Hydrolysis of the silyl group was effected by dissolving **37a/39a** (40.0 mg, 0.142 mmol) in freshly distilled THF (3 mL) followed by addition of 3 drops of H_2O and 1 drop of 1 M HCl and allowing the solution to stand for 5 min. The product was obtained by concentration in vacuo and preparative TLC ($CHCl_3$/MeOH, 9:1) yielding a mixture of lactam alcohols **37b/39b** as a clear, colorless oil (28.5 mg, 96%) in the same 5:4 diastereomeric ratio: IR (film) 3600–3200, 3000–2800, 1680, 1430, 1310, 1260, 860 cm^{-1}; ^{1}H NMR (200 MHz) δ 5.87 (d, 1/2 H, $J = 4.78$ Hz), 5.81 (minor epimer) (d, ~1/2 H, $J = 5.48$ Hz), 4.32–4.08 (m, 3 H), 2.82–2.65 (m, 1 H), 2.50–2.0 (m, 5 H), 2.0–1.28 (m, 6 H), 0.96 and 0.95 (2 t, 3 H); ^{13}C NMR δ 173.1, 172.7, 140.9, 140.5, 121.1, 118.1, 72.7, 70.24, 55.5, 55.4, 38.1, 36.4, 35.7, 35.5, 31.4, 31.2, 28.9, 26.2, 25.5, 23.60, 18.7, 18.1, 13.4, 13.4; MS (CI, $m/e - 1$, rel intensity) 209 (M^+, 100), 191 ($M^+ - H_2O$, 21).

It was found that 10 mg of lactams could be separated by employing a medium-pressure liquid chromatography apparatus[31] using a 2 × 30 cm column filled with silica gel (Woelm 0.023–0.063 mm), eluting with 20:1 $CHCl_3$–MeOH, providing 5 and 4 mg of each diastereomer. The 200-MHz ^{1}H NMR spectra of these isomers were very similar to that of the mixture.

(±)-1,5,6,8a-Tetrahydro-8-(1-oxobutyl)-3(2*H*)-indolizinone (22a). Pyridinium chlorochromate (15 mg, 0.07 mmol) was added to the mixture of alcohols **37b/39b** (10.5 mg, 0.05 mmol) dissolved in CH_2Cl_2 (1 mL) and the mixture was stirred for 1 h.[14] The mixture was chromatographed on 2 g of Florisil (ethyl acetate) yielding lactam enone **22a** (6.75 mg, 66%): IR (film) 3000–2850, 1680, 1420 cm^{-1}; ^{1}H NMR δ 6.9 (t, 1 H, $J = 3$ Hz), 4.5–4.0 (m, 2 H), 2.9–2.0 (m, 7 H), 2.20–1.0 (m, 4 H), 0.90 (t, 3 H, $J = 7$ Hz).

1,2,3,5,6,8a-Hexahydro-α-propyl-8-indolizinemethanol (elaeokanine B) (4). Diisobutylaluminum hydride (0.6 mL, 0.6 mmol, 1.0 M in hexanes) was added dropwise under N_2 to a solution of epimeric lactams **37b/39b** (25.2 mg, 0.120 mmol) in THF at room temperature. Stirring was continued for an additional 0.5 h. The solution was hydrolyzed with 5 mL of 1 M HCl and extracted with 10 mL of $CHCl_3$. The aqueous layer was basified with solid Na_2CO_3 and extracted with three 20-mL $CHCl_3$ portions. Drying over anhydrous Na_2SO_4 and concentration in vacuo yielded the diastereomeric amino alcohols (elaeokanine **B**) (**4**) as a clear oil which decomposed slowly at room temperature but was stable for several weeks below 0 °C (21.2 mg, 91%): IR (film) 3500–3200, 3000–2700, 1260, 1050, 800 cm^{-1}; ^{1}H NMR (200 MHz) δ 5.65 (s, 1 H), 4.04–3.74 (m, 2 H), 3.10–1.28 (m, 15 H), 0.86 (t, 3 H, $J = 6$ Hz); MS (CI, $m/e - 1$, rel intensity) 195 (P, 40), 194 (20), 193 (33), 177 (P – H_2O, 100); MS (EI, m/e measured, rel intensity, m/e calcd) 195.1607 (M^+, 14, 195.1623), 194.1582 ($M^+ - 1$, 23, 194.1545), 122.0967 (100, 122.0970).

The diastereomeric amino alcohols **40** and **41** could be separated, although with difficulty, by preparative TLC on silica gel ($CHCl_3$/ether/MeOH/28%NH_4OH, 40:35:20:5). Each epimer gave 200-MHz ^{1}H NMR spectra identical with the compound prepared by reduction of the individual lactams **37b** and **39b**. The TLC's of pure compounds **40** and **41** prepared by either method were identical. NMR spectra of each isomer was nearly identical with that of the mixture.

(±)-1-(1,2,3,4,6,8a-Hexahydro-8-indolizinyl)-1-butanone (elaeokanine A) (3). Trifluoroacetic acid (32 mg, 0.15 mmol) was added under N_2 to a stirred solution of dimethyl sulfoxide (16 mg, 0.20 mmol) in CH_2Cl_2 at –78 °C.[35] This cold solution was stirred under N_2 for 20 min. Epimeric alcohol **4** (20.0 mg, 0.102 mmol) in CH_2Cl_2 (1 mL) was then added. Stirring at –78 °C under N_2 was continued for 1 h and the reaction mixture was quenched with 3 drops of triethylamine, warmed to room temperature over 10 min, and hydrolyzed with 1 mL of H_2O. Extraction with three 3-mL portions of CH_2Cl_2, drying over anhydrous Na_2SO_4, and concentration in vacuo yielded crude racemic elaeokanine A (**3**). Chromatography on preparative silica gel G plates (saturated NH_4OH in ether, methanol, $CHCl_3$, 2:2:1) gave the alkaloid as a clear oil (12.2 mg, 62%) identical in spectral properties to natural elaeokanine A.[19,34] IR ($CHCl_3$) 3100–2800, 1665, 1200, 1040 cm^{-1}; ^{1}H NMR (200 MHz) δ 6.887 (d of t, 1 H, $J = 4.1$, 1.6 Hz), 3.30 (m, 1 H), 2.99–2.28 and 1.92–1.25 (m, 14 H), 0.925 (t, 3 H, $J = 7.4$ Hz); UV λ_{max} (ϵ): 229 (10,000); MS (CI, $m/e - 1$, rel intensity) 194 (13), 193 (M^+, 100), 192 (11), 191 (17); MS (EI, m/e measured, rel intensity, m/e calcd) 193.1463 (M^+, 35, 193.1466), 192.1391 ($M^+ - 1$, 17, 192.1388), 173.1239 (17, 173.1231), 165.1158 (11, 165.1154), 164.1069 ($M^+ - C_2H_5$, 9, 164.1075), 151.0949 (12.5, 151.0952), 150.0904 ($M^+ - C_3H_7$, 100, 150.0919), 123.1041 (19, 123.1048), 122.0981 ($M^+ - C_4H_7O$, 40, 122.0970), 120.0821 (9, 120.0813).

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Reaction of Benzophenone Triplets with Allylic Hydrogens. A Laser Flash Photolysis Study

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Abstract: The quenching of benzophenone by olefins having allylic hydrogens leads to hydrogen abstraction in addition to quenching by the π system. The fraction of quenching events that leads to hydrogen abstraction in benzene at 27 °C ranges from ~0 for conjugated dienes to 94% for 1,4-cyclohexadiene. For cyclohexene the rate constant for abstraction is 1.7×10^7 M^{-1} s^{-1} and accounts for 23% of the quenching events. Deuteration leads to a decrease in the fraction of abstraction, which for cyclohexene-d_{10} is 11%. Hydrogen abstraction has a higher activation energy than quenching by the double bond; as a result its importance increases with increasing temperatures. The absolute rate constants for the reactions of *tert*-butoxy radicals with the olefins were also measured.

Introduction

The interaction of carbonyl triplets with double bonds has been the subject of numerous studies.[3-18] The predominant process is known to involve interaction with the π system leading to a 1,4-biradical, probably via a charge-transfer precursor.[5-7,10] This

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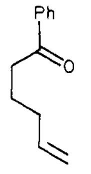
biradical can (after intersystem crossing) lead to oxetanes[3] or fragment to yield the starting materials with concurrent olefin cis–trans isomerization.[10] Fragmentation–cyclization competitions of this type are common in the chemistry of 1,4-biradicals.[20,21]

The olefins used in quenching studies of the type mentioned above frequently have allylic hydrogen atoms; these are known to be highly reactive toward *tert*-butoxy radicals,[22] a species whose behavior usually parallels that of radical-like ketone triplets such as the one from benzophenone.[20,25,26] However, very little is known about the reactivity of allylic hydrogens in these systems. Several studies using cyclohexene have indicated the presence of products that suggest hydrogen abstraction,[6,12,13] and in the case of the acetone–2,3-dimethyl-2-butene system, a detailed product study by Carless[11] revealed the presence of products resulting from combination reactions of radicals generated in the abstraction of allylic hydrogens. In the case of intramolecular processes, the possibility of hydrogen abstraction has been examined for molecules **1**–**3** by Wagner and by us.[27-29] In all cases allylic abstraction takes place, although the yield of type II biradicals is low in the cases of **2** and **3**.[28,29]



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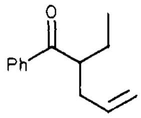

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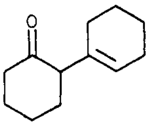

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It is perhaps important to note that while in most cases the reactivity of allylic hydrogens may not be evident from the product studies available in the literature, this should not be taken as evidence against hydrogen abstraction. For example, it has been pointed out that 1,4-cyclohexadiene quenches acetophenone triplets quite efficiently without chemical reaction.[15] We find that *in the benzophenone–1,4-cyclohexadiene system 94% of the quenching involves hydrogen abstraction* (vida infra)! This is perhaps not surprising, since similar observations have recently been made in other systems. For example, the well-known *inefficient* reaction of benzophenone triplets with aliphatic amines[30] has recently been shown to produce free radicals with unity quantum yields.[31] In fact, the inefficient generation of products in this system is probably the result of radical disproportionations that mask the actual yields of primary photoproducts.[31]

This study was undertaken in order to establish the fraction of quenching by olefins that involves hydrogen abstraction. In doing so we have also obtained absolute rate constants for these processes, and in the case of cyclohexene, the corresponding Arrhenius parameters. Attempts to detect the 1,4-biradicals involved in the photocycloaddition reaction were unsuccessful, despite some encouraging preliminary results (vide infra). The rates of reactions of *tert*-butoxy radicals with olefins were also determined in order to provide a suitable set of values for the comparison of ketone and alkoxy reactivities.

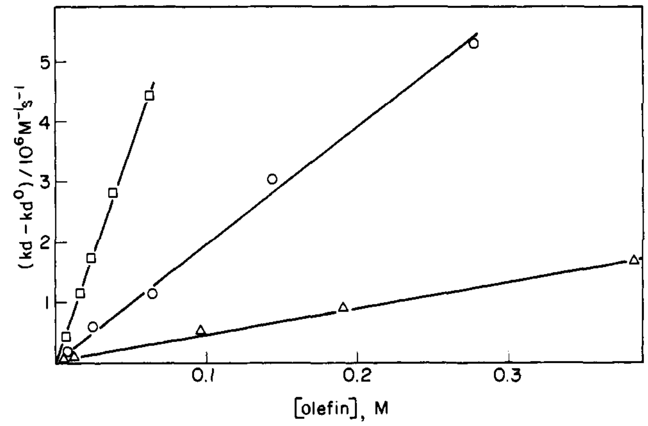

Figure 1. Plots showing the effect of olefin addition on the rates of triplet decay monitored at 540 nm in benzene at 27 °C. Data for cyclooctene (□), 1-octene (△), and *trans*-4-methyl-2-pentene (○). The rate of decay in the absence of olefin (k_d^0) has been substracted from the rate of triplet decay (k_d).

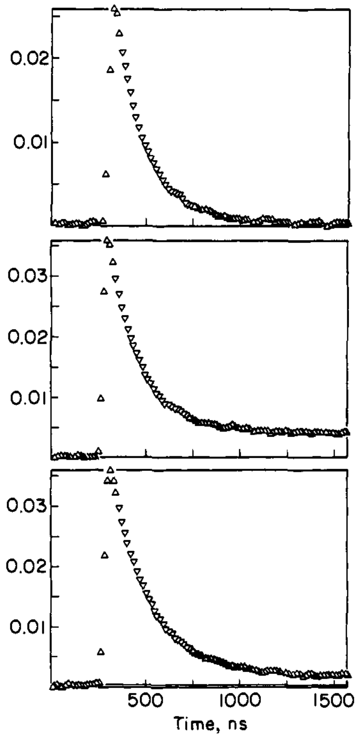

Figure 2. Traces obtained in the benzophenone–cyclohexene system (0.08 M) in benzene at 27 °C: top, monitored at 600 nm; center, monitored at 540 nm; bottom, monitored at 540 nm for cyclohexene-d_{10}.

Results

All the experiments described herein have been carried out in oxygen-free samples using the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a nitrogen laser for excitation. Transient absorptions were monitored using a computerized system described elsewhere.[32]

The rates of benzophenone triplet quenching by olefins were obtained by monitoring absorption in the 500–600-nm region (typically at 540 nm) in the presence of variable concentrations of olefin. The triplet lifetime in benzene in the absence of olefin was usually 2–3 μs and should simply be regarded as the lifetime

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Table I. Kinetic Parameters at 27 °C in Benzene

substrate	$k_q{}^a$	$k_a{}^a$	$k_\pi{}^a$	$F_k{}^b$	$k^a(Bu^tO\cdot)$
1,3-cyclooctadiene	3000	<30^c		~0	3.6
1,3-octadiene	6700	<50^c		~0	5.6
2,3-dimethyl-2-butene	900	(60)	840	0.035	15
cyclooctene	72	11	61	0.15	2.6
cyclohexene	73	17	56	0.23	5.8
cyclohexene-d_{10}	54	6	48	0.11	2.0
2-methyl-2-pentene	72	19	53	0.25	14.5
1,5-cyclooctadiene	81	22	59	0.26	8.9
trans-trans-2,8-decadiene	38	14	24	0.35	2.6
1-octene	4.4	1.6	2.8	0.37	1.5
trans-4-methyl-2-pentene	19	10	9	0.51	3.6
1,4-cyclohexadiene	290	273	(17)	0.94	53^d

[a] In units of $10^6\ M^{-1}\ s^{-1}$. [b] See eq 5; typical errors are ±0.02 or 10%, whichever is higher. [c] Assuming the limit of detection as ca. 1%. [d] From ref 24.

under our experimental conditions and may be partially controlled by trace impurities in the solvent.[33] The laser pulse was attenuated using neutral density filters in order to avoid triplet–triplet annihilation processes. The bimolecular rate constant for triplet quenching by olefin was obtained from a plot of the rate of decay (k_d) for benzophenone triplet vs. the olefin concentration. Typical plots are shown in Figure 1.

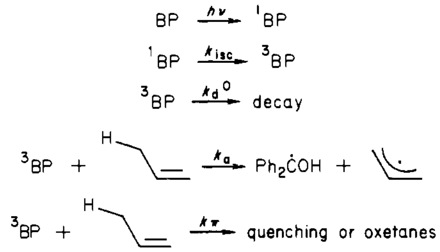
Some representative triplet decay traces obtained in the benzophenone–cyclohexene system are shown in Figure 2. The top trace was obtained at 600 nm (considerably displaced from the maximum for the triplet state),[34] at a wavelength where the ketyl radical, $Ph_2\dot{C}OH$, has virtually no absorption; as a result the traces return to approximately the prepulse level. The center trace corresponds to benzophenone triplet quenching by cyclohexene monitored at 540 nm, where both, the triplet state and the ketyl absorb, the latter having a lower extinction coefficient.[35] The "tail" absorption corresponds to $Ph_2\dot{C}OH$; its characterization was confirmed by a detailed spectral analysis in the 300–700-nm region. It should be noted that the ketyl radical is a stable species in the time scale of our experiments. The bottom trace in Figure 2 corresponds to the benzophenone–cyclohexene-d_{10} system under conditions identical with those shown in the center trace. The center and bottom traces show two differences: the pseudo-first-order rate of decay for 0.08 M cyclohexene-d_{10} is slightly slower with $k_d = 5.02 \times 10^6\ s^{-1}$, compared with $6.03 \times 10^6\ s^{-1}$ for the center trace. The other difference is larger and more important: the yield of ketyl radicals is lower with the deuterioquencher. This will be discussed quantitatively below.

The rest of the results reported in this section are based on the assumption that quenching of benzophenone by olefins takes place by two competing mechanisms, one in which the triplet state abstracts hydrogen in a radical-like process, and the other one in which the triplet state is quenched by interaction with the double bond, according to Scheme I, where BP stands for benzophenone and the superscripts indicate the multiplicity. The experimentaly determined rate constant for quenching is given by eq 1 and corresponds to both quenching processes.

$$k_q = k_a + k_\pi \tag{1}$$

In order to separate the values of k_a and k_π it is necessary to have an actinometer suitable for flash experiments, so that the quantum yields of ketyl radical formation can be determined. We have chosen for this purpose the reaction of the benzophenone triplet with triethylamine, which, according to Inbar, Linschitz, and Cohen[31] produces ketyl radicals quantitatively, a conclusion based on the critical assumption that the quantum yield of ketyl generation in the benzophenone–diphenylmethanol system is 2.0.[36]

Scheme I



An additional advantage of reaction 2 as an actinometer is the fact that the signals from $Ph_2\dot{C}OH$[35] and $CH_3\dot{C}HN(C_2H_5)_2$[38] do not overlap in the region of interest.

$$^3BP + (C_2H_5)_3N \rightarrow Ph_2\dot{C}OH + CH_3\dot{C}HN(C_2H_5)_2 \tag{2}$$

The determination of relative ketyl yields is straightforward, since they are proportional to the ratio of transient absorptions (A_{rt}) by the ketyl radical and the triplet.[31]

$$A_{rt} = \frac{\text{absorption after triplet decay (ketyl)}}{\text{absorption at } t = 0 \text{ (triplet)}} \tag{3}$$

Inbar, Linschitz, and Cohen[31] carried out their measurements at 530 nm. We have preferred to work at 540 nm, where the ratio of extinction coefficients is more favorable to the ketyl radical. This is an important difference in some of the systems leading to low yields.

The ratio of quantum yields for the system of interest (superscript x) and for the actinometer (superscript A) is simply given by the ratio of A_{rt}^x to A_{rt}^A; however, the value of interest is not the quantum yield but, rather, the fraction of the quenching events that lead to ketyl radical generation, F_k. As mentioned before, this value is taken as 1.0 for the actinometer.

In order to estimate F_k it is also necessary to know the fraction of triplets quenched, F_T. This is given by the lifetimes in the absence of quencher ($\tau_T{}^0$) and at the concentration at which A_{rt} was determined, according to eq 4.

$$F_T = 1 - (\tau_T/\tau_T{}^0) \tag{4}$$

The value of F_K is then determined from

$$F_K = \frac{A_{rt}^x\,F_T^A}{A_{rt}^A\,F_T^x} \tag{5}$$

The separate values of k_a and k_π are then derived from

$$k_a = F_k k_q \tag{6a}$$

$$k_\pi = k_q - k_a \tag{6b}$$

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(33) There is no question that longer lifetimes could be obtained by exhaustive purification of the solvent. This would not lead to any significant advantage and, in fact, would promote T–T annhilation processes, a far better candidate as an error source.

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(36) Even if this yield were somewhat lower, the errors introduced are not expected to be large, and would be well within the error limits given in our tables (vide infra). In a related system (acetophenone–1-phenylethanol) the primary yields of radicals are substantially lower than unity.[37]

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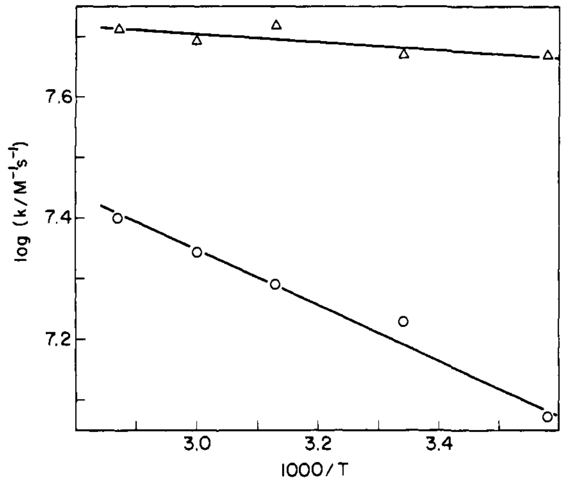


Figure 3. Arrhenius plots for cyclohexene in benzene for hydrogen abstraction (○) and quenching by the π system (△).

Table II. Solvent Effects at 27 °C

olefin	solvent	$k_a{}^a$	$k_\pi{}^a$	F_k
cyclohexene	benzene	17	56	0.23
cyclohexene	acetonitrile	31	65	0.32
2-methyl-2-pentene	benzene	19	53	0.25
2-methyl-2-pentene	acetonitrile	16	49	0.25

^{a} In units of 10^6 M^{-1} s^{-1}.

Table I summarizes the data obtained in benzene at 27 °C. A more detailed study was carried out in the cyclohexene case, where we examined the temperature dependence, as well as solvent and isotope effects. Figure 3 shows Arrhenius plots for k_a and k_π, from which we obtain

$$\log k_a = (8.66 \pm 0.30) - (2000 \pm 400)/\theta$$

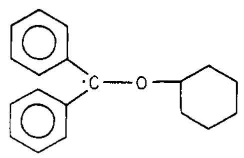
$$\log k_\pi = (7.88 \pm 0.20) - (300 \pm 200)/\theta$$

where $\theta = 2.3RT$ and RT in cal/mol.

The deuterium isotope effect, based on studies with cyclohexene-d_{10} at 27 °C in benzene, was $k_H/k_D = 2.8 \pm 0.2$ for the abstraction and 1.1 ± 0.2 for the interaction with the double bond.

A few experiments were carried out in acetonitrile in order to examine the effect of solvent polarity (Table II). The values obtained for cyclohexene are $k_a = 3.1 \times 10^7$ M^{-1} s^{-1} and $k_\pi = 6.5 \times 10^7$ M^{-1} s^{-1} at 27 °C. We note that these values are subject to considerably more error than the ones in benzene, because of the apparent formation of some $Ph_2CO^{-}\cdot$ (absorption in the 600–700-nm region). The basicity of triethylamine probably makes the ratio of ketyl to radical–anion absorption different in the amine and olefin systems, thus introducing some error.

A series of experiments were carried out in the hope of detecting the biradicals which are expected intermediates in photocycloaddition reactions. Structure **4** shows the expected species in the case of cyclohexene.



4

A few systems gave encouraging preliminary results (e.g., 1-octene, 2,8-decadiene, and 1,5-cyclooctadiene) with absorptions in the 390–450-nm region. However, in all the examples examined herein we were able to eliminate these absorbing species by careful purification of the olefins. The only species detectable after complete triplet decay is the ketyl, whose spectrum is shown in Figure 4 and is in full agreement with the spectrum reported in the literature and with the one that can be obtained by irradiation of di(*tert*-butyl) peroxide–diphenylmethanol mixtures. Quite obviously, allylic radicals are also formed in our experiments; however, our results indicate that their extinction coefficients at λ >300 nm, must be much smaller than those for $Ph_2\dot{C}OH$.

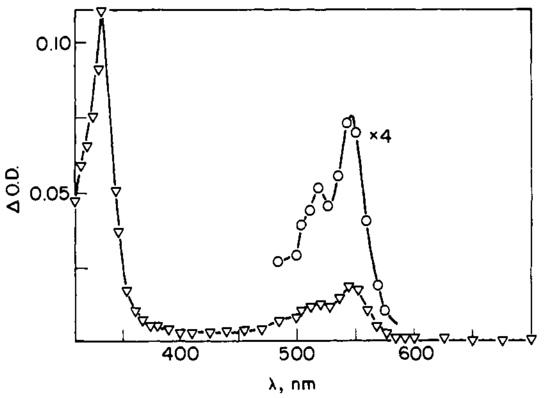


Figure 4. Transient spectra of ketyl radicals obtained following the quenching of benzophenone triplets by 0.3 M *trans*-4-methyl-2-pentene (in benzene at 27 °C).

We have also examined the reactivity of *tert*-butoxy radicals photogenerated from the peroxide with the same olefins examined in the case of the benzophenone triplet. The method used for these measurements uses diphenylmethanol as a probe, and is the same described earlier;[22] the method has proven quite versatile in a number of earlier studies.[22-24,39] It should be remarked that this technique measures molecular reactivity and that any addition to the double bond (particularly irreversible addition) will be incorporated into the rate constant. For the examples examined herein, abstraction was expected to be the predominant reaction path (vide infra).[40] The rate constants measured at 27 °C in 1:2 benzene/di(*tert*-butyl) peroxide (v/v) have also been included in Table I.

Discussion

The results reported here show that hydrogen abstraction can account for anywhere from ~0 to 94% of the quenching events. Virtually zero ketyl yields were obtained with conjugated dienes where triplet energy transfer is favorable, while the highest ketyl yields were obtained when double allylic hydrogens are available, as in the case for 1,4-cyclohexadiene. The rate constants for hydrogen abstraction are systematically higher (by a factor of 4–5) for benzophenone triplets than for alkoxy radicals, although the same trends are observed for both species. This similarity is well documented in the literature.[20,25,26,41] The only olefin which deviates considerably from the behavior described above is 2-methyl-2-pentene which is more reactive toward *tert*-butoxy radicals than one would expect. We can only speculate that addition to the double bond may be making a significant contribution in this case. A plot of $k(Bu^tO\cdot)$ vs. k_a (except the data for 2-methyl-2-pentene) is linear, with a slope of 0.19 and a correlation coefficient of 0.997.

The reactivity trends observed for different types of allylic hydrogens are also similar to those obtained in the case of polyunsaturated fatty acids.[23]

Quenching by 1,3-cyclooctadiene occurs by energy transfer and in this particular case is slower than for other dienes, a fact that has already been documented in the literature.[42]

As pointed out in the Introduction, there are numerous reports on the quenching of carbonyl triplets by olefins,[3-18] and it would be redundant to discuss here the kinetics of these processes and the way in which the rates are affected by molecular structure.

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Suffice to say that in those cases where direct kinetic comparisons are possible,[6] or where similar systems have been examined,[3-6,8,10,17,18] our data agree well with the values in the literature.

The rate constants for hydrogen abstraction reflect the type and number of hydrogens available (primary < secondary < tertiary), the degree of conjugation (double allylic > allylic), the type of hydrocarbon (cyclic > acyclic) and to some extent the substitution at the double bond. In the case of cyclohexene hydrogen abstraction is favored by an increase in temperature because its activation energy is higher than for interaction with the double bond; the latter is almost temperature insensitive. The Arrhenius parameters associated with k_π compare well with those reported for k_q in other systems.[17] The tendency of hydrogen abstraction to increase with increasing temperatures can be expected to be quite general. The Arrhenius parameters for cyclohexene are the first absolute values reported for hydrogen abstraction by a carbonyl triplet. The few values available in the literature are either based on competitive studies or have not evaluated the yield of ketyls;[35b,43,44] i.e., they represent the temperature dependence of k_q, not of k_a.

The isotope effect observed for k_a in the case of cyclohexene is 2.8 for the benzophenone triplet and 2.9 for *tert*-butoxy. They are reasonable for fast reactions of this type; for comparison, for *tert*-butoxy radicals typical values are 1.23 for Bu_3SnH,[45] 1.4 for $(CH_3)_3N$,[39c] and 2.8 for tetrahydrofuran,[22] while for benzophenone triplet the value is 1.27 for Bu_3SnH.[46]

As expected,[5] isotope effects on k_π are small or negligible, a result that reflects the fact that the C–H bonds are not directly involved in this process.

Changes in the polarity of the solvent have only minor effect on the rate constants for the processes responsible for triplet quenching. The results have been summarized in Table II. We are somewhat reluctant to draw significant conclusions from the minor differences observed because of the problems (possible involvement of $Ph_2CO^{-}\cdot$) mentioned before.

All the arguments presented herein have been based on the assumption that abstraction and interaction with the π system are two parallel processes. An alternative mechanistic assumption would be that both processes occur via an exciplex which partitions between abstraction and quenching (or oxetane) products. While we favor the former interpretation because of the parallel between k_a and alkoxy reactivities, we cannot entirely rule out the possibility of a common intermediate for both processes.[47]

Finally, we come to the question of biradical intermediacy and the possibility of detection. Quite recently Hayashi[18] reported the detection of the biradical involved in the interaction of benzophenone triplets with *cis*-3-methyl-2-pentene. This species was reported to have a lifetime of 6 μs in cyclohexane. While we did not examine this particular molecule, the structure of the ones examined is indeed quite close to it, and a wide range of structures has been covered. We could not detect any species that we could characterize as the biradical. In fact, the spectrum reported by Hayashi is identical with the UV band of the ketyl radical, $Ph_2\dot{C}OH$ (λ_{max} 332 nm), a species that is produced in all the systems with allylic hydrogens. While the spectrum of the biradical could conceivably be similar to that of the ketyl, it is hard to see what would make the biradical in the case of *cis*-3-methyl-2-pentene particularly long lived or easily detectable.[48]

Experimental Section

All the olefins used in this study are commercially available. In all cases they were chromatographed on activated alumina and distilled. The procedure was repeated whenever necessary. The purity of the materials was checked by gas chromatography on an OV-101 column. 1,5-Cyclooctadiene proved particularly difficult to purify. In the experiments with 1,4-cyclohexadiene, the absence of the 1,3 isomer was confirmed by gas chromatography before and after the experiments. Benzophenone was recrystallized twice from ethanol and the solvents (benzene, Aldrich Gold Label) and acetonitrile (Baker, Reagent grade) were used as received.

Diphenylmethanol (Eastman) and di(*tert*-butyl) peroxide (MCB) were purified as reported earlier.[22]

All experiments were carried out in nitrogen purged samples using for excitation the pulses from a Molectron UV-24 nitrogen laser. The detection system makes use of an RCA-4840 photomultiplier. Typical benzophenone concentrations were in the 0.001 to 0.008 M range. Our instrument has been fully interfaced to a PDP11/03L computer which controls the experiment, gathers data, and provides suitable processing and storage facilities. Full details have been reported elsewhere.[32]

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(47) Such an approach would associate the experimental Arrhenius parameters with the formation of the exciplex. A paper unpublished while this manuscript was under revision uses that viewpoint: Maharaj, U.; Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 2328–2333.

(48) Hayashi[18] detected only weak signals in the 520-nm region, which could not be distinguished from thermal lensing. It should be pointed out that the ketyl signals at 520 or 540 nm in a system leading to low yields are difficult to detect because they are weaker than those at 330 nm and overlap with the triplet state absorptions, thus making them be difficult to monitor without suitable averaging and background subtracting techniques.[32]