J. Am. Chem. Soc. **1987**, *109*, 3050–3057

ammonium fluoride trihydrate (TBAF·3H_2O, Aldrich). This flask was attached to a vacuum line (<2 mmHg) and heated at 45 °C for 48 h.[8] To the dry TBAF (calcd 16% H_2O loss) was added a mixture of tosyl fluoride (3.56 g, 0.0204 mol) and 1-(hydroxymethyl)-2-vinylcyclopropane (1.0 g, 0.0102 mol) in 30 mL of diethyl ether (dried from $LiAlH_4$ onto activated 4Å sieves). The TBAF/TsF/alcohol mixture formed two layers upon combination. The TBAF formed an orange gelatinous solid which could be stirred freely upon use of ultrasonics (E/MC Model 250, RAI Reseach) and slight heating (not >40 °C). This mixture was stirred for 61 h. At this time the product mixture (2 layers) was poured into a 200-mL separatory funnel and 20 mL of deionized H_2O was added. The ether layer was separated and the aqueous layer extracted with 2 × 20 mL diethyl ether. The ether layers were combined, dried with $MgSO_4$, and filtered. The ether was removed at atmospheric pressure pot temperature <48 °C). The yellow oil was vacuum transferred twice. The cis and trans isomers of **1-(fluoromethyl)-2-vinylcyclopropane** (10) (24%) were separated by GC.

The *cis*-1-(fluoromethyl)-2-vinylcyclopropane was further GC purified on a 10 ft × $^1/_4$ in., 10% ODPN column (98% GC pure). The kinetic studies were done on this purified sample.

***trans*-1-(Fluoromethyl)-2-vinylcyclopropane**: ^{1}H NMR (300 MHz), δ 5.42 (ddd, 1 H, C—Ch=C), 5.10 (dd, 1 H, *t*—C=CH), 4.92 (dd, 1 H, *C*—C=CH), 4.28 (ddd, 2 H, CH_2F) 1.5–0.7 (complex m, 4 H, cyclopropyl H); ^{19}F NMR, ϕ 210.46 (t d, J^2_{HF} = 48.9 Hz), J^3_{HF} = 7.3 Hz); mass spectrum, *m*/*z* (relative intensity) 101 (M^+ + 1, 1.36), 100 (M^+, 30.07).

***cis*-1-(Fluoromethyl)-2-vinylcyclopropane**: ^{1}H NMR (200 MHz), δ 5.7 (m (ddd?), 1 H, C—CH=C), 5.2 (m (dd?), 1 H, *t*—C=CH, 5.1 (m (dd?), 1 H, *C*—C=CH), 4.4–4.0 (ddm, 2 H, CH_2F), 1.8–0.5 (complex m, 4 H, cyclopropyl H); ^{19}F NMR, ϕ 211.3 (t, J^2_{HF} = 48.9 Hz); ^{13}C NMR, δ 135.8 (s, HC=), 115.9 (s, =CH_2, 84.0 (d, $J_{C\text{-}F}$ = 166 Hz, CH_2F), 19.7 (d, J_{CF} = 5 Hz, H_2C cyclopropyl), 17.8 (d, J_{CF} = 25 Hz, H*C*—CH_2F cyclopropyl), 9.6 (d, J_{CF} = 5 Hz, H*C*—C= cyclopropyl); mass spectrum, *m*/*z* (relative intensity) 101 (M^+ + 1, 1.50), 100 (M^+, 27.46).

Thermal Rearrangement of *cis*-1-(Fluoromethyl)-2-vinylcyclopropane. *cis*-1-(Fluoromethyl)-2-vinylcyclopropane (80.0 mm) was expanded into a well-conditioned pyrolysis bulb and pyrolyzed at five temperatures between 193.25 and 227.25 °C. The reaction was followed by GC with a 10 ft. × $^1/_8$ in., 10% ODPN column at 55 °C. The rate constants are given in Table III. The pyrolysis afforded only two products: (*Z*,*Z*)-1-fluoro-1,4-hexadiene (**12**) and (*E*,*Z*)-1-fluoro-1,4-hexadiene (**11**) in the ratio of 65:35, respectively.

(*Z*,*Z*)-1-Fluoro-1,4-hexadiene: ^{19}F NMR, ϕ 131.64 (ddt, J^1_{HF} = 85.4 Hz, $J^3_{trans\ HF}$ = 42.6 Hz, J^5_{HF} = 1.7 Hz, =CHF).

(*E*,*Z*)-1-Fluoro-1,4-hexadiene: ^{19}F NMR, ϕ 131.87 (ddt, J^1_{HF} = 85.5 Hz, $J^3_{cis\ HF}$ = 18.8 Hz, J^5_{HF} = 2.6 Hz, =CHF).

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

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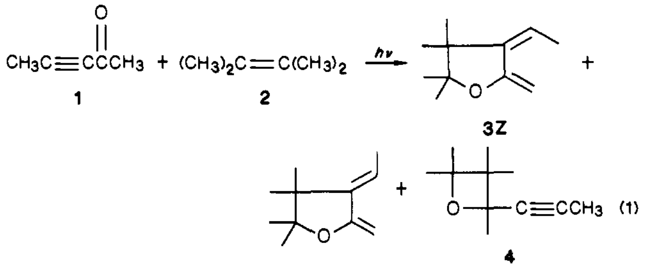
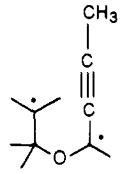
Abstract: The photochemistry of 4,4-dimethyl-1-mesityl-2-pentyn-1-one (**7**) in solution has been examined by using a combination of product studies, quantum yield measurements, and laser flash photolysis techniques. The main products of reaction are the indanones **10** and **11**, believed to be formed via the intermediacy of carbene **9**. Transient phenomena are dominated by the photoenolization of the parent ketone **7**, which occurs following hydrogen abstraction by the triplet leading to biradical (or triplet enol) **8**. The biradical has a lifetime of 38 ± 4 ns in methanol and 45 ± 7 ns in heptane (for **7D**) at room temperature. Biradical decay leads to a mixture of enols **18Z** and **18E**. The syn enol **18Z** usually accounts for >90% of the mixture and decays with first-order kinetics with $k_d = 2.7 \times 10^7\ s^{-1}$ in hexane at 293 K. For comparison the deuterio analogue **18Z-D** decayed with $k_d = 3.7 \times 10^6\ s^{-1}$ under the same experimental conditions. The anti enol was extremely long-lived, and under carefully controlled conditions its lifetime was 22 s in hexane at room temperature.

Several recent reports have provided a number of examples of photochemical [3 + 2] cycloaddition of α,β-acetylenic ketones with various olefins, e.g.,[5–7] eq 1. The reaction has been proposed to involve the intermediacy of biradical **5**, which cyclizes to carbene **6**, which is ultimately responsible for product formation. The products of [3 + 2] cycloaddition have been shown to be triplet-derived, and trapping studies, in particular using alcohols, have provided unequivocal evidence for the intermediacy of carbene **6**.



1 **2** **3Z** **3E** **4** (1)



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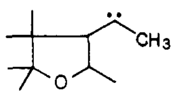

6

The biradical shown above (**5**) and all those included in the earlier publications contain an oxygen atom in their backbone; this is known to have a great influence on the biradical lifetimes in other systems.[8] Recently, Agosta et al. have reported an example of a reaction involving an all-carbon alkyl propargyl

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(1) Issued as NRCC-27495.

(2) The Rockefeller University.

(3) University of Texas.

(4) National Research Council.

(5) Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 6902.

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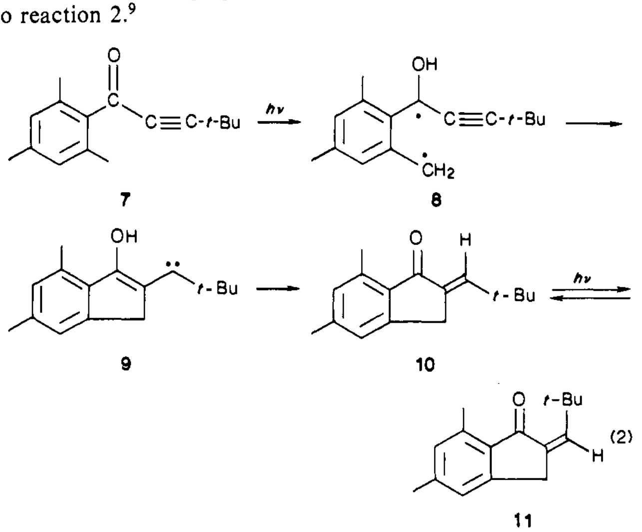
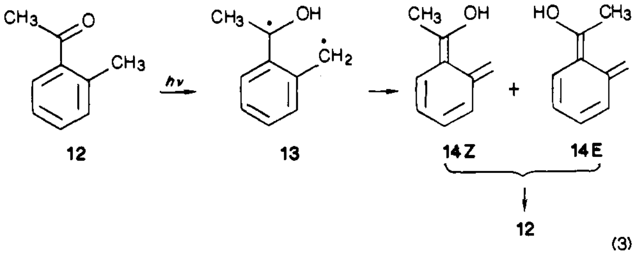
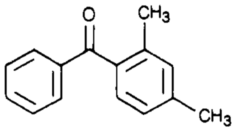
biradical, which was proposed to close to a vinyl carbene, according to reaction 2.[9]



During the last decade, biradicals generated in the Norrish Type II and related reactions have been the subject of many direct time-resolved studies.[10,11] In particular, a number of studies have examined the biradicals (i.e., triplet enols) produced in the photoenolization of ortho alkyl-substituted aromatic ketones, such as *o*-methylacetophenone, i.e.,[12-15] eq 3.



The lifetimes of these biradicals are strongly dependent on the substitution at the carbonyl center and in some cases on the polarity of the solvent. For example, the biradicals from **12** and from 2,4-dimethylbenzophenone (**15**) have lifetimes of 900 and $\sim$30 ns, respectively, in methanol at room temperature, while in hydrocarbon solvents their lifetimes are 130 and $\sim$30 ns, respectively.[14] Examination of literature lifetimes for a variety of biradicals produced in photoenolizations and in the Norrish Type II reaction suggests that **15** is unusual in that the biradical generated via intramolecular hydrogen abstraction (**16**) shows virtually no solvent sensitivity.



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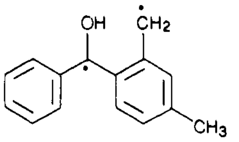
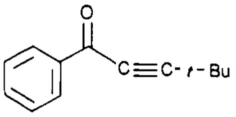
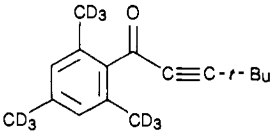


16

7 provides an interesting source for a new type of biradical-triplet enol that has not been examined by using flash techniques. The relationship (or lack thereof) of any transients observed to the mechanism of formation of **10** and **11** was an important impetus to this work. In this paper, we report jointly the results of detailed studies of the photochemistry of **7**, covering product and quantum yield studies, isotope exchange studies, quenching experiments, and phosphorescence and extensive laser flash photolysis work under a variety of experimental conditions. In addition, a number of experiments on **17** are also reported; this molecule serves as a useful control substrate since it cannot undergo photoenolization.



17

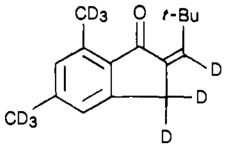


7D

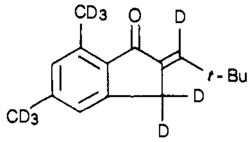
Results

Synthesis. The mesityl alkynyl ketone **7**[9] was readily available through reaction of mesitaldehyde with the Grignard reagent from *tert*-butylacetylene and subsequent oxidation of the crude alcohol with Jones's reagent.[16] For synthesis of **7D** mesitaldehyde-d_9 was used. This was prepared through base-catalyzed exchange[17] of sodium mesitoate with deuterium oxide to form mesitoic acid labeled in the methyl groups. Reduction of the derived ester with lithium aluminum hydride and reoxidation furnished labeled mesitaldehyde, which was then converted to **7D**. Nuclear magnetic resonance (NMR) measurements on **7D** indicated that the ring methyl groups were greater than 95% fully labeled. Ketone **17** was prepared from benzaldehyde by using the procedure described above for **7**.

Preparative Chemistry. Irradiation of a degassed benzene solution of **7** (0.020 M, $\geq$340 nm) for 6 h yielded 74% of a 84:16 mixture of the isomeric indanones **10** and **11**, which could be separated and purified by flash[18] or gas chromatography. Longer irradiation times gave an increasing proportion of **11**, and very low conversion furnished essentially only **10**. From the behavior of related compounds[19] photochemical isomerization of **10** to **11** is expected to be efficient. The structures of **10** and **11** are fully supported by their infrared (IR) and 300-MHz proton NMR spectra.[20] Similar irradiation of **7D**, using glassware and solvent benzene that had been carefully dried, led to **10D** and **11D** with some loss of the olefinic deuterium atom, presumably due to exchange with adventitious water. Recovered **7D** had lost no deuterium within the limits of NMR analysis (±5%); the location of deuterium in all cases could be determined unambiguously by proton NMR measurements.



11D



10D

Quantum Yields and Quenching Studies. A quantum yield of $\sim$0.097 for the rearrangement of **7** in cyclohexane at 313 nm was determined against concurrent formation of acetophenone from valerophenone in ethanol, a reaction for which the quantum yield is known.[21] The reaction was quenched by 2,3-dimethyl-1,3-butadiene and followed Stern–Volmer kinetics[22] over the range

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(20) We have also studied[9] the analogous photoisomerization of 1-(*o*-tolyl)-2-butyn-1-one, where the products are the known (*E*)- and (*Z*)-2-ethylidene-1-indanones, whose spectroscopic properties agreed with those previously reported[19] for these substances.

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(22) Wagner, P. J. In *Creation and Detection of the Excited State*; Marcel Dekker: New York, 1971; Vol. 1, Part A, p 173.

0–3.2 M quencher, with $k_q\,\tau_T \approx 0.29$ M^{-1}.

Photolysis of 7 in Benzene/D_2O. Irradiation of **7** as described above, but in benzene saturated with deuterium oxide,[23] furnished **10** and **11** carrying ~45% deuterium at the olefinic hydrogen and no deuterium at other positions. Recovered **7** contained no incorporated deuterium within the limits of NMR analysis (±5%). In a similar experiment deuterium levels were measured mass spectrometrically; **10**, **11**, and recovered **7** contained ~54, 44, and 7% of one deuterium atom, respectively. Experiments in dry benzene and benzene/H_2O showed that quantum yields are relatively insensitive to water (or D_2O) addition. Control experiments for unirradiated samples in the three solvents showed no deuterium incorporation in the starting material under these conditions. Furthermore, addition of D_2O to the reaction mixture after photolysis of **7** in benzene alone gave no deuterium incorporation in the products after 24 h at 30 °C in the dark.

Photolysis of 7 in Methanol. Irradiation of **7** as described above but in solvent methanol for 16 h gave essentially no reaction. Gas chromatographic analysis indicated ~95% of **7** remained unchanged.

Phosphorescence. The phosphorescence spectrum of **7** in a methylcyclohexane glass at 77 K showed the typical well-resolved structure of an n,π^* ketone with a 0,0 band at 423.5 nm, corresponding to a triplet energy of 67.5 kcal/mol. Ketone **17** gave a very similar phosphorescence spectrum (0,0 band at 419.5 nm, 68.2 kcal/mol).

Time-Resolved Studies. These experiments were carried out at two different locations, NRC in Ottawa and CFKR in Austin. The two systems, while far from identical, have similar capabilities. Experiments at NRC used 337- or 308-nm excitation, while at CFKR 266 or 353 nm were used. Some details and appropriate references are given in the Experimental Section. Unless otherwise indicated, experiments were carried out at room temperature (ca. 293 K) in samples deaerated by bubbling oxygen-free nitrogen. Control experiments showed that only minor substrate depletion took place during the laser experiments and that periodically stirred static samples (as opposed to a flow system) were adequate.

Control Experiments with 17. Laser photolysis of **17** in hexane or methanol using 337-nm excitation did not lead to any readily detectable signals in the 340–650-nm range. In benzene a weak transient with a 26-ns lifetime was observed at 330 nm and may be attributed to triplet **17**.

The triplet lifetime for **17** in hexane was estimated from quenching studies by using 1-methylnaphthalene (MeN) as an energy acceptor. Under these conditions, energy transfer from triplet **17** leads to readily detectable MeN triplets; their transient absorption (A_{420}) was monitored at 420 nm. This technique, which has been widely used to study "undetectable" triplets,[24] yields $k_q\tau_T$ from eq 4, where k_q is the rate constant for triplet energy transfer,

$$\frac{1}{A_{420}} = \alpha + \frac{\alpha}{k_q\tau_T[\text{MeN}]} \qquad (4)$$

τ_T the triplet lifetime, and [MeN] the concentration of 1-methylnaphthalene. The corresponding plot is shown in Figure 1 and leads to $k_q\tau_T = 160$ M^{-1}. On a first approximation the value of k_q can be assumed to be the same as for benzophenone, since the triplet energies and chromophores are quite similar. For benzophenone the value has been independently determined in benzene and led to $k_q = 7.4 \times 10^9$ M^{-1} s^{-1}. Using this value we obtain $\tau_T = 22$ ns. While short, this value is not outside the time domain of the techniques employed; its determination by this technique was preferred in order to provide a direct comparison with **7** (vide infra).

Triplet Lifetime for 7. While transient signals are readily detectable following laser excitation of **7**, all attempts to characterize triplet **7** directly using nanosecond techniques were unsuccessful; i.e., no intermediate quenchable by oxygen and conjugated dienes could be detected. This result is consistent with product quenching studies, which led to $k_q\tau_T = 0.29$ M^{-1} in cyclohexane with 2,3-dimethyl-1,3-butadiene as a quencher (vide supra).

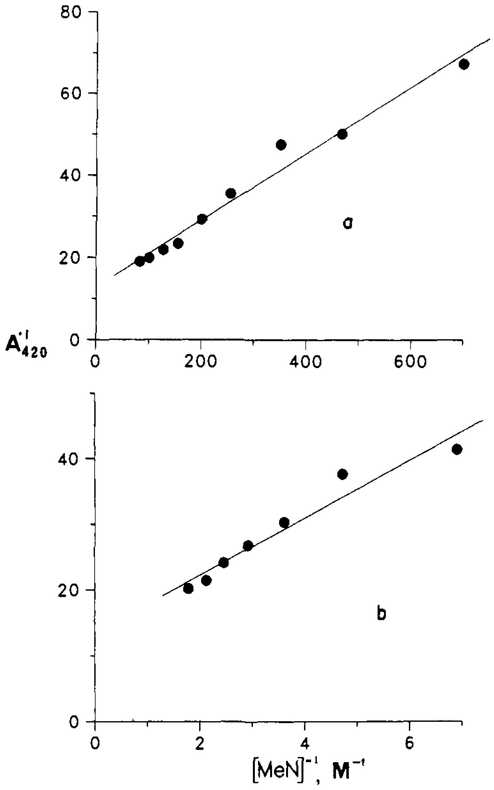

Figure 1. Plot of the reciprocal optical density at 420 nm (A_{420}) vs. the reciprocal methylnaphthalene concentration for **17** (a) and **7** (b).

Experiments with MeN, using the same technique described above for **17**, led to $k_q\tau_T = 3.0$ M^{-1} in hexane (Figure 1), corresponding to a triplet lifetime in the neighborhood of 0.4 ns. The difference between the $k_q\tau_T$ values derived from products and from the laser is not entirely surprising.[25] At concentrations as high as those required here (>0.5 M), MeN is not completely transparent at 337 nm and some of the assumptions in this technique break down. In any event, the laser experiments support the short lifetime determined in the product quenching studies, but the value derived from the latter is preferred. The same type of experiments could not be repeated in methanol because the enol signals (vide infra) interfere with the measurement of A_{420} for the MeN triplet.

Characterization of Ground-State Enols from 7. Although from a mechanistic point of view biradicals (i.e., **8**) precede the formation of enols, the latter are the dominant feature of the transient measurements. For this reason these results are presented before those leading to the characterization of **8**. Ground-state enols **18E** and **18Z** are expected products of biradical decay, i.e., eq 5.

Laser photolysis of **7** (typically 0.5–1 mM) in methanol led to very strong signals with $\lambda_{max} \approx 400$ nm (Figure 2). Approximately 94–95% of the signal decayed with first-order kinetics with a lifetime of 1.5 ± 0.1 μs (see insert in Figure 2). However, the residual 5–6% of the absorption was extremely long-lived (~60 μs). The decay of the faster signal was not affected by oxygen saturation of the solution, although this led to a small decrease in the yield of transient. The slower signal was somewhat affected by oxygen, $k_q(O_2)$ = ca. 3×10^5 M^{-1} s^{-1}, very close to the value observed for the long-lived enol from 2-methylacetophenone by Haag, Wirz, and Wagner.[14] Neither transient lifetime was affected by addition of 1,3-cyclohexadiene or di-*tert*-butyl nitroxide, both of which are excellent triplet quenchers. Di-*tert*-butyl ni-

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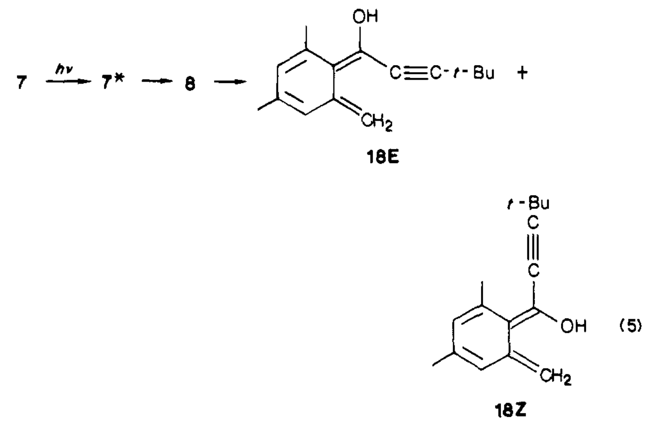
[23] The solubility of water in benzene at 20 °C is 0.021 M: Joris, G. G.; Taylor, H. S. *J. Chem. Phys.* **1948**, *16*, 45.

[24] Scaiano, J. C.; Netto-Ferreira, J. C. *J. Photochem.* **1986**, *32*, 253 and references therein.

[25] Triplet quenching by dienes is usually slower than by 1-methylnaphthalene: Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 1539. Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *Ibid.* **1985**, *107*, 5806.



18E

18Z

(5)

troxide and oxygen are also well-known to be efficient biradical quenchers.

The short- and long-lived components in this decay show virtually identical spectra, suggesting that the two species have very similar chromophores. We assign the short- and long-lived 400-nm transients to ground-state enols **18Z** and **18E**, respectively. There is abundant precedent in the literature showing that the two isomeric enols usually have very different lifetimes.[14] The formation of the 400-nm transients is not instantaneous in our time scale, but under certain conditions it is possible to detect a well-resolved growth of the transient; these results provide further evidence for the enol assignments and are presented together with the experiments leading to the characterization of biradical **8**.

Laser irradiation of **7** in hexane or heptane leads to readily detectable but short-lived signals that also show a residual long-lived component. The long-lived transient decays with a lifetime of ~22 s in hexane at room temperature. Figure 3 shows its absorption and decay after irradiation at room temperature for 30 s at 313 nm. At ice temperature the spectrum remains for at least a half hour.

In order to facilitate characterization of the short-lived transient we carried out two types of experiments that lead to considerably longer *Z* enol lifetimes in hydrocarbon solvents. In one set of experiments **7** was replaced by **7D**. The enol decay rate constant (short component) was 3.7×10^6 s^{-1}, much slower than the value for the hydrogen analogue **7**, for which we obtained an extrapolated (vide infra) value of 2.3×10^7 s^{-1}. A direct measurement for **7** gave $k_d \approx 2.7 \times 10^7$ s^{-1}, but the extrapolated value is prefered because it avoids problems due to biradical interference (vide infra). Large isotope effects for enol decay in related systems are well-established[15] and would be expected for the thermal 1,5 shift of hydrogen to revert to **7**.

In another series of experiments, we examined the temperature dependence of the decay of **18Z** in hexane between 206 and 280 K. Arrhenius analysis of the data (Figure 4) led to

$$\log (k_d/\mathrm{s}^{-1}) = (9.6 \pm 0.1) - (3000 \pm 130)/2.3RT$$

with RT in cal/mol. The preexponential factor is lower than that observed in the case of enol **14Z**; however, these plots tend to be nonlinear even if over a limited temperature range they may approach linearity (Figure 4).[15] The fraction of residual absorption following decay [i.e., **18E**/(**18E** + **18Z**)] was ca. 12% at 206 K and ~19% at 280 K although the latter value may be the subject of considerable error. As in the case of methanol the spectra of the transients responsible for the fast and slow decay are virtually identical.

Oxygen saturation at 205 K in hexane did not change significantly the lifetime or yield of *Z* enol. Addition of either methanol or di-*tert*-butyl nitroxide (Table I) led to longer lifetimes for the *Z* enol and an increase in the relative yield of the *E* enol; the effect is attributed to hydrogen bonding to the hydroxylic position in the enol.

Several experiments with **7** and **7D** were also carried out in dioxane/H_2O mixtures. These results have been summarized in Table II. Deuteriation of the substrate has a dramatic effect on the *Z* enol lifetime, but the solvent composition has no detectable effect, indicating that H/D exchange does not take place during the *Z* enol lifetime or in the stages (biradical) leading to its

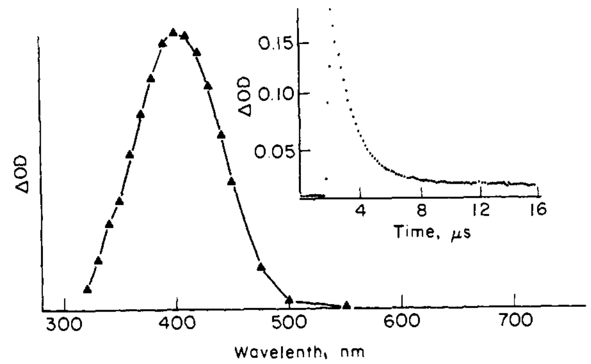


Figure 2. Transient absorption spectrum recorded 1 μs after 308-nm excitation of **7** in methanol. Insert: a decay trace monitored at 400 nm.

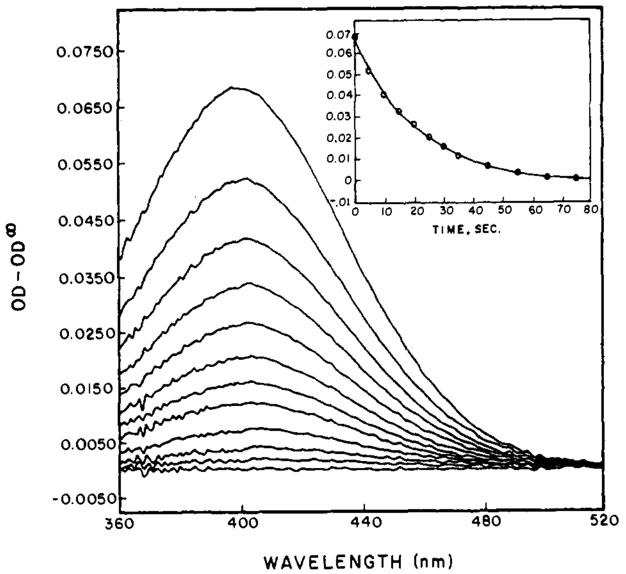


Figure 3. Absorbance due to **18E** on the 0–75-s time scale following irradiation of **7** (4×10^{-3} M) at 313 nm. The absorbance at 80 s is subtracted as a base line. Insert: decay of the absorbance at 402 nm.

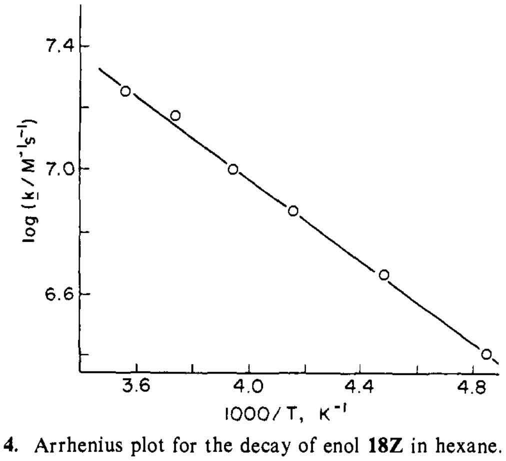


Figure 4. Arrhenius plot for the decay of enol **18Z** in hexane.

Table I. Effect of Various Substrates on the Lifetime of Enol **18Z** in Hexane at 210 K

substrate	concn, M	τ, ns
none		354
oxygen	(saturated at 210 K)	335
methanol	0.0057	2200
di-*tert*-butyl nitroxide	0.001	463
di-*tert*-butyl nitroxide	0.002	680
di-*tert*-butyl nitroxide	0.003	722

Table II. Effect of Deuteriation on the Decay of Enol **18Z** in Dioxane/Water

substrate	cosolvent[a]	k_{decay}, s^{-1}
7	H_2O	1.10×10^6
7	D_2O	1.11×10^6
7D	H_2O	1.05×10^5
7D	D_2O	1.04×10^5

[a] In a 9:1 dioxane/H_2O or dioxane/D_2O solvent.

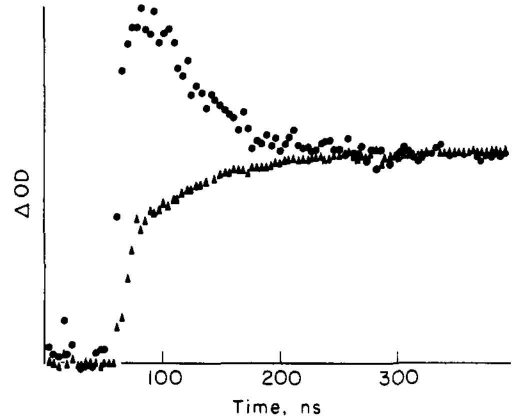


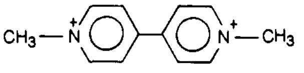
Figure 5. Growth and decay traces monitored at 400 and 330 nm, respectively, following 308-nm excitation of 7 in methanol at 220 K.

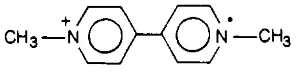
formation. This agrees well with the small amount of deuterium incorporation in 7 recovered after partial photolysis in benzene/D_2O.

Experiments in acetonitrile led to a lifetime of 0.35 μs for **18Z**. As in the other solvents the "early" and "late" spectral components were very similar.

Lifetime and Reactivity of Biradical 8. As already pointed out, the mixture of isomeric enols **18** is not produced "instantly" on a nanosecond time scale, and a growth can be readily detected under some conditions. Figure 5 shows a comparison of traces recorded at 400 and 330 nm showing growth and decay processes occurring approximately in the same time following 308-nm laser excitation of 7 in methanol at 220 K. The lifetime obtained from these measurements was ~50 ns. Similar experiments at room temperature led to a (38 ± 4 ns) decay at 330 nm and a (35 ± 3 ns) rise at 400 nm.

This 330-nm transient is not quenched by dienes, clearly indicating that it is not the triplet state of 7. In order to establish if its characterization as biradical 8 was correct, we carried out a series of trapping experiments with methyl viologen.

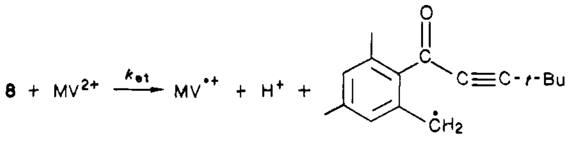

MV^{2+}


$MV^{\bullet+}$

Methyl viologen has been widely used as a scavenger for biradicals bearing ketyl radical sites, and the techniques for determining biradical lifetimes and reactivities are now well-established.[10,13] Trapping of **8** by MV^{2+} is expected to lead to the formation of $MV^{\bullet+}$, which can be readily characterized from its absorption spectrum. The formation of $MV^{\bullet+}$ was monitored at 600 nm following laser excitation at 353 nm; a representative trace is shown as an insert in Figure 6. The formation of $MV^{\bullet+}$ follows pseudo-first-order kinetics according to eq 6 where k_{growth} is the

$$k_{\text{growth}} = \tau_\beta^{-1} + k_{\text{et}}[MV^{2+}] \quad (6)$$

experimental rate constant for the formation of $MV^{\bullet+}$ according to reaction 7 and τ_β and k_{et} are the biradical lifetime and the rate constant for reaction 7, respectively. Analysis of the quenching


(7)

data (Figure 6) leads to $\tau_\beta^{-1} = (2.7 \pm 0.1) \times 10^7\ s^{-1}$ and $k_{\text{et}} = (6.8 \pm 0.5) \times 10^8\ M^{-1}\ s^{-1}$ (errors as $\pm 2\sigma$). This gives a lifetime of 37 ± 2 ns for biradical **8**, in excellent agreement with the value obtained by direct detection. We emphasize that the MV^{2+} technique does not require any assumptions regarding the identity of any of the intermediates produced in the direct photolysis of 7.[10]

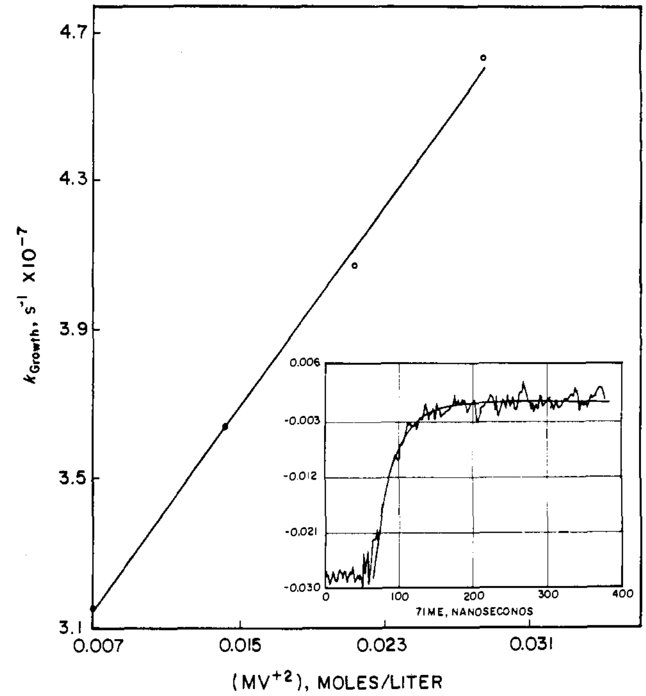


Figure 6. Plot of the first-order rate constant for growth of $MV^{\bullet+}$ absorbance at 600 nm vs. the MV^{2+} concentration. Insert: a representative trace at 600 nm.

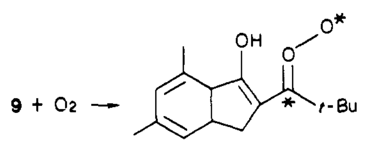
Biradical studies in hydrocarbon solvents were difficult because the biradical and *Z* enol lifetimes are rather similar. In hydrocarbon solvent only the use of **7D** permitted any kinetic resolution at room temperature since **8** and unlabeled **18Z** evidently have nearly identical lifetimes. Figure 7 shows the decays from 7 and **7D** respectively at 330 nm. The former shows good single exponential behavior, and the latter clearly shows **18Z-D** as a longer component. For **7D** in heptane, the fast 330-nm decay (44 ± 5 ns) corresponds well to the 405-nm rise (45 ± 7 ns). The good correspondence shows the 330-nm transient to be a precursor of **18Z** and **18E** and reinforces its assignment as **8**.

Studies in acetonitrile, where **18Z** is longer lived, suggest that **8** has a lifetime of 7–10 ns.

Attempts To Detect Carbene 9. All transients observed from 7 can be assigned to biradical **8** or enols **18Z** or **18E**. No direct evidence for the intermediacy of a carbene was obtained from any of the laser flash experiments. Carbenes are readily trapped by alcohols, and one could not expect to detect them directly in solvents such as methanol. Further, in this solvent product yields are too low for them to have any significant role in determining the transient phenomena. One must conclude that in methanol reversible photoenolization is responsible for the strong absorption signals observed. Although the transient data in hydrocarbons are quantitatively different from those in methanol, the main qualitative features remain much the same, and the quantitative differences are well-precedented.

A detailed spectroscopic study was carried out for a 5×10^{-4} M solution of 7 in hexane saturated with oxygen at 218 K. This experiment was undertaken in the hope of detecting carbonyl oxide signals that could result from oxygen trapping of the carbene (reaction 8).

No signals that could be attributed to **20** were observed, although it should be noted that typical carbonyl oxide absorptions usually fall in the 400–450-nm region.[26] If there was any carbonyl

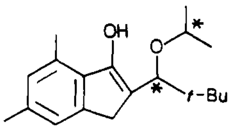


20

(8)

oxide in this system, it was not distinguishable from the other transients absorbing in the 400-nm region produced in the photochemistry of 7 (see Figure 2). Similar problems were experienced in acetonitrile, where carbene-derived nitrile ylides have been reported to absorb in the 400-nm region.[27]

In another attempt we tried to trap carbene 9 with acetone to yield carbonyl ylide 21.



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In this experiment 7 was irradiated in acetone as solvent by using 337-nm excitation (acetone being transparent at this wavelength). Several other carbenes are known to react with ketones to yield readily detectable carbonyl ylides with absorptions in the 450–650-nm region.[28] However, photolysis of 7 in acetone yielded only a transient (λ_{max} = 410 nm, τ_{decay} = 1.2 μs, τ_{growth} ≈ 30 ns) very similar to that observed in methanol. No signals attributable to a carbonyl ylide were observed.

A low-temperature ESR experiment was also carried out to see if the proposed carbene could be detected. Photolysis of 1 in a 2-methylbutane glass at 15 or 77 K gave no signals attributable to carbene 9. This result is not surprising since formation of the carbene would be expected to show a considerable activation energy and may not occur at low temperature. Consistent with this, the ketone is strongly phosphorescent at 77 K and below.

Discussion

The results of the laser work on the photochemistry of 7 leave no doubt that the photoenolization reaction dominates the transient phenomena. The triplet state of 7 leads in a subnanosecond process to the formation of biradical 8. The lifetime of triplet 7 is nearly 2 orders of magnitude shorter than that of 17, clearly indicating the importance of the new decay mode leading to 8. The biradical (or triplet enol) 8 must be formed as the syn conformer but presumably undergoes rapid conformational equilibration. Its lifetime at room temperature is 35–40 ns in methanol, 40–45 ns in hydrocarbons (hexane or heptane), and ~7 ns in acetonitrile. Biradical decay leads to the formation of the isomeric enols **18E** and **18Z**. The **8** → **18** conversion can be detected as a decay in the 330-nm region, where the biradical absorption dominates, while in the 400-nm region we observe a signal growth concurrent with the decay at 330 nm. The absence of a significant difference in biradical lifetime between methanol and heptane is unusual, but not unprecedented; **16**, which is also very short-lived, shows similar lifetimes (i.e., ~30 ns) in both polar and nonpolar solvents.[14]

Enols **18E** and **18Z** absorb strongly at ~400 nm and have very similar spectra but show different kinetic behavior. **18Z** is very short-lived in hydrocarbon solvents, being only about 40 ns in heptane, but in the presence of hydrogen-bonding substrates the lifetime is much longer; e.g., in methanol τ ≈ 1.5 μs. Even in view of the known[14] effect of H-bond accepting solvents, which increase *Z* enol lifetimes, it is rather remarkable that even a small amount of methanol added to a hydrocarbon solvent can lead to a substantial enhancement of the lifetime; for example, at 210 K in hexane 0.0057 M methanol changes the lifetime of **18Z** from 354 to 2200 ns.

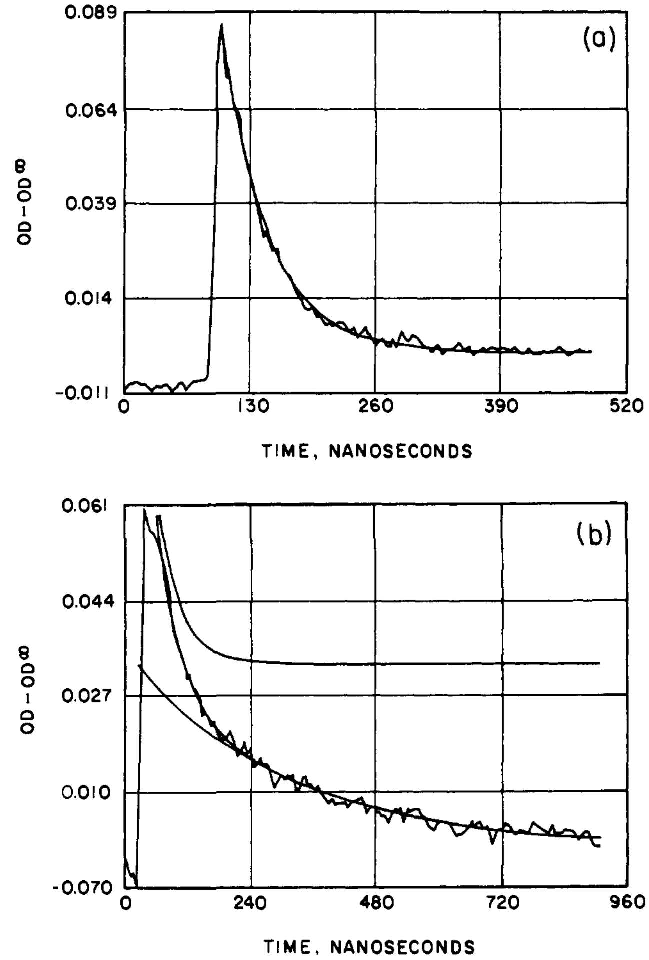

Figure 7. (a) Decay from unlabeled 7 at 330 nm in N_2-saturated heptane. The decay rate constant is (2.15 ± 0.1) × 10^7 s^{-1}. (b) Decay from **7D** at 330 nm in N_2-saturated heptane. Simultaneous fit to two first-order decays using the (known) base line due to **18E** gives (2.3 ± 0.2) × 10^7 s^{-1} and (2.3 ± 0.4) × 10^5 s^{-1} for the decays of **8D** and **18Z-D**, respectively.

Deuteriation of the three methyl groups in the mesityl moiety does not introduce any significant change in the biradical lifetime, but it changes by roughly 1 order of magnitude the rate of decay of **18Z**. All these results are consistent with the rate of back hydrogen transfer, **18Z** → **7**, being the rate-determining step for the disappearance of **18Z**. Thus, this rate can be decreased by deuteriation, lowering the temperature, or engaging the hydroxyl group in hydrogen bonding.

While deuteriation at the precursor level (i.e., 7) has a dramatic effect on the lifetime of **18Z**, addition of D_2O to the solvent (see Table II) has no effect on the lifetime. This clearly shows that triplet 7, biradical 8, and **18Z** do not undergo D/H exchange under these conditions. Similarly, while saturation of benzene with D_2O leads to significant deuterium incorporation in the products, incorporation in 7 is only very minor. This is rather surprising, since the return to starting material is clearly the main process in the photochemistry of 7.

The anti enol **18E** is usually very long-lived, e.g., in methanol its lifetime was ~60 μs, although lifetimes were much longer in hydrocarbon solvents. Quite clearly conformational effects are of importance in the decay of the isomeric enols since the suprafacially allowed 1,5-H shift is only possible intramolecularly with the *Z* isomer.

A prime reason for undertaking a thorough study of the transients was to obtain evidence for or against the unusual biradical-carbene rearrangement of eq 2. The failure to detect

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Table III. Quantum Yields of Formation of **10** and **11** in Hexane at Various Wavelengths

UV wavelength, nm (intensity)[a]	visible wavelength,[b] nm (intensity)[a]	ϕ_{10}[c]	ϕ_{11}[c]
313 (4.4)		0.007	0.045
313 (24.7)		0.009	0.037
366 (62.3)		0.012	0.046
313 (4.4)	405 (17.6)	0.009	0.066
313 (4.4)	436 (27)	0.008	0.047
366 (13.3)	436 (27)	0.009	0.040

[a] In einsteins/minute per sample × 10^7; 3-mm slits with Hg/Xe arc lamp, Bausch & Lomb SP-200 monochromator. [b] Samples irradiated with overlapped light from the two wavelengths. [c] Computed Solely on the basis of the UV intensity. Assumes response factors of **7**, **10**, and **11** are identical on FID detection. Precision ±5% estimated.

carbene **9** is in this sense disappointing, and alternative mechanisms involving the transients actually observed require serious consideration.

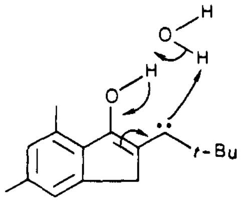
The effect of deuterium on the transient lifetimes and the deuterium incorporation studies of **7** and **11** clearly show that ^{3}**7**, **8**, and **18Z** cannot be immediate precursors of products **10** and **11**. The sequence ^{3}**7** → **8** → **18Z** (+ **18E**) seems incontrovertible, and that **18Z** retains the original isotope distribution expected from **7** without exchange during its lifetime is inconsistent with the extensive D incorporation into **10** and **11** in D_2O-saturated benzene in any direct process. The requirement for a revised mechanism to be consistent with all the data, in particular the deuterium incorporation results, is the presence, on the pathway to products, of an intermediate capable of efficient isotope exchange, but which undergoes no (or very inefficient) back reaction to regenerate **7**. For example, a modification that would allow for two kinetically distinct biradicals, **8Z** and **8E**, with the latter being responsible for product formation would be consistent with the data if isotope exchange occurs at the **8E** state or following its decay. Modifications of the sort **8** → **10** or **18Z** → **10** are permissible in view of the data if participation of a molecule of water via a 7-membered-ring transition state is preferred over the analogous 5-membered-ring transition state without the water molecule. However, **8** → **10** would require concerted formation of two bonds and spin inversion if it were a direct process, which is altogether unlikely. Were **18Z** involved, the order of magnitude increase in lifetime in methanol would have promoted the formation of **10** and **11** while the observation is that methanol retards their formation.

Enol **18E** is an attractive possible precursor to **10** and **11** since its very long lifetime in hydrocarbon solvent would be consistent with deuterium exchange and its much shorter lifetime in methanol consistent with a lowered steady-state concentration and thus the diminished rate of formation of **10** and **11**. A species with a 22-s lifetime could even build up to concentrations high enough to be sensitive to incident light, so the photochemical path **7** → **18E** $\xrightarrow{h\nu}$ **9** → products was considered.

The results of Table III, however, rule out either photochemical or thermal involvement of **18E**, assuming that the two processes would not yield the same products with the same yields (even if with different rates). The two photon nature of the photochemical path would predict: (a) increased quantum yield at higher light intensity and (b) enhancement of the reaction by light which **18E** absorbed but **7** did not. Neither a factor of 6 increase in light intensity at 313 nm nor the addition of 436-nm light in experiments in which the ketone was excited at 313 or 365 nm affected the quantum yield of appearance of **10** and **11** significantly. In the latter case the quantum yield was calculated on the basis of the 313- or 365-nm intensity only since 436 nm is not absorbed by **7**. Partial absorption of 405-nm light by **7** occurs at the concentration employed, and this is responsible for the slightly enhanced apparent quantum yield of **11** when 405-nm light is used.

There is thus no significant two-photon path to **10** and **11**. Further, we noted that the yellow color of **18E** was bleached almost instantly (within 1–2 s) if irradiated at 436 or 405 nm. If **18E** gave **10** and **11** thermally, the strong enhancement of its decay by visible light should have decreased their quantum yield of formation. That the quantum yield was unaffected also rules out thermal involvement of **18E**.

Mechanism of Formation of 10 and 11. Involvement of all observed transients as *direct* precursors of **10** and **11** is thus ruled out, and we are left with the originally proposed mechanism, with minor elaboration, as that which best satisfies the data. The modification is that the slow deuterium exchange in **8** and **18Z** seems likely to extend to carbene **9**, also an enol with expected pK_a around 10. The deuterium incorporation results then are best accommodated by the version of the original mechanism that uses a molecule of water and a 7-membered-ring transition state, when water is present, as a preferred alternative to the 5-ring transition state without water. The 7-ring case is analogous to hydrogen bonding in a 1,4-diol and the 5-ring case to that in a 1,2-diol; the 1,4-diols afford substantially stronger intramolecular hydrogen bonds as measured by O–H infrared frequency shifts.[29]



Experimental Section

Equipment and general procedures were described in ref 6 and references therein. Solvent for infrared (IR) spectra was CCl_4 and for nuclear magnetic resonance (NMR) spectra, $CDCl_3$. All compounds were colorless oils unless otherwise noted; melting points are corrected. All gas chromatography employed a 4 ft × 0.25 in. column of 25% QF-1 on 45/60 Chromosorb W unless otherwise stated. The spectrum of **18E** (Figure 3) was recorded on a HP 8450A UV-vis diode array spectrophotometer. Irradiation of samples at 313 nm and recording of absorption spectra were carried out in a dark room. Phosphorescence spectra were recorded on a Perkin-Elmer LS-5 instrument.

Laser Flash Photolysis. Experiments at NRC used either 337 (Molectron UV-24 nitrogen laser, ≤5 mJ/pulse) or 308 nm (Lumonics TE-860-2 excimer laser, XeHCl mixture, ≤40 mJ/pulse) for excitation. Samples were contained in 3 × 7 or 7 × 7 mm^2 quartz cells and were deaerated by purging with oxygen-free nitrogen. Further details have been described elsewhere.[30]

Experiments at CFKR used the third (355 nm) or fourth (266 nm) harmonic of either a Q-switched (fwhm 10 ns) or mode-locked (fwhm, including broadening by electronics, 1.75 ns) Nd-YAG laser. The system has been previously described.[31]

4,4-Dimethyl-1-(2,4,6-trimethylphenyl)-2-pentyn-1-one (7). A solution of *tert*-butylacetylene (2.5 g) in tetrahydrofuran (THF) (10 mL) was added with cooling to a 2.7 M solution of ethylmagnesium bromide in THF (15 mL). The mixture was stirred 10 min, heated at reflux 30 min, and then treated dropwise with mesitaldehyde (4.5 g) in THF (10 mL). The resulting mixture was heated at reflux 2 h, cooled, quenched with aqueous NH_4Cl, and worked up with ether. The crude alcohol product (6 g) was dissolved in acetone (30 mL) and the solution titrated with Jones's reagent[16] with cooling. Standard workup and distillation gave analytically pure **7** (5.4 g, 79%) that could be crystallized from methanol to give white crystals: mp 33–35 °C; IR 2980 (s), 2940 (m), 2215 (s), 1660 (s), 1615 (m), 1270 (s), 1255 (w), 1055 (w) cm^{-1}; NMR (300 MHz) δ 6.852 (s, 2 H, ArH), 2.345 (s, 6 H, 2 $ArCH_3$), 2.286 (s, 3 H, $ArCH_3$), 1.282 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.98; H, 8.90.

Preparation of Mesitaldehyde-*d*$_9$. An ethereal solution of mesitoic acid-d_9 (1.713 g, 9.9 mmol), prepared by the method of Atkinson et al.,[17] was treated with diazomethane to yield the ester (1.833 g, 99%) that was subsequently reduced with $LiAlH_4$ in Et_2O to give the alcohol (1.551 g, 99%). The crude alcohol was oxidized with pyridinium chlorochromate (4.31 g)[32] to afford the desired aldehyde (1.458 g, 95%).

Preparation of 7D. Following the same method employed for **7**, the labeled ketone was obtained in 75% overall yield from mesitaldehyde-d_9.

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Integration of NMR spectra (300 and 60 MHz) of VPC purified material (185 °C) using the *tert*-butyl group as an internal standard (9H) indicated that the methyl groups on the aromatic ring were 96.5% labeled.

4,4-Dimethyl-1-phenyl-2-pentyn-1-one (17). A solution of *tert*-butylacetylene (3.0 g) in 5 mL of THF was added dropwise to a solution of ethylmagnesium bromide (1.0 equiv) in 30 mL of THF. After being stirred for 30 min, the mixture was treated dropwise with benzaldehyde (3.2 g) in 5 mL of THF. The mixture was worked up as for **7** to give the crude alcohol (85%) that was oxidized with Jones's reagent.[16] The crude ketone was purified by flash chromatography on silica gel using 4% EtOAc/hexane to give **17** as a colorless oil: NMR (500 MHz) δ 8.10–8.15 (m, 2 H), 7.62–7.42 (m, 3 H), 1.38 (s, 9 H); MS, *m/e* (%) 186 (30.3), 171 (11.4), 143 (43.1), 128 (30.8), 105 (100.0). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.02; H, 7.73.

Irradiation of 7. A solution of **7** (228 mg) in benzene (50 mL) was degassed and irradiated with a 450-W Hanovia lamp for 6 h through a uranium glass filter. Removal of solvent and flash chromatography[18] (5% Et_2O in hexanes) gave **11** (28 mg, 13%), **10** (140 mg, 66%), and **7** (18 mg, 8%). Yields are based on unrecovered **7**; longer irradiation increased the ratio **11**:**10**. Analytical samples of **10** and **11** were prepared by preparative gas chromatography. For (*E*)-5,7-dimethyl-2-(2,2-dimethylpropylidene)-1-indanone (**10**): mp 88–90 °C; IR 2970 (s), 1700 (s), 1650 (s), 1615 (s), 1325 (s), 1250 (s), 1190 (m), 1150 (m), 1108 (w) cm^{-1}; NMR (300 MHz) δ 7.090 (s, 1 H, ArH), 6.936 (d, J = 0.46 Hz, 1 H, ArH), 6.774 (t, J = 2.1 Hz, 1 H, olefinic), 3.747 (s, 2 H, CH_2), 2.656 (s, 3 H, CH_3), 2.392 (s, 3 H, CH_3), 1.231 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.27; H, 8.99. For (*Z*)-5,7-dimethyl-2-(2,2-dimethylpropylidene)-1-indanone (**11**): mp 86–88 °C; IR 2950 (s), 2920 (m), 2860 (m), 1695 (s), 1628 (s), 1610 (s), 1370 (m), 1320 (m), 1250 (m), 1190 (m), 1150 (m), 1025 (w) cm^{-1}; NMR (300 MHz) δ 7.025 (s, 1 H, ArH), 6.909 (s, 1 H, ArH), 6.186 (t, J = 1.6 Hz, 1 H, olefinic), 3.578 (s, 2 H, CH_2), 2.646 (s, 3 H, CH_3), 2.376 (s, 3 H, CH_3), 1.336 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: 83.77; H, 8.72.

Stern–Volmer Quenching of Rearrangement of 7 to 10. Degassed solutions of **7** (9.08 mM) in cyclohexane containing tetradecane (0.97 mM) as internal standard and containing different concentrations of 2,3-dimethyl-1,3-butadiene (0, 0.20, 0.80, 1.60, 2.40, and 3.20 M) were irradiated in duplicate at 25 °C through a 1-cm path of a K_2CrO_4 (0.002 M in 1% aqueous K_2CO_3) filter (~313 nm).[21] Products **10** and **11** were analyzed by gas chromatography; results were plotted in the usual fashion[22] and yielded $k_q\tau \approx 0.29$ M^{-1}.

Quantum Yield Determination. (**a**) **313 nm.** Duplicate solutions (3.0 mL) of **7** (9.35 mM) in cyclohexane containing tetradecane (5 mM) as internal standard were placed in Pyrex test tubes, degassed with N_2, and sealed. These were irradiated on a merry-go-round apparatus simultaneously with duplicate tubes of valerophenone (10.3 mM) in ethanol containing tetradecane (5 mM), using the output of a 450-W Hanovia lamp filtered through the K_2CrO_4 filter described above. Conversion was $\leqslant$14%. Yields of **10** and **11** and acetophenone were determined by calibrated GC. From the known[21] quantum yield for formation of acetophenone from valerophenone, the quantum yield for products is ~ 0.097. (**b**) **Various Wavelengths.** Samples in hexane degassed by three or four freeze–pump–thaw cycles and sealed were irradiated with various combinations of UV and visible wavelengths isolated from Hg/Xe arc lamp sources by Bausch and Lomb SP-200 monochromators.

Irradiation of 7D. A solution of **7D** (117 mg) in anhydrous benzene (70 mL) was irradiated to 95% conversion in a toroidal vessel that was rinsed with D_2O before being dried in an oven for 1.25 h. The residue remaining after removal of solvent was purified by preparative GC (185 °C) to afford **11D** and **10D** in a ratio of 1:5. NMR spectra of these products indicated that in each case the olefinic hydrogen atom was 83% deuterium. Recovered starting acetylenic ketone was 95.5% labeled.

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Intramolecular Charge-Transfer Interactions in Triplet Keto Sulfides

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Abstract: The photochemistry of β-, γ- and δ-phenacyl sulfides, sulfoxides, and sulfones has been studied. The first group undergoes no irreversible reaction. The other two undergo type II photoelimination but in low quantum efficiency. Analysis of triplet lifetimes and product quantum yields indicates that all undergo rapid internal quenching, which is ascribed to a charge-transfer (CT) process. The positional dependence of rate constants for this CT reaction is $\beta > \gamma > \alpha \gg \delta > \epsilon$. Some rate constants (units of 10^8 s^{-1}) for $PhCO(CH_2)_nSBu$ are as follows: n = 1, 16; n = 2, 55; n = 3, 29; n = 4, 1.7; n = 5, $\leq$0.2. These values are interpreted as representing relative equilibrium constants for achieving cyclic orientations in which the sulfur lone pair and the half-empty oxygen n-orbital overlap substantially. The rate constants are very sensitive to the oxidation state of sulfur; for the n = 3 sulfoxide, $k = 35 \times 10^8$; for the n = 3 sulfone, $k = 0.35 \times 10^8$. The δ-substituted ketones undergo elimination to form 4-benzoyl-1-butene, by β-elimination of sulfur-centered radicals from the biradicals that intervene in the type II elimination. Actual radical cleavage rate constants lie in the order SNC > PhS ~ BuS(O) $\gg$ BuS, $BuSO_2$, CH_3CO–S and range from 10^9–3×10^5 s^{-1}. Rate constants for triplet state γ-hydrogen abstraction were found to correlate well with the σ_I values of the various sulfur groups, except for δ-sulfinyl, which apparently participates in the reaction.

As part of a systematic investigation of intramolecular charge-transfer (CT) quenching of triplet ketones, we have studied the photochemistry of ω-phenacyl sulfides of the structure $PhCO(CH_2)_nSR$, together with their corresponding sulfoxides and sulfones. Sulfides are known to quench triplet ketones bimolecularly.[1] The mechanism is thought to involve CT interactions, particularly since rate constants correlate with those of other electron donors.[1,2] Since the actual values of the bimolecular quenching rate constants are well below the diffusion limit,[1] rate constants for analogous intramolecular quenching processes should depend on the equilibrium constants for formation of the requisite cyclic orientations.[3,4] The donor orbital of sulfides is a lone pair

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