123.6 (C-8), 117.8 (C-12), 114.4 (C-7), 89.3 (C-16), 61.5 (C-3), 58.2 and 57.3 (C-5 and C-21), 38.3 (C-17), 35.6 (C-20), 34.3 (C-15), 32.6 (C-19), 28.2 (C-14), 21.2 (C-6), 7.64 ppm (CH_3); MS (EI) *m/e* (relative intensity) 296 (50), 295 (59), 282 (13), 278 (51), 250 (13), 249 (100), 221 (13), 210 (13), 167 (21), 156 (10), 152 (20), 150 (38), 149 (50), 136 (13), 124 (16), 122 (18), 110 (16), 97 (54), 96 (13), 95 (13), 84 (12), 83 (15), 77 (15), 71 (30), 70 (21). Anal. Calcd for $C_{19}H_{24}N_2O$: C, 76.99; H, 8.16; N, 9.45; O, 5.40. Found: C, 76.95; H, 8.19; N, 9.46; O, 5.40.

Irradiations in CCl_4 and in EtOH were performed in a similar manner. When CCl_4 was used as solvent, chloride anion formation was not detected ($AgNO_3/HNO_3$ test).

The conversion of **1** was poor (conversion 10%; **2** yield 9%) when it was irradiated in hexane with an external high-pressure mercury lamp in a Pyrex container (higher energy cutoff 290 nm). No phototransformation was detected when **1** (in hexane and in CCl_4 solution) was irradiated with a tungsten lamp.

Compound **2** was not detected as a photoproduct when a solution of **1** in hexane (quartz container, external low-pressure mercury lamp, irradiation time 1 h) was irradiated under N_2 atmosphere.

Irradiation of 1 in the Presence of HBr. The alkaloid **1** (10 mg, 0.355×10^{-4} mol) was dissolved in hexane (1000 mL), and the solution was placed in a quartz Erlenmeyer flask and in a Pyrex Erlenmeyer flask. Then, HBr(g) was slowly bubbled (≤ 0.05 mL/min) in both solutions.

Method A. The solution contained in the Pyrex Erlenmeyer flask (A solution) was kept in the dark while that contained in the quartz Erlenmeyer flask (B solution) was irradiated according to the above described method, with the low-pressure mercury lamp. HBr(g) was bubbled in both solutions simultaneously. The irradiation was stopped when a light yellow precipitate (A precipitate) was observed in the A solution. The crystalline A precipitate that formed was filtered off and then characterized as the monohydrobromide (−)-quebrachamine salt by the $AgNO_3/HNO_3$ test and by the Volhard method. The HBr concentration in the mother A liquors was determined by the Volhard method and the alcaloid **1** concentration by GC analysis.

The precipitate formed in the irradiated B solution (B precipitate) was collected by vacuum filtration and analyzed by TLC, GC, GC/MS, and by Volhard method. Then, B precipitate was dissolved in CH_2Cl_2 and extracted with H_2O, dried over anhydrous Na_2SO_4, and evaporated. The residue obtained was worked up as usual. The mother B liquors were analyzed as usual.

Method B. Both solutions, A and B, were kept in the dark while HBr(g) was bubbled in both containers. The HBr bubbling in the A solution was initiated 0.5 s before than the bubbling in the B solution. The HBr bubbling was stopped when a light turbidity was shown by A solution. In that moment, the irradiation of the B solution, with the low-pressure mercury lamp, was started while A solution was kept in the dark. After 1 h of irradiation, the usual workup and GC analysis of both solutions gave the **1** conversion, **2** yield, and **2** quantum yield values mentioned in the text.

Irradiation of 1 in AcOH. A solution (0.355×10^{-4} M) of (−)-quebrachamine in AcOH (glacial) was irradiated with the low-pressure mercury lamp, contained in a quartz Erlenmeyer flask. After 1 h of irradiation the light brown solution was diluted with H_2O: (i) First, the acidic aqueous solution was extracted with benzene and then with CH_2Cl_2, (ii) then, the aqueous solution was neutralized with NaOH(aq) and extracted with benzene and then with CH_2Cl_2. The organic layers were separated and washed with H_2O and then with $NaHCO_3$(aq). The residues obtained by evaporation of the solvent were analyzed by TLC, GC, and GC/MS.

Photosensitized Irradiation of 1. The photosensitized reactions of **1** (10 mg) were performed by employing Rose Bengal (RB) and Hematoporphirine (HP) (0.6 mg) dissolved in EtOH (RB) and in CCl_4 (HP) (1000 mL). The solutions were irradiated with a tungsten lamp for 18 h. The progress of the reaction was followed as usual, and **2** was not detected as product of the dye photosensitized reaction of (−)-quebrachamine (**1**).

Acetylation of 2. The monoacetyl derivative (**3**) was obtained from **2** as an oily compound from hexane: MS (EI) *m/e* (relative intensity) 338 (0.7), 279 (54), 278 (100), 263 (5), 250 (46), 249 (81), 236 (50), 235 (49), 222 (9), 221 (65), 207 (23), 181 (44), 167 (22), 118 (6), 110 (5). Anal. Calcd for $C_{21}H_{26}N_2O_2$: C, 74.52; H, 7.74; N, 8.28; O, 9.46. Found: C, 74.50; H, 7.75; N, 8.29; O, 9.46.

The diacetyl derivative **4** was obtained, in very poor yield, as impurity of **3**, and it was characterized by GC/MS: MS (EI) *m/e* (relative intensity) 380 (0.5), 321 (23), 320 (100), 277 (18), 263 (10), 250 (27), 249 (78), 236 (47), 235 (23), 222 (8), 221 (63), 207 (15), 181 (32), 167 (18), 118 (5), 110 (7).

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Registry No. **1**, 4850-21-9; **2**, 120411-05-4; **3**, 120385-95-7; **4**, 120416-95-7; **5**, 3384-38-1.

Photochemistry of 4,4-Dimethyl-1-phenyl-2-pentyn-1-one[1]

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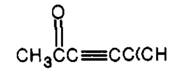
The photochemistry of 4,4-dimethyl-1-phenyl-2-pentyn-1-one has been examined by a combination of laser flash photolysis experiments and product studies. The triplet ketone is relatively long-lived in inert solvents such as acetonitrile but reacts readily with hydrogen donors via hydrogen abstraction to give the corresponding ketyl radical and with substituted aromatics via charge-transfer quenching. For example, rate constants for quenching by cyclohexane and anisole are 2.9×10^7 and 2.8×10^8 M^{-1} s^{-1}, respectively, in acetonitrile. The ketone undergoes efficient photodecomposition in cyclohexane ($\Phi = 0.86$) to give the expected radical coupling products but is unreactive in benzene. The ketone radical anion ($\lambda_{max} = 510$ nm in acetonitrile) is formed directly by quenching the triplet with 1,4-diazabicyclo[2.2.2]octane. It may also be generated indirectly in the reaction with triethylamine by reduction of the parent ketone by the amine-derived radical produced by hydrogen abstraction by the triplet ketone.

Despite the wide amount of attention that α,β-enone systems have received,[3] there have been relatively few investigations of the analogous α,β-acetylenic ketones.[4-14] Most of the available examples indicate that these compounds undergo the typical hydrogen abstraction, α-cleavage, and cycloaddition reactions of triplet ketones. For example, 5,5-dimethyl-3-hexyn-2-one (1) in 2-propanol undergoes photoreduction to yield pinacols[11] and ketone **2** gives type II γ-hydrogen abstraction products with a quantum yield of 0.43 in benzene.[9] Ketone **3** undergoes efficient intramolecular hydrogen abstraction to give a biradical, which has been suggested to rearrange to a vinyl carbene that is ultimately responsible for product formation.[4] This ketone has been examined by laser flash photolysis with the detection of both biradical and enol intermediates.[8] Type I cleavage followed by loss of carbon monoxide and rearrangement of the resulting biradical has been reported for ketone **4**.[14]



$CH_3\overset{O}{\overset{\|}{C}}C{\equiv}CC(CH_3)_3$

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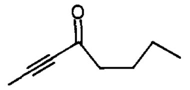

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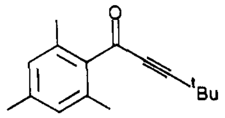

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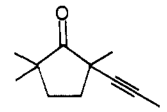

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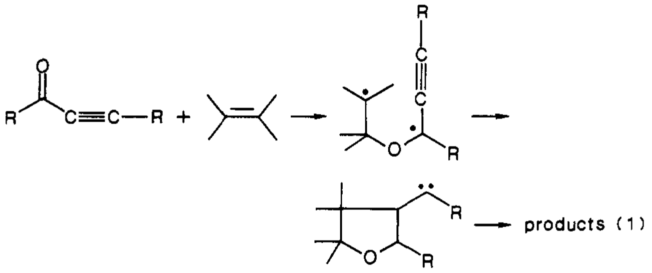
In addition to the above reactions, α,β-acetylenic ketones also undergo both [3 + 2] and [2 + 2] cycloaddition reactions with various olefins.[5-7,10] Recently, a number of examples have been reported in which what is overall a [3 + 2] photochemical cycloaddition has been shown to proceed through a biradical which cyclizes to a carbene (reaction 1).[5-7] The products then result from intramolecular rearrangement of the carbene or for some substrates from closure of the biradical to an oxetane.



(1)

The above examples indicate that α,β-acetylenic ketones show typical carbonyl reactivity although the final products may result from rearrangements involving the triple bond. However, the irradiation of 1-phenyl-2-propyn-1-one in alcohols has recently been suggested to result in hydrogen abstraction from the alcohol by the triple bond rather than by the carbonyl oxygen.[12,13] The final product in this case is a 2,5-disubstituted furan resulting from cyclization and dehydration of the 1:1 adduct of ketone plus alcohol (reaction 2).

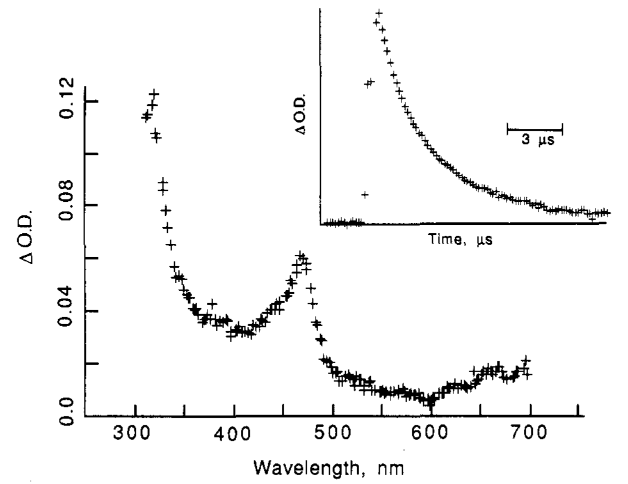
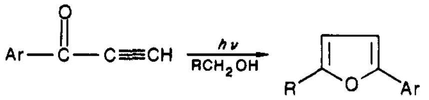
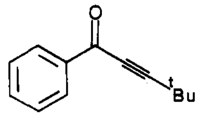


Figure 1. Triplet–triplet absorption spectrum for ketone **5** measured 1 μs after 308-nm excitation in acetonitrile. Insert: Transient decay at 475 nm.



(2)

The above conflicting results concerning the expected reactivity of α,β-acetylenic ketones have prompted us to examine ketone **5** using a combination of laser flash photolysis and product studies in order to evaluate the extent to which the triple bond modifies the carbonyl reactivity. The results reported herein demonstrate that triplet **5** is relatively long-lived in inert solvents and reacts rapidly with hydrogen donors to generate ketyl radicals and with some amines to generate radical anions. Product studies confirm that hydrogen abstraction is an efficient reaction in solvents such as cyclohexane. The triplet is also readily quenched by substituted benzenes, presumably via a charge-transfer mechanism, which explains the previously reported 25-ns lifetime for triplet **5** in benzene.[8]



5

Results

Characterization of Triplet 5. Excitation (308 nm) of ~0.5 mM solutions of **5** in acetonitrile yielded the transient spectrum shown in Figure 1, with λ_{max} at 320 and 475 nm. Decay kinetics monitored at either of these two wavelengths were identical and indicated a lifetime in excess of 5 μs for the transient (see insert in Figure 1). The decays were not strictly first order, probably indicating the presence of a small second-order component due to triplet–triplet annihilation. This transient is readily assignable to triplet **5** based on the following observations.

Phosphorescence from ketone **5** could be measured at room temperature and was similar to that recorded in an EPA (ethanol, isopentane, ether, 2:5:5) glass at 77 K ($E_{0,0}$

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(1) Issued as NRCC 30198.

(2) Co-op student; University of Sherbrooke.

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Table I. Rate Constants for Reaction of Triplet 5 with Various Substrates in Acetonitrile at Room Temperature

substrate	k_q, M^{-1} s^{-1}
1,3-cyclohexadiene	$(9.9 \pm 0.4) \times 10^9$
oxygen	$(2.1 \pm 0.2) \times 10^9$
1-methylnaphthalene	$(8.6 \pm 0.7) \times 10^9$
cyclohexane	$(2.8 \pm 0.2) \times 10^7$
methanol	$(7.1 \pm 0.5) \times 10^6$
2-propanol	$(2.7 \pm 0.4) \times 10^7$
cyclohexene	$(9.7 \pm 0.3) \times 10^8$
1,4-cyclohexadiene	$(1.90 \pm 0.07) \times 10^9$
triethylamine	$(1.2 \pm 0.2) \times 10^9$
1,4-diazabicyclo[2.2.2]octane	$(1.8 \pm 0.2) \times 10^{10}$
chlorobenzene	$(3.8 \pm 0.1) \times 10^6$
benzene	$(1.01 \pm 0.05) \times 10^7$
tert-butylbenzene	$(3.4 \pm 0.2) \times 10^7$
toluene	$(4.32 \pm 0.08) \times 10^7$
toluene-d_8	$(5.2 \pm 0.3) \times 10^7$
p-xylene	$(1.2 \pm 0.1) \times 10^8$
anisole	$(2.8 \pm 0.2) \times 10^8$
durene	$(1.15 \pm 0.05) \times 10^9$

= 413.5 nm; 69.2 kcal/mol). Furthermore, the phosphorescence decay observed at room temperature was identical with the decay of the triplet–triplet absorption measured under similar experimental conditions. The phosphorescence spectrum at 77 K showed the vibrational structure and short lifetime (2.0 ms in EPA) normally observed for n,π^* carbonyl triplets.[15]

Additional support for the triplet assignment was provided by the characteristic quenching of the transient by typical triplet quenchers such as oxygen and 1,3-cyclohexadiene ($k_q = 2.1 \times 10^9$ and 9.9×10^9 M^{-1} s^{-1}, respectively, Table I). Efficient quenching was also observed with 1-methylnaphthalene ($k_q = 8.6 \times 10^9$ M^{-1} s^{-1}) with the concomitant production of its triplet state.

Similar results were obtained in Freon-113 but in solvents such as benzene, cyclohexane, or methanol the triplet was much shorter lived. Triplet lifetimes of approximately 30 ns were measured in both benzene and methanol, and the transient phenomena were dominated by the presence of other species as discussed in the next section.

Reaction of Triplet 5 with Hydrogen Donors. Triplet **5** was readily quenched by a variety of hydrogen donors as indicated in Table I. The experimental rate constants (k_{exp}) for triplet decay as a function of quencher decay were plotted according to reaction 3, where k_0 is the

$$k_{exp} = k_0 + k_q[Q] \qquad (3)$$

first-order rate constant for triplet decay in the absence of quencher. This approach gave rate constants (k_q) of 2.8×10^7 M^{-1} s^{-1} and 2.7×10^7 M^{-1} s^{-1} for cyclohexane and 2-propanol, respectively. The triplet quenching was accompanied by the formation of a new transient with a considerably longer lifetime. The spectrum of the new species in methanol is shown in Figure 2, and is quite similar to that of the triplet ketone. This species may be readily assigned to the ketyl radical formed by hydrogen abstraction from triplet **5**. The spectra of ketyl radicals are normally quite similar to those of their triplet precursors.[16] The insert in Figure 2 shows a decay trace monitored at 470 nm for the quenching of triplet **5** by methanol in acetonitrile. The short-lived component is the triplet, and the long-lived residual absorption is due to the radical.

Reaction of Triplet 5 with Aromatics. Substantial yields of ketyl radical were produced by the reaction of triplet **5** with 1,4-cyclohexadiene, alcohols, and cyclohexane in acetonitrile. However, triplet quenching by substituted aromatics (e.g. toluene, anisole) showed little or no production of ketyl radical. Consistent with these observations is the fact that the quenching rate constant for toluene was not decreased by deuterium substitution (Table I) as would be expected if hydrogen abstraction was a major pathway. The relative quenching rate constants for a number of substituted aromatics were observed to decrease with increasing oxidation potential of the substrate, as expected for a charge-transfer quenching process similar to that which has been observed for other aromatic ketones.[17-20] A plot of log (k_q) versus quencher oxidation potential is shown in Figure 3. The observed quenching rate constants are all considerably higher than those for ketones such as benzophenone. For example, benzophenone is quenched by benzene with a rate constant of 2.7×10^4 M^{-1} s^{-1} [20] while ketone **5** reacts with a rate constant of 1.0×10^7 M^{-1} s^{-1}. Consistent with this enhanced

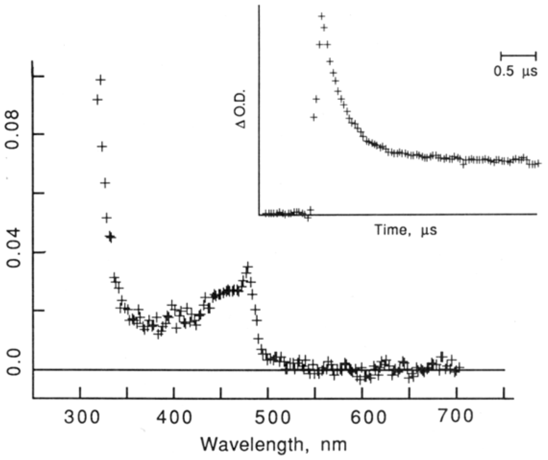

Figure 2. Transient absorption spectrum of the ketyl radical recorded 1 µs after 308-nm excitation of **5** in methanol. Insert: Decay trace monitored at 470 nm for quenching of triplet **5** with 0.454 M methanol.

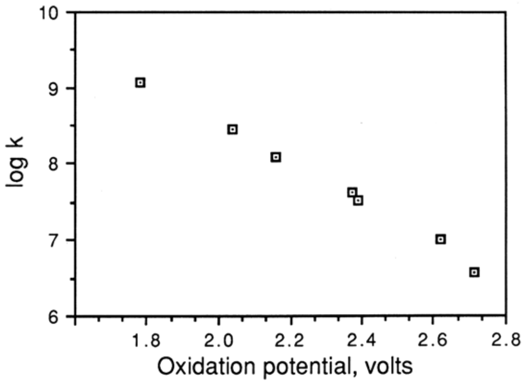

Figure 3. Correlation between the oxidation potentials of various aromatics and the rate constants for triplet quenching. The quenchers (E_{ox}) in order of increasing oxidation potential are durene (1.78), anisole (2.04), *p*-xylene (2.16), toluene (2.37), *tert*-butylbenzene (2.39), chlorobenzene (2.61), and benzene (2.71). The oxidation potentials are taken from ref 21 and are against SCE.

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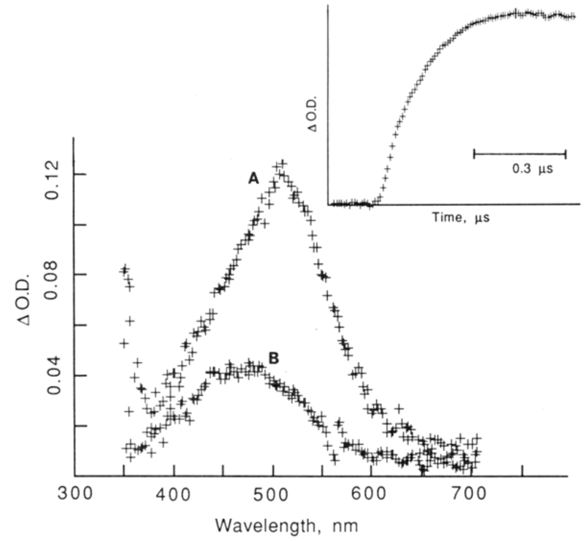

Figure 4. Transient absorption spectrum produced by 308-nm excitation of ketone **5** in acetonitrile plus 0.6 mM DABCO under air at 80 ns (A) and 250 ns (B) delays. Insert: Growth trace for $5^{\bullet -}$ at 525 nm for 0.32 mM DABCO in nitrogen-purged acetonitrile.

triplet reactivity is the fact that the ground state of ketone **5** has a reduction potential of −1.64 V in acetonitrile as compared to −1.85 V for benzophenone measured under the same conditions.

Reaction of Triplet 5 with Amines. For none of the substituted aromatics was there any evidence for the formation of radical ions as a result of the quenching process. However, reaction of triplet **5** with DABCO (1,4-diazabicyclo[2.2.2]octane) in acetonitrile produced a new species with a broad absorption to the red of the triplet (λ_{max} at 510 nm). This species had a growth lifetime that increased with increasing amine concentration and that was identical with the triplet decay at low quencher concentrations. At higher DABCO concentrations the strong absorption due to the new species made it difficult to measure the triplet decay at 470 nm. A plot of k_{exp} (based on the growth at 525 nm) against DABCO concentration gave a rate constant of 1.8×10^{10} M^{-1} s^{-1}. The spectrum of the new transient is shown in Figure 4 along with a growth trace monitored at 525 nm in the presence of 3.2×10^{-4} M DABCO.

The transient decay could not be adequately fitted by either a first- or a second-order decay. Furthermore, the decay rate was observed to decrease with lower laser intensities and to more closely approximate a first-order decay. The half-life even at higher laser doses was always in excess of 4 μs. The transient was efficiently quenched by oxygen as evidenced by its 90-ns lifetime in aerated acetonitrile.

The above observations are all consistent with the formation of the radical anion from **5**. This is further confirmed by the spectra in the presence of air which show the radical anion at short delays and the DABCO radical cation at longer delays (Figure 4). The latter has a characteristic absorption in the 400–500-nm region[22] and is not readily quenched by oxygen. However, since it has a much weaker extinction coefficient than the radical anion it is only readily detectable when the latter is removed by reaction with oxygen. The increase in lifetime of the anion at lower laser doses is consistent with back-electron transfer to the amine radical cation being the primary decay pathway; such a process will depend upon the concentration of the radical ions and, thus, upon the initial laser intensity.

The growth of the radical anion continued to increase with increasing amine concentration up to ca. 3 mM, at which point the growth lifetime was ca. 20 ns. There is, therefore, no evidence for the formation of the radical anion via deprotonation of an initially formed radical. Similar results to those described above were also obtained in 9:1 acetonitrile/water, except that the radical anion spectrum was blue-shifted by approximately 30 nm.

Reaction of triethylamine with triplet **5** in 9:1 acetonitrile/water also produced the radical anion. However, in this case the growth lifetime of $5^{\bullet -}$ did not continue to increase with increasing amine concentration, but rather levelled off at lifetimes of ≤150 ns. Furthermore, the growth lifetime was observed to depend upon the initial ketone concentration when sufficient amine had been added to reach the amine-independent region. These results are consistent with formation of the radical anion by attack of the methyl(dimethylamino)methyl radical (generated by hydrogen abstraction by the triplet ketone from the amine) upon the ground-state ketone (reaction 4). The amine-dependent growth of $5^{\bullet -}$ at lower amine concentrations reflects the kinetics of formation of the methyl(dimethylamino)methyl radical by hydrogen transfer to triplet **5**. Analysis of the rate of growth as a function of

$$CH_3\dot{C}HN(Et)_2 + \mathbf{5} \rightarrow \mathbf{5}^{\bullet -} + CH_2{=}CN(Et)_2 + H^+ \qquad (4)$$

ketone concentration led to a rate constant of $\sim 3 \times 10^9$ M^{-1} s^{-1}. Similar results have been observed previously for both both benzophenone and benzil.[23,24] The growth of the radical anion monitored at 525 nm where there was no interference from the radical or triplet did not show a fast component due to direct formation by quenching of the triplet. Under these conditions the radical anion was much longer lived (>100 μs) than in the DABCO experiments described above, since back-electron transfer is no longer the rate-limiting step for its decay. The absence of radical anion formation when the ketyl radical from **5** is produced by reaction with 1,4-cyclohexadiene or 2-propanol in 9:1 acetonitrile/water is also consistent with formation of $5^{\bullet -}$ via reaction 4.

Similar results were obtained for triethylamine quenching of triplet **5** in 7:3 acetonitrile/water. However, in this case the signals due to radical anion were considerably stronger, and at high amine concentrations there were both instantaneous and slow pathways for its formation. The latter may be assigned to reduction of the ketone by the amine-derived radical; the former is attributed to the direct formation of the anion by quenching of the triplet. At high ketone concentrations there were approximately equal amounts of the instantaneous and delayed process, consistent with production of two radical anions per ketone triplet.

Product Studies. Irradiation of **5** in cyclohexane at 300 nm results in efficient photochemistry to give the expected radical coupling products, as shown in reaction 5. Products **6** and **7** were isolated and identified as outlined in the Experimental Section. HPLC analysis of product mixtures indicated that the pinacol dimer **6** was formed in approximately 60% yield based on decomposition of the starting ketone, while the cross-coupling product accounted for an additional 20–25%. A number of other minor products were detected by HPLC, but these were formed in small amounts and were not isolated. One of these was readily identified as the alcohol (4,4-di-

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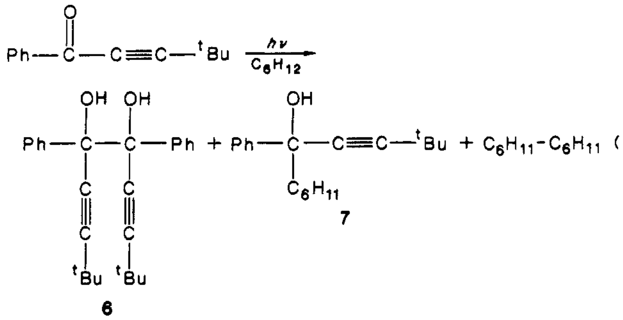

(5)

methyl-1-hydroxy-1-phenyl-2-pentyne) formed by hydrogen abstraction by the ketyl radical, on the basis of comparison of retention time and UV and mass spectra to those of an authentic sample. The other minor products may arise partly from further thermal or photochemical decomposition of the primary products. In this regard it should be noted that there was some decomposition of **6** in cyclohexane. However, approximately 5 h was required to see a detectable change by HPLC for a sample of the isolated dimer. Therefore, this decomposition was not a problem as long as the photolyzed samples were analyzed immediately after irradiation since typical irradiation times were 0.5–1.5 h. Dicyclohexyl was analyzed by GC since it does not have a suitable chromophore for HPLC analysis using UV detection.

A quantum yield for loss of starting material of 0.86 in cyclohexane was measured relative to the production of acetophenone from valerophenone in benzene.[25] The much smaller extinction coefficient, even at 235 nm, for the major product (**6**) compared to that of the ketone made it difficult to measure a quantum yield based on product appearance at low conversion.

The photochemistry of **5** was also investigated briefly in several other solvents. Irradiation of **5** in benzene for 90 min gave <4% loss of starting material, and no products were detected by HPLC. In contrast, irradiation of a similar concentration of **5** in cyclohexane under matched conditions resulted in ≥85% decomposition of the starting material. Similarly, **5** was efficiently photolyzed in methanol. HPLC analysis indicated that there were two major products. The LC retention time, UV spectrum, and LC/MS data were consistent with one of these being pinacol dimer **6**. The other major product showed UV and mass spectra consistent with its assignment to a furan as had been previously observed.[13]

Discussion

The above transient experiments and product studies confirm that the triplet state of **5** shows qualitatively similar behavior to that of other phenyl ketones. The phosphorescence data indicate that the triplet energy is almost identical with that of benzophenone and suggest that the lowest triplet is n,π^* in nature. However, triplet **5** does show enhanced reactivity toward both hydrogen donors and substituted aromatics. For example, benzophenone and acetophenone react with cyclohexane with rate constants of 7.5×10^5 and 3.4×10^5 M^{-1} s^{-1},[26] respectively, in acetonitrile, whereas the rate constant for **5** is 2.8×10^7 M^{-1} s^{-1}. Similar rate enhancements are also observed for other hydrogen donors. Despite these large differences, the net photochemistry is very similar for both **5** and benzophenone. The measured quantum yield for decomposition of **5** indicates that the interaction of cyclohexane with triplet **5** produces ketyl radicals with a high efficiency. The slightly lower than unity quantum yield may reflect a small amount of disproportionation of the ketyl–cyclohexyl radical pair. Furthermore, the high yields of the expected radical coupling products suggest that attack of radicals at the triple bond of starting material does not complicate the photochemistry, at least with cyclohexane as the donor.

Triplet **5** also shows efficient charge-transfer quenching by aromatics, as demonstrated by the correlation between the quenching rate constant and the oxidation potential of the donor shown in Figure 3. Even for aromatics that are reasonably good hydrogen donors in other systems (e.g. toluene or durene) there is no evidence for the formation of ketyl radicals, or for that matter, any other transients as a result of the quenching process. These results differ substantially from those for benzophenone for which k_q for toluene is 4.1×10^5 M^{-1} s^{-1} and which gives a high yield of ketyl radical,[26] although it should be noted that low radical yields have also been observed for quenching of benzophenone with more easily oxidized aromatics such as anisole.[27] The low yield of hydrogen abstraction for **5** is more in line with the behavior observed for decafluorobenzophenone, which reacts with toluene with a k_q of 1.24×10^9 M^{-1} s^{-1} but which gives only a 9% yield of ketyl radical.[19] Note that the rate constant for quenching of triplet **5** by toluene (4.3×10^7 M^{-1} s^{-1}, Table I) indicates a reactivity that is intermediate between that of benzophenone and decafluorobenzophenone. The stability of **5** to irradiation in benzene is consistent with unreactive quenching via a charge-transfer process.

The present results are not consistent with the previous suggestion that the photochemistry of ketone **5** and its substituted derivatives in alcohol solvents involves hydrogen abstraction by the acetylenic moiety.[13] Rather, our experiments indicate that the photochemistry of **5** is that expected for a triplet carbonyl, although the reactivity is considerably enhanced compared to some other systems. These results also agree well with the previous observation of the expected radical coupling products in the photochemistry of **1** in 2-propanol.[11] Given the low yields (~10%) of isolated furan products and the long irradiation times in the previous reports,[12,13] it is possible that these products resulted from a minor reaction pathway, perhaps involving attack of intermediate solvent-derived radicals on the acetylenic group of the starting ketone. In this regard it may also be important to note that we have observed that the pinacol dimer is not particularly stable in solution.

The production of radical anion by quenching triplet **5** with amines agrees well with previous studies in benzophenone systems.[23,28,29] For example, the quenching of benzophenone with DABCO produces radical anion directly and under certain conditions the rate of disappearance is limited by back electron transfer, as we have observed for $\mathbf{5}^{\bullet-}$.[23] It has been suggested[29] that the stability of $DABCO^{\bullet+}$ is responsible for the lack of proton transfer to give radicals in the initial BP–DABCO charge-transfer complex, and the same rationalization presumably applies for ketone **5**. In contrast, there is now considerable evidence to suggest that the initial charge transfer complex

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for BP–triethylamine decays by either proton transfer to give radicals or by dissociation to yield radical ions, with the competition between the two being solvent-dependent.[29,30,31] Our results indicate that proton transfer is the dominant decay route for the initial complex for the **5**/triethylamine complex in acetonitrile. However, in aqueous mixtures the rapid production of $\mathbf{5}^{\bullet-}$ suggests that ion pair separation competes effectively with proton transfer. This is similar to the situation observed for benzophenones substituted with electron-withdrawing groups.[23]

The efficient reduction of ground state **5** by the triethylamine-derived radical is consistent with the reduction of various benzophenones and benzil by amine-derived radicals.[23,24] The observed rate constants are close to those observed for some of the more readily reducible benzophenones, in good agreement with the observed reduction potential for ketone **5**.

In summary, ketone **5** has been shown to undergo hydrogen abstraction reactions, charge-transfer quenching by aromatics, and electron-transfer processes.[32] Both transient experiments and product studies confirm that the photochemistry of **5** is that expected for a typical phenyl ketone, although there are some quantitative differences that presumably result from the presence of the acetylenic moiety.

Experimental Section

Materials and Methods. Ketone **5** was synthesized as described in the literature.[8] Cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and triethylamine were distilled before use, and durene and DABCO were recrystallized from benzene and ethanol, respectively. Other quenchers and solvents (spectro grade) were used as received.

Phosphorescence spectra at 77 K were measured on a Perkin-Elmer LS-5 spectrofluorimeter. HPLC measurements were done on a Hewlett-Packard 1090 liquid chromatograph equipped with a reverse-phase column (RP-18; 5 μm) and a diode array detector. Methanol/water solvent mixtures were used, and signals were monitored at 235, 254, and 320 nm. LC/MS measurements were carried out on a Hewlett-Packard 5988A instrument with a similar column and solvent system. GC analyses were done on a Perkin-Elmer 8320 gas chromatograph with a 12-m BP1 on vitreous silica column.

Laser Flash Photolysis. A Lumonics TE860-2 excimer laser with Xe/HCl gas mixtures (308 nm; 5 ns pulses; $\leq$20 mJ/pulse) was used for excitation. Spectra were recorded using an EG&G gated and intensified optical multichannel analyzer with a model 1420 detector with a 20-ns gate. Samples were contained in 7 × 7 mm^2 quartz cells and were deaerated by bubbling nitrogen gas. Several experiments were carried out with flow samples to check that there were no complications due to sample depletion or product buildup. Static samples were found to be sufficient for most purposes. The other details of the flash photolysis setup have been reported elsewhere.[33]

Product Studies. Samples of **5** in cyclohexane (0.025 M) were deaerated and irradiated for 0.5–1.5 h using 300-nm Rayonet lamps. Products were analyzed by HPLC using an internal standard and known mixtures of ketone **5** and dimer **6** for calibration purposes. The pinacol dimer was not sufficiently stable for GC analysis, although GC was used to confirm the presence of dicyclohexyl. Products **6** and **7** were isolated from a preparative scale irradiation (150 mg of **5** in 20 mL of cyclohexane) by chromatography on silica gel using a chromatotron with 4% ethyl acetate/hexane as the eluent. Dimer **6** was further purified by recrystallization from hexane to give white crystals; mp 119–121 °C; ^{1}H NMR (δ, CDCl$_3$) 7.4–7.1 (m, 10 H), 3.1 and 2.9 (s, total of 2 H) and 1.28 and 1.24 (s, total of 18 H) for a mixture of the meso and *dl* isomers; LC/MS (*m/e* (intensity)) 357 (51) for $M^+ - OH$ and 187 (100). Anal. Calcd: C, 83.38; H, 8.07. Found: C, 83.18; H, 8.20. Product **7** was obtained as an oil; LC/MS (*m/e* (intensity)): 253 (100), $M^+ - OH$.

Quantum Yields. Samples of **5** in cyclohexane and valerophenone in benzene with matched optical densities at 310 nm were deaerated with nitrogen and irradiated through Pyrex with Rayonet 3000 lamps for 6 and 12 min, respectively. The irradiated samples were analyzed by HPLC and GC for **5** and the actinometer, respectively, using appropriate internal standards and calibration solutions. The quantum yield for disappearance of **5** was calculated based on the known quantum yield of 0.3 for acetophenone production from valerophenone. Triplicate runs were done for both sample and actinometer.

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