025	.0665	.852	1.14
.082	.0025	.133	.720	1.35
.082	.0025	.399	.525	1.86
.082	.0025	.665	.353	2.76

[a] $\tau = .36 \times 10^{-7}$ sec.

TABLE LXXXVI. Quenching of p-Trifluoromethylbutyrophenone[a] by 2-Methyl-2-butene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.082	.0025	0	.975	
.082	.0025	0	.968	
.082	.0025	.0246	.785	1.24
.082	.0025	.0492	.688	1.41
.082	.0025	.1476	.423	2.29
.082	.0025	.1476	.423	2.29
.082	.0025	.1968	.353	2.75

[a] $\tau = .36 \times 10^{-7}$ sec.

TABLE LXXXVII. Quenching of p-Trifluoromethylbutyrophenone[a] by Norbornene

[Butyrophenone]	[$C_{14}H_{30}$]	[Olefin]	$\frac{\text{Counts Acetophenone}}{\text{Counts } C_{14}H_{30}}$	Φ^0/Φ
.096	.00202	0	1.73	
.096	.00202	0	1.74	
.096	.00202	.179	1.16	1.50
.096	.00202	.358	.825	2.11
.096	.00202	.537	.704	2.47
.096	.00202	.716	.596	2.92

[a] $\tau = 0.6 \times 10^{-7}$ sec.