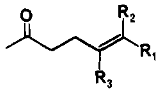
Organic Photochemistry with 6.7-eV Photons: γ,δ-Unsaturated Ketones

William J. Leigh and R. Srinivasan*

Contribution from the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598. *Received November 19, 1981*

Abstract: The photochemistry of a series of acyclic, aliphatic γ,δ-unsaturated ketones in pentane solution with 185-nm light has been investigated. The variety of products formed can be rationalized as arising from discrete reactions of the individually excited chromophores. Neither intramolecular energy transfer nor internal conversion leading to population of the lowest (n,π^*) singlet state are competitive with product formation at 185 nm. The mechanism of alkyne formation in the solution-phase photolysis of these and terminal alkenes at 185 nm is elucidated by using a deuterated derivative, and the reaction is postulated to proceed from the olefinic π,π^* singlet state.

The photochemistry of bichromophoric organic molecules in the far ultraviolet[1,2] displays distinctly different characteristics from what has generally been observed at longer wavelengths.[3] These characteristics result from (i) the reactive chromophore (at 185 nm) being transparent at longer wavelengths and reacting faster than internal energy transfer can take place[1], and (ii) photochemistry ensuing from upper excited states which are the result of through-bond and through-space mixing of the isolated chromophores.[2] A further result of ii is that the overall photochemistry cannot be accounted for in terms of the sum of the separate parts. Published work in this area encompasses olefin/olefin[1]- and olefin/cyclopropyl[2]-type systems. In this report we examine the far ultraviolet photochemistry of linear, nonconjugated ketone/olefin bichromophoric systems, **1a**–**d**.



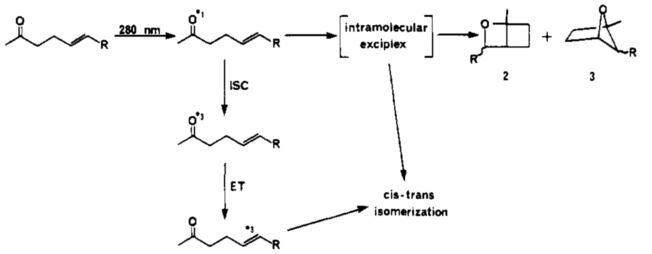
1

a, $R_1 = CH_3$, $R_2 = R_3 = H$; b, $R_1 = R_2 = R_3 = H$;
c, $R_1 = R_2 = D$, $R_3 = H$; d, $R_1 = R_2 = H$, $R_3 = CH_3$

The long wavelength photochemistry of γ,δ-unsaturated ketones has been extensively studied[4] and can be simply characterized as that of an n,π^* aliphatic ketone in the presence of an alkene (Scheme I). The (initially excited) n,π^* singlet state of the carbonyl moiety undergoes intramolecular oxetane formation, in competition with intersystem crossing to the n,π^* triplet state followed by intramolecular energy transfer to the olefinic end of the molecule and resultant cis–trans isomerization. The formation of **2** and **3** as well as ca. 67% of the total observed cis–trans isomerization is presumed to involve the intermediacy of an intramolecular exciplex.[3a,4e]

The excited-state manifold in this system, depicted in the energy level diagram in Figure 1, is expected to be complex in the 185-nm region. The ultraviolet absorption spectra of both aliphatic ketones and alkenes in hydrocarbon solution reveal absorption bands in this region.[5] In aliphatic ketones, this band corresponds to excitation to the second excited singlet state and has been identified as the n_0,3s(R) Rydberg or (more likely) n,σ^* valence shell transition.[6] The exact identity of this state is subject to controversy; at any rate, the solution-phase photochemistry of aliphatic ketones in the far-UV has not been investigated in detail. In mono- and disubstituted aliphatic olefins, the absorption in this region is composed of two bands, corresponding to excitation to the π,3s(R) Rydberg and π,π^* singlet states; the relaxed (orthogonal) π,π^* state is believed to be lowest in energy. Fluorescence emission studies suggest that internal conversion from the π,3s(R) state to the π,π^* singlet state is extremely rapid in mono- and disubstituted systems.[7] While the photochemistry of tri- and tetrasubstituted acyclic alkenes has been extensively investigated,[8] that of simple terminal alkenes has received limited attention.

Scheme I



Given the complexity of the excited state manifold in this system, there are several possibilities that may occur upon excitation of **1** with 185-nm light. Photobehavior may be dominated by carbonyl photochemistry, which may result in either unique reactivity or enhanced n,π^* reactivity depending on how fast internal conversion to the lowest (n,π^*) singlet state occurs. On the other hand, olefin photochemistry may dominate, providing that intramolecular energy transfer to the carbonyl group (leading again to enhanced n,π^* photoreactivity) is not competitive. Also, the possibility exists that this spectral region contains transition(s) to mixed states, in which case unique photochemistry may again be observed. Our results enable some distinction to be made between the various possibilities outlined above, as well as a definition of the photochemical behavior of this system and simple alkanes at 185 nm.

Results

The ultraviolet absorption spectra in the region below 220 nm of *trans*-**1a** and **1b** in pentane solution are shown in Figure 2.

The photochemistry of *trans*-5-hepten-2-one (**1a**) in pentane solution at 185 (+254) nm is summarized in eq 1. The oxetanes **2a** and **3a** which were also formed and a fraction of the *cis*-**1a** obtained were established to result from irradiation with the

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[1] Srinivasan, R.; Brown, K. H.; Ors, J. A.; White, L. S.; Adam, W. *J. Am. Chem. Soc.* **1979**, *101*, 7424.

[2] (a) Srinivasan, R.; Ors, J. A.; Brown, K. H.; Baum, T.; White, L. S.; Rossi, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 5297. (b) Srinivasan, R.; Baum, T.; Brown, K. H.; Ors, J. A.; White, L. S.; Rossi, A. R.; Epling, G. A.; *J. Chem. Soc. D* **1981**, 973.

[3] (a) Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383. (b) Morrison, H. *Org. Photochem.* **1979**, *4*, 143.

[4] (a) Srinivasan, R. *J. Am. Chem. Soc.* **1960**, *82*, 775. (b) Morrison, H. *Tetrahedron Lett.* **1964**, 3653. (c) Morrison, H. *J. Am. Chem. Soc.* **1965**, *87*, 932. (d) Yang, N. C.; Nussim, M.; Coulson, D. R. *Tetrahedron Lett.* **1965**, 1525. (e) Kurowsky, S. R.; Morrison, H. *J. Am. Chem. Soc.* **1972**, *94*, 507.

[5] "DMS UV Atlas of Organic Compounds"; Plenum Press: New York, **1968**; Vol. 4.

[6] Robin, M. B. "Higher Excited State of Polyatomic Molecules"; Academic Press: New York, **1975**; Vol. 2.

[7] Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1975**, *62*, 576.

[8] Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1.

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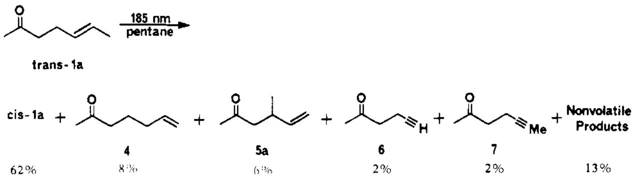
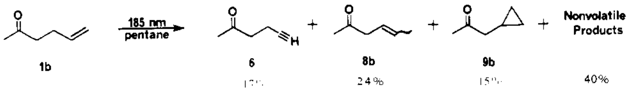


(1)

254-nm component of the lamp output. No other product besides **2a**, **3a**, and *cis*-**1a** was detectable in the 254-nm photolysate. *cis*-**1a** is apparently comparatively unreactive at 185 nm (as well as at 254 nm[4e]), since concentration vs. time plots for the formation of **2a** and **4**–**7** are noticeably curved. The yield of *cis*-**1a** was calculated (by GC) after 15-min photolysis, while those of **4**–**7** were calculated from the initial slopes of the concentration vs. time plots in Figure 3, relative to the slope of the [*trans*-**1a**] vs. time plot after correcting for the 254-nm component. The nonvolatile products were shown by GC to consist of at least 15 high-boiling materials, none in appreciable yield; the total yield was determined after 120-min photolysis.

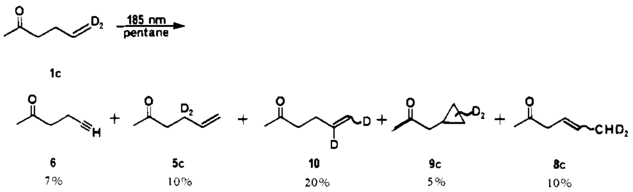
Photolysis of 5-hexen-2-one (**1b**) at 185 (+254) nm in pentane solution gave the product mixture summarized in eq 2. Nonvolatile products (40%), determined at 19% conversion, were not isolated but were shown (by GC) to consist of more than 15 products, none in greater than 2% yield. The oxetanes were shown to result entirely from irradiation with the 254-nm component of the lamp output. No other products besides **2b** and **3b** were detected in a 254-nm photolysis under identical conditions. Straight lines were obtained in all cases from concentration vs. time plots for the products and starting material, and yields were determined from the calculated slopes, after correcting for the 254-nm component. Other minor products included 1-butene (2%) and ketene (trapped with methanol, ca. 2%).



(2)

Photolysis of **1b** at 185 (+254) nm as a film at −70 °C under high vacuum was carried out to determine the formation of gaseous products. Fractional distillation of the trapped materials lead to the identification (by IR) of acetaldehyde, acetylene, ketene, 1,3-butadiene, and 1-butene as minor products. The bulk of the photolysate was similar in all respects to that obtained in the solution phase photolysis.

Photolysis of 5-hexen-2-one-*6,6-d*$_2$ (**1c**) at 185 (+254) nm in pentane solution gave a product mixture which was identical with that obtained from the photolysis of **1b** (see eq 3). Gas chromatographic isolation of **6**, followed by infrared and mass spectral analysis, showed it to be ca. 10% deuterated in the terminal position.[9,10] Recovered 5-hexen-2-one was examined by deuterium NMR spectroscopy. The proton-decoupled spectrum consisted of three singlets at δ 2.28, 4.99, and 5.85 in the ratio 1:8:1. These signals correspond presumably to deuterium in the 4-, 6-, and 5-positions, respectively, and thus indicate that the recovered starting material (after 40% apparent conversion) consisted of **1c** (70%), **5c** (10%), and **10** (20%). No detectable scrambling of deuterium was evident in **1c** recovered after a 254-nm photolysis run under comparable conditions. Product yields, not corrected for 254-nm products, were determined by GC at 40% conversion, taking deuterium scrambling (leading to **5c** and **10**) into account.



(3)

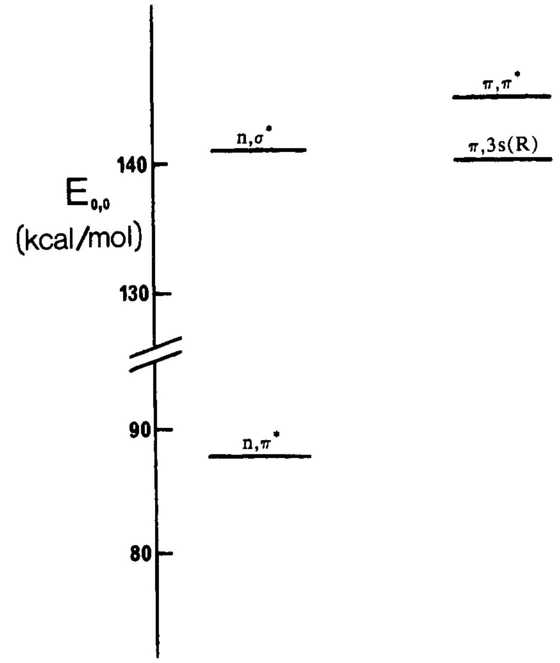


Figure 1. Excited-state energies for 5-hexen-2-one (**1b**).

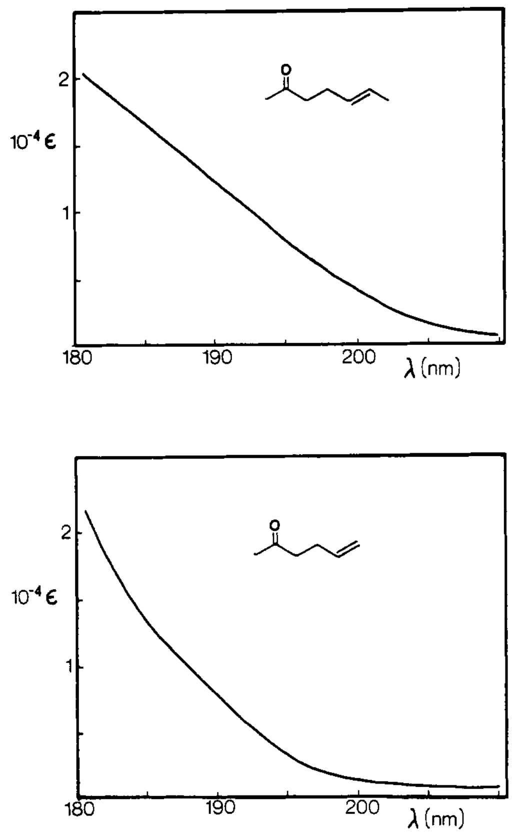


Figure 2. Ultraviolet absorption spectra (pentane solution) of *trans*-**1a** and **1b**.

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[9] Comparison of the mass spectra of **6** isolated from the photolyses of **1b** and **1c** indicates that the latter is less than about 10% deuterated. For a review of the mass spectra of alkynes, see: Dolejsek, Z.; Hanus, V.; Vokac, K. *Adv. Mass Spectrom.* **1966**, *3*, 503–514.

[10] The infrared spectrum clearly shows two bands attributable to alkyne C–H and C–D stretches at 3295 and 2600 cm^{-1}, respectively, with an intensity ratio of I_{3295}/I_{2600} = 12.0. It has been determined that the ratio of intensities of the C–H and C–D stretches in 3,3-dimethyl-1-propyne and 3,3-dimethyl-1-propyne-*1-d* is $I_{C-H}/I_{C-D} \simeq 0.9$;[11] this leads to an estimate of ca. 7% deuterium at the 6-position in **6**.

[11] (a) Hoffmann, V.; Stehlik, G.; Zeil, W. *Z. Naturforsch., A* **1970**, *25A*, 572. (b) Gastilovich; Shigorin; Komarov *Opt. Spektrosk.* **1965**, *19*, 354.

Table I. Rates of Alkenone Disappearance and Product Formation in the Photolyses of 1 and 1-Octene[a]

	k_{dis}[b]		k_2[b]							
	254[d]	185 (+254)[e]	254[d]	185 (+254)[e]	k_4[b,c]	k_5[b,c]	k_6[b,c]	k_7[b,c]	k_8[b,c]	k_9[b,c]
1a	4.83	26.7	1.17	2.18	1.63	1.10	0.32	0.32		
1b	3.00	8.50	0.72	1.05			0.72		1.05	0.62
1d	6.00	19.33	3.20	5.58				0.25	0.82	
1-octene[f]		7.20								

[a] 0.05 M, degassed pentane solution, 15 °C, 40-W lamp. Obtained from the slopes (or initial slopes for **1a**) of concentrations vs. time plots. [b] $\times 10^5$ s; error is ±5%. [c] These products are formed only at 185 nm. [d] In nm. Vycor filter, $\%T_{254} = 69$. [e] In nm. Unfiltered. [f] $k_{1\text{-octyne}} = 1.28$.

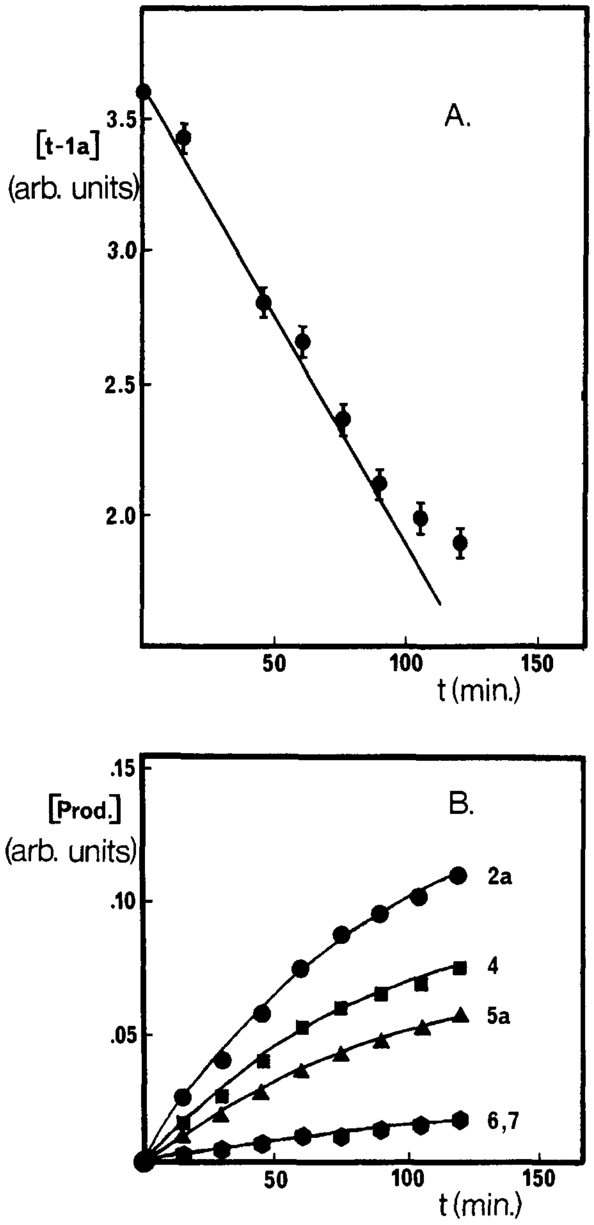
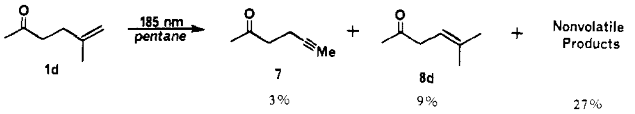


Figure 3. Concentration versus time plots for the photolysis (185 (+254) nm) of trans-**1a** (pentane solution, 0.05 M, 15 °C): A, disappearance of *trans*-**1a**; B, formation of **2a**, **4**, **5a**, and **6**.

8c and **9c** were not isolated in this case.

Photolysis of 5-methyl-5-hexen-2-one (**1d**) at 185 (+254) nm in pentane solution gave the product mixture shown in eq 4. The oxetanes were shown to result primarily from irradiation with the 254-nm component of the lamp output. No other products besides **2d** and **3d** were detected in a 254-nm photolysis under identical conditions. The yields of **7** and **8d** were determined by GC relative to reacted starting material at 12% conversion, while the yield of nonvolatile products (not isolated) was determined at 25% conversion (corrected for 254-nm component). Straight lines were obtained from concentration vs. time plots for all products and starting material up to 20% conversion.

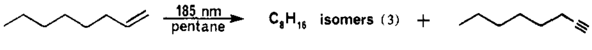


3%   9%   27%

(4)

Rate data for disappearance of the starting material and formation of the products are collected for **1a,b,d** in Table I for both 185 (+254)-nm and 254-nm photolyses. The solution concentrations (0.05 M) were such that all of the incident radiation at 185 nm was absorbed; the rates of formation of the products should therefore be proportional to their quantum yields. A quantum yield of 0.015 was determined for the formation of **2a** from *trans*-**1a**.[4c] The lamp output at 254 nm is estimated to be ca. 6 times greater than its output at 185 nm.

Photolysis of 1-octene at 185 nm in pentane solution lead to the formation of four products (eq 5). Three of these, formed in yields of 32%, 16%, and 6%, were determined by GC/MS to be isomeric with the starting material. The fourth product (18%) was identified as 1-octyne on the basis of a comparison of its IR and mass spectra and GC retention times with those of an authentic sample. Rate data for the photolysis of 1-octene are collected as well in Table I.



54%   18%

(5)

Discussion

As Figure 2 reveals, the ultraviolet absorption spectra of *trans*-5-hepten-2-one (**1a**) and 5-hexen-2-one (**1b**) in the region below 220 nm are featureless and offer no indication of the presence of mixed transitions; they are probably best viewed as the superposition of the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ absorption spectra of the isolated carbonyl and olefinic chromophores. Since absorption in this region is about a factor of 10 greater in olefins ($\epsilon_{185} \sim 10^4$) than in alkyl ketones ($\epsilon_{185} \sim 10^3$),[5] one can conclude that the bulk of the incident radiation at 185 nm is absorbed by the olefinic portion of the molecule. As expected, the spectrum of *trans*-**1a** extends to longer wavelengths than does that of **1b**, in accord with the known effect of increasing alkyl substitution on the absorption spectra of aliphatic olefins.[6]

The photochemistry of the four compounds (**1a–d**) investigated at 185 nm is generally analogous to that of acyclic 1,5-dienes[12] and can be rationalized as resulting primarily from excitation of the isolated carbon–carbon double bond. Thus, cis–trans isomerization (accounting for 62% of the isolable products in the case of *trans*-**1a**) provides the dominant mode of excited-state decay, while [1,3]-hydrogen migration (leading to **4** from **1a** and **8** from **1b–d**), [1,2]-hydrogen migration, and [1,3]-acylmethyl migration are of secondary importance. In contrast to our proposed [1,2]-H shift mechanism to account for the formation of **9** and **10** from **1a,c** via the carbene intermediate shown in eq 6, it is noteworthy

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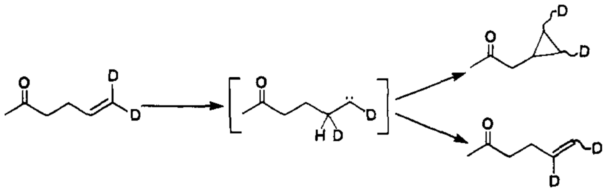
[12] Manning, T. D. R.; Kropp, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 889.


(6)

that analogous allylcyclopropane formation in the photolysis of 1,5-dienes has been shown to result from initial [1,2]-*allyl* migration followed by closure of the resulting 1,3 biradical.[12] However, [1,2]-H(D) migration is the only pathway which accounts for deuterium scrambling (into the 5-position) in the photolysis of **1c**. Although the corresponding methylcyclopropane was not detected in the photolysis of either **1a** or **1d**, one cannot rigorously exclude the possibility of its presence in minor amount. [1,3]-Acylmethyl migration (leading to **5** from **1a,c**) has been observed previously upon short wavelength irradiation of a cyclic γ,δ-unsaturated ketone[13] and the conclusion that this reaction proceeds from an upper excited state is substantiated by our results.

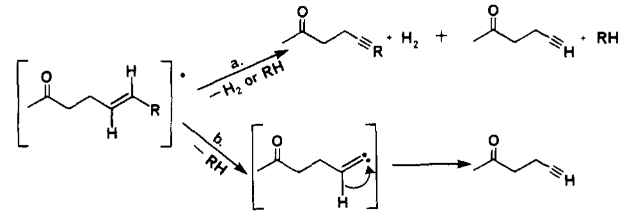
The photoelimination of RH (R = CH_3 or H), leading to alkynones **6** and **7**, is noteworthy in that it has not been previously recognized as a common photoreaction of alkenes *in solution*, though well-known in the gas phase.[14] The identification of 1-octyne as a major product (18%) in the 185-nm photolysis of 1-octene clearly indicates its generality, and the occurrence of this reaction in the photolyses of **1a–d** is thus not due to any special interaction between the olefinic and carbonyl groups.

There are at least two possible mechanisms for the formation of **6**, from 5-hexen-2-one (**1b**), and these are illustrated in Scheme II. Path "a" involves elimination of H_2 (or RH) across the double bond, leading to the alkynone directly. This is the only mechanism by which **7** can be formed in the photolysis of *trans*-**1a**. Path "b" involves loss of RH from the 6-position (shown formally as leading to a vinylidene intermediate[15]) followed by, or in concert with, [1,2]-hydrogen migration from the 5- to the 6-position. Both pathways are known to occur in the gas-phase photolyses of olefins,[14,16] although considerably higher energy excitation is usually necessary. The present study indicates that both occur as well in solution, though with varying importance depending upon the degree and pattern of substitution at the double bond. Mass[9] and infrared[10] spectral analysis of the 5-hexyn-2-one (**6**) isolated from the photolysis of 5-hexen-2-one-*6,6-d*$_2$ (**1c**) and the absence of **6** in detectable amount in the photolysis of 5-methyl-5-hexen-2-one (**1d**) indicates that elimination proceeds at least 90% via path "b" in terminal (mono- and 1,1-disubstituted) olefins, while the formation of both **6** and **7** in the photolysis of 5-hepten-2-one (**1a**) indicates that alkyne formation proceeds at least 50% via the alternate pathway ("a") in the case of 1,2-disubstituted olefins. It is important to recognize that the formation of **7** from **1d** requires [1,2] migration of a methyl group.[17]

Alternate scission of the C_4–C_5 bond, leading to acetylene and 2-butanone from **1b** presumably also occurs, although to a lesser extent. Acetylene was detected as a minor product in the photolysis of **1b** as a frozen film.

The nonvolatile material formed in significant yields in the photolyses of **1a–d** could have arisen from a number of sources, though no single compound was formed in sufficient yield to enable isolation. The formation of ketene/1-butene and acetaldehyde/1,3-butadiene as minor products in the photolysis of **1b** suggests that α cleavage is a minor reaction pathway, arising from population of the weakly absorbing carbonyl n,σ^* state, so it may be that the nonvolatile materials are formed as a result of the production of free radicals.

Scheme II



The differences in the rates of oxabicyclohexane (**2**) formation in the unfiltered and Vycor-filtered photolyses (Table I) can be accounted for by the reduction in intensity of the 254-nm light as a result of the transmittance characteristics of the Vycor filter. The implication that very little or none of these products (i.e., **2** and **3**) are formed at 185 nm[18] leads to the important conclusion that the lowest (n,π^*) state of **1** is not populated to any significant extent upon absorption of 185-nm light. This means, first, that intramolecular energy transfer from the olefinic S_1 state to the carbonyl n,π^* state must be slow relative to the rate of reaction of olefinic singlets, in spite of the facts that such a process would be exothermic by at least 30 kcal/mol and that a significant fraction of molecules must be in such an orientation when excited to enable energy transfer to occur at a rate considerably faster than the normal bimolecular diffusion-controlled rate (ca. 2×10^{10} M^{-1} s^{-1} in *n*-pentane[19]). However, while the lower limit for the rate constants[20] for formation of the olefin-derived products from **1** is only 10^{10} s^{-1}, the poor overlap between alkene emission[7] and ketone absorption spectra may slow the rate of intramolecular $\pi,\pi^* \rightarrow n,\pi^*$ singlet–singlet energy transfer considerably due to Franck–Condon factors.[19] Second, the apparent absence of n,π^* products upon 185-nm excitation may imply that carbonyl $S_2 \rightarrow S_1$ internal conversion is slow as well in these compounds, although caution should be exercised in this interpretation. Despite the fact that the large energy difference (30 kcal/mol) between the zero–zero bands of S_2 and S_1 may make rapid internal conversion unlikely,[19] only 10% of the light at 185 nm is absorbed by the carbonyl moiety, and the yield of n,π^* products formed as a result of $S_2 \rightarrow S_1$ internal conversion would be within our limits of error.[18] The observation of α-cleavage products (ca. 2%) in the 185-nm photolysis of **1b** does indicate, however, that $S_2 \rightarrow S_1$ internal conversion is, at most, competitive with reaction from the carbonyl n,σ^* state.

Finally, there remains the question as to which excited state(s) is involved in the olefin-derived photoreactions observed for **1a–d**. It has been suggested that [1,3]-hydrogen migration and [1,2] migrations leading to carbenes are derived from the Rydberg state.[8] If this is the case, then it may be that the alkynes are derived from the π,π^* state. This is consistent with the assigned ordering of the π,3s(R) and π,π^* states in alkyl olefins.[6] Heavily alkylated olefins, in which the lowest singlet state is π,3s(R), do not give alkynes upon photolysis but instead yield [1,3]-hydrogen migration and carbene-derived products and react with nucleophiles. Upon proceeding to tri-, di-, and monosubstituted olefins, the π,3s(R) state increases in energy relative to the π,π^* state, and these reactions decrease in importance (especally nucleophilic trapping) at the expense of alkyne formation.

Experimental Section

Infrared spectra were recorded in carbon tetrachloride solution on a Beckman Acculab 6 spectrometer and are reported in wavenumbers. ^1H NMR spectra were recorded on a Varian T60 spectrometer and are reported in parts per million downfield from Me_4Si. Inverse gate proton-decoupled ^2H NMR spectra were recorded on an IBM Instruments

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[13] (13) Crandall, J. K.; Mayer, C. F.; Arrington, J. P.; Watkins, R. J. *J. Org. Chem.* **1974**, *39*, 248.

[14] (14) McNesby, J. R.; Okabe, H. *Adv. Photochem.* **1964**, *3*, 157.

[15] (15) Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P. von R. *Chem. Phys. Lett.* **1981**, *79*, 408.

[16] (16) Okabe, H.; McNesby, J. R. *J. Chem. Phys.* **1962**, *36*, 601.

[17] (17) (a) Gilbert, J. C.; Luo, T. *J. Org. Chem.* **1981**, *46*, 5237. (b) Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *Ibid.* **1976**, *41*, 745.

[18] (18) **2b** and **3b** are formed in ca. 2% chemical yield upon photolysis of a degassed, 0.05 M pentane solution of 5-hexen-2-one (**1b**) with a defocused argon fluoride laser (λ = 193 nm; fluence = ca. 15 mJ/cm^2). The product distribution is otherwise identical with that obtained in the 185 (+254) nm irradiations: Leigh, W. J.; Srinivasan, R. unpublished results.

[19] (19) Turro, N. J. "Modern Molecular Photochemistry", Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978; Chapter 9.

[20] (20) Estimated from the absorption spectrum of 2-pentene.[5]

NR80 spectrometer, calibrated with a benzene-d_6 external reference, and are reported in parts per million downfield from Me_4Si. Ultraviolet absorption spectra of GC purified materials were recorded in pentane (Baker Photrex-grade) solution on a Cary 17D spectrometer and are reported in nanometers. Mass spectra were recorded on a Hewlett-Packard 5995A gas chromatography/mass spectrometer equipped with either 3% Carbowax 20M (12 ft × 0.25 in.) or 3% OV-101 (12 ft × 0.25 in.) glass columns.

Analytical and preparative gas chromatographic separations were carried out on a Hewlett-Packard 5750B gas chromatograph equipped with a thermal conductivity detector and the following columns: (a) 10% Carbowax 20M, 14 ft × 0.25 in.; (b) 10% OV-101, 14 ft × 0.25 in.; (c) 20% Apiezon L, 14 ft × 0.25 in.

***trans*-5-Hepten-2-one (1a)** was prepared by the method of Kimel and Cope.[21] The product was distilled through a 12-in. spinning band column, affording material (bp 142 °C) which was >99% pure by GC and contained less than 5% of the cis isomer.

5-Hexen-2-one (1b) was Eastman reagent grade and was purified by passage through an alumina column followed by two fractional distillations over anhydrous sodium sulfate through a 15-in. Vigreux column. The material (bp 121 °C) was >99% pure by GC.

5-Hexen-2-one-*6,6*-d_2 (1c) was prepared by the Wittig reaction of (3-(2-methyl-1,3-dioxan-2-yl)propyl)triphenylphosphonium bromide[22] and paraformaldehyde-d_2. The phosphonium salt (13.7 g, 0.03 mol) and anhydrous ether (125 mL) were placed in a 250-mL round-bottom flask fitted with condenser, magnetic stirrer, and nitrogen line. A 2.4 M solution of *n*-butyllithium (17 mL, 0.035 mol) was added, and the mixture was stirred for 2 h at room temperature. Paraformaldehyde-d_2 (CPL; 1.8 g, 0.056 mol) was added to the orange mixture, and stirring was continued for a further 24 h. The creamy, slightly yellow mixture was filtered through Celite, the filter cake was washed repetitively with ether, and the solvent was evaporated to yield a yellow oil (2.2 g).

The oil was redissolved in ether (10 mL), 2 N hydrochloric acid (10 mL) was added, and the mixture was stirred vigorously for 3 h at room temperature. The layers were separated, and the aqueous portion was washed with ether (5 × 8 mL). The ether extracts were combined with the mother liquors, washed with saturated bicarbonate (5 mL), water (5 mL), and saturated brine (5 mL), dried over anhydrous magnesium sulfate, and filtered. Evaporation of solvent yielded the ketone as a yellow oil (1.2 g, 0.012 mol, 40%), which was purified twice by GC using column a (110 °C) and finally column b (70 °C) to yield material which was >99% pure. The GC retention times on both columns matched those of **1b**: IR (CCl_4) 3000 (m), 2910 (m, br), 2310 (w), 2220 (w), 1715 (s), 1430 (m), 1360 (s), 1160 (s) cm^{-1}; ^{1}H NMR (CCl_4) δ 2.02 (3 H, s), 2.15–2.60 (4 H, m), 5.70 (1 H, br s); ^{2}H NMR (pentane) δ 5.0 (s); MS, *M/e* (relative intensity) 43 (100), 57 (10), 40 (7), 100 (7).

5-Methyl-5-hexen-2-one (1d) was prepared by condensation of ethyl acetoacetate with 3-chloro-2-methylpropene[23] followed by ester hydrolysis and decarboxylation with refluxing 5% sodium hydroxide. The product was purified by two distillations through a 15-in. Vigreux column (bp 142–145 °C) followed by one distillation through a 12-in. spinning band column. The fraction boiling at 142–143 °C was >99% pure by GC.

1-Octene (99.5%) was used as obtained from Albany Chemicals Co.

Apparatus. All photolyses were conducted on a preparative scale in pentane (Baker Photrex-grade) solution in a Type K reactor. It consists of a quartz immersion well (55 × 100 cm) fitted with a Suprasil (38 × 98 cm) inner sleeve. The light source was a 40-W American Ultraviolet Co. G3716VH low-pressure mercury resonance lamp, which was encased by a Vycor tube (T_{254} = 70%) for the 254-nm photolyses. The lamp was cooled with a stream of nitrogen, and the entire apparatus was immersed in a large Pyrex container through which cold water (ca. 15 °C) was flowed.

Procedure. A 0.05 M solution of the ketone in pentane was placed in the irradiation vessel and was flushed with dry nitrogen for 30–45 min. Methylcyclohexane or isooctane (Baker Photrex grade, 0.2 equiv) was included as internal standard in quantitative runs. Photolyses were generally carried to conversions of <20%, aliquots being withdrawn at various time intervals for GC analysis. Yields were determined relative to reacted starting material from concentration vs. time plots constructed for both starting material and products from the measured ($h \times w_{1/2}$) areas of the respective peaks in the GC trace, after we corrected for the loss of starting material due to irradiation with the 254-nm component of the light source. GC detector response was assumed to be the same for all starting materials and products. After photolysis, the pentane was removed by distillation and the residue was connected to a high vacuum (ca. 10^{-2} torr) via a liquid-nitrogen cold trap. Evacuation was maintained at room temperature for a period of 1.5 h in all cases. The remaining residue was weighed to give the yield of nonvolatile products. In all cases, the residue consisted of at least 15 high-boiling products (by GC, column b) and was devoid of starting material and all volatile products. Isolation of these products was not attempted since none were present in significant quantity. The contents of the cold trap consisted of unreacted starting material and volatile products (**2**–**9**), which were isolated by GC (columns a and b).

Photolysis of *trans*-1a. Irradiation was carried out as described above. Nonvolatile products amounted to 13% (0.072 g from 1.121 g of *trans*-**1a**; 47% conversion). Separation of volatile materials by GC (column a) gave *cis*-**1a** (62%), identified by comparison of its IR, ^{1}H NMR, and mass spectra with published ones,[4c] **4** (8%), **5a** (6%), **6** (2%), and **7** (2%). **4**, **5a**, and **7** were identified by comparison of their IR, ^{1}H NMR, and mass spectra and GC retention times with those of authentic samples (prepared from ethyl acetoacetate and 4-chloro-1-butene,[23] diketene, and crotyl alcohol,[21] and ethyl acetoacetate and 1-chloro-2-butyne,[24] respectively). Alkynone **6** was identified on the basis of the following: IR (CCl_4) 3295 (s), 2130 (2), 1721 (2), 1364 (m), 1162 (m), 637 (s) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.75 (t, 1 H), 2.10 (s, 3 H), 2.24–2.70 (m, 4 H); mass spectra *M/e* 96, base peak *M/e* 43; its 2,4-dinitrophenylhydrazone, mp 133–134 °C (lit.[25] 136 °C). Also present were the oxetane **2a**, identified by comparison of its spectra data with those published,[4d] and cyclopentenols arising from GC decomposition of oxetane **3a**.[4d] These products were also present along with *cis*-**1a** in a 254-nm photolysate, run under the same conditions as above. The rate of formation of **2a** in the 254-nm run was 57% as great as that obtained with the unfiltered lamp. The yield of nonvolatile products was <2%.

Photolysis of 1b. Irradiation and photolysate distillation, carried out as described above, gave nonvolatile products in a yield of 40% (0.064 g from 1.007 g of **1b**, 19% conversion). Separation of volatile materials by GC (column a) gave **6** (17%), *cis*-**8b** (12%), *trans*-**8b** (12%), and **9b** (15%). The structures of *cis*- and *trans*-**8b** were assigned on the basis of their IR, ^{1}H NMR, and mass spectra,[4b] after final GC purification using column b. *cis*-**8b**: IR (CCl_4) 1715 (s), 1351 (m), 1158 (m), 680 (w) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.66 (d, 3 H), 2.10 (s, 3 H), 3.09 (m, 2 H), 5.57 (m, 2 H); MS, *M/e* (relative intensity) 29 (100), 27 (71), 55 (70), 39 (29), 54 (27). *trans*-**8b**: IR (CCl_4) 1716 (s), 1355 (m), 1155 (m), 962 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.76 (m, 3 H), 2.10 (s, 3 H), 3.05 (m, 2 H), 5.52 (m, 2 H); MS, *M/e* (relative intensity) 43 (100), 27 (25), 29 (16), 39 (12), 55 (10), 98 (3). Cyclopropane **9b** was identified by comparison of its GC retention time, IR, ^{1}H NMR, and mass spectra with those of an authentic sample.[26] Also present were the oxetane **2b**, identified by comparison of its spectral data with those published,[4a] and cyclopentenols arising from GC decomposition of oxetane **3b**.[4d] These products were also present in the 254-nm photolysate run under the same conditions as above. The rate of formation of **2b** in the 254-nm run was 69% as great as that obtained with the unfiltered lamp. The yield of nonvolatile products was <2%.

The 185 (+254)-nm run described above was also monitored by GC (column b) for low-boiling hydrocarbon products. The major low-boiling product was 1-butene (2%), identified by comparison of its GC retention times on two columns (b and 3% DOPN, 24 ft × 0.25 in.) with those of an authentic sample. The yield was determined by GC (calibrated).

Photolysis of 1b as a Film. A sample of **1b** was placed in an evacuable Pyrex irradiation vessel with a Suprasil inner sleeve. The vessel was evacuated, warmed slightly, and then plunged into a dry ice/acetone bath. The material was visibly condensed on the walls of the vessel as a thin film. The sample was irradiated at −70 °C with the unfiltered output from a 10-W Osram low-pressure mercury resonance lamp while connected to a high vacuum (ca. 10^{-4} torr) via a liquid-nitrogen cold trap. Irradiation was continued for 4 h. The contents of the cold trap were warmed to −70 °C while volatile materials were condensed in a gas infrared cell. The infrared spectrum of this fraction showed clearly the presence of ketene and acetylene. The cold trap was then warmed to room temperature, and the second volatile fraction was condensed in the gas infrared cell. The infrared spectrum of this fraction showed the presence of acetaldehyde, 1,3-butadiene, and 1-butene by comparison with published spectra.[27] The residue in the irradiation vessel, analyzed

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by GC (column a) consisted of unreacted **1b**, **6**, **8b**, **9b**, **2b**, and the cyclopentenols derived from **3b** in comparable yields to the pentane photolysis described above.

Photolysis of 1b in Pentane/Methanol. A 0.05 M solution of **1b** in pentane/methanol (100:1) was irradiated with the 10-W Osram lamp for 5 h. GC analysis (column a) of the yellow photolysate indicated the presence of methyl acetate in 1–2% yield.

Photolysis of 1c. A 0.02 M solution of **1c** was irradiated as described above. GC analysis indicated the formation of **6** (7%), *cis*- and *trans*-**8c** (10%), and **9c** (5%). The yields were calculated by taking deuterium scrambling of the starting material (see below) into account but are not corrected for 254-nm products. Alkynone **6** was isolated and analyzed by infrared and mass (10-eV) spectroscopy. The ratio of intensities of the $\nu(C{\equiv}C{-}H) = 3295\ cm^{-1}$ and $\nu(C{\equiv}C{-}D) = 2600\ cm^{-1}$ peaks in the IR spectrum was $\equiv C{-}H/{\equiv}C{-}D = 12.0$. The soft-ion mass spectrum contained four peaks in the molecular ion region: 95:96:97:98 = 100:17.7:4.9:1.4, as compared to the same region in the corresponding spectrum of undeuterated **6** (95:96:97 = 100:10.4:1.4). Starting material was isolated after photolysis and its ^2H NMR spectrum examined. The inverse gate decoupled spectrum showed three singlets at δ 2.28, 4.99, and 5.85 in the ratio 1:8:1. Photolysis of a 0.02 M solution of **1c** at 254 nm leads only to the formation of oxetanes. Examination of reisolated starting material by deuterium NMR showed that no detectable scrambling of deuterium had occurred.

Photolysis of 1d. Irradiation of a 0.05 M solution was carried out as described above. Non-volatile products amounted to 27% (0.056 g from 1.117 g of **1d**; 31% conversion). Separation of volatile materials by GC (column a) gave **7** (3%) and **8d** (9%), identified on the basis of its spectral properties:[29] IR (CCl_4) 1715 (s), 1380 (m), 1358 (m), 1157 (m); ^1H NMR (CCl_4) δ 1.58 (br s, 3 H), 1.80 (br s, 3 H), 2.10 (s, 3 H), 3.04 (d, 2 H), 5.12–5.53 (m, 1 H); MS, M/e 43 (100), 41 (73), 27 (29), 39 (29), 69 (18), 112 (5). Alkynone **6** could not be detected in the photolysis mixture. Also present were the oxetane **2d**, identified by comparison of its spectral data with those published,[4d] and cyclopentenols arising from GC decomposition of oxetane **3d**.[4d] These products were also present in a 254-nm photolysate, run under the same conditions as above. The rate of formation of **2d** in the 254 nm was 58% as great as that obtained with the unfiltered lamp. The yield of nonvolatile products was <2%.

Photolysis of 1-Octene. A 0.05 M solution of 1-octene was irradiated as described above. Analysis by gas chromatography (column c) showed three products (not isolated) in yields of 32%, 16%, and 6%. The mass spectra of these products showed them to be isomers of the starting material. GC analysis using column a demonstrated the production of 1-octyne in 18% yield, the identity of which was established by comparison of its GC retention times (columns a and c), infrared, and mass spectra with those of an authentic sample.

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Registry No. *cis*-**1a**, 4535-61-9; *trans*-**1a**, 1071-94-9; **1b**, 109-49-9; **1c**, 82065-02-9; **1d**, 3240-09-3; **4**, 21889-88-3; **5a**, 61675-14-7; **5c**, 82065-03-0; **6**, 2550-28-9; **6** 2,4-DNP, 82065-04-1; **7**, 22592-18-3; *cis*-**8b**, 51024-76-1; *trans*-**8b**, 763-92-8; *cis*-**8c**, 82065-05-2; *trans*-**8c**, 82065-06-3; **8d**, 28332-44-7; **9b**, 4160-75-2; **9c**, 82080-59-9; **10**, 82065-07-4; (3-(2-methyl-1,3-dioxan-2-yl)propyl)triphenylphosphonium bromide, 82065-08-5; 1,1-dideuterio-4-(2-methyl-1,3-dioxan-2-yl)but-1-ene, 82065-09-6; ethyl acetoacetate, 141-97-9; 3-chloro-2-methylpropene, 563-47-3; 1-octene, 111-66-0; 1-octyne, 629-05-0.

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Laser Photochemistry: Trapping of Quinone–Olefin Preoxetane Intermediates with Molecular Oxygen and Chemistry of the Resulting 1,2,4-Trioxanes[1]

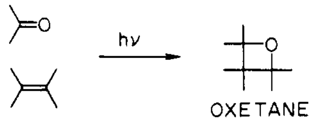
R. Marshall Wilson,* Stephen W. Wunderly, Thomas F. Walsh, Arlene K. Musser, Russell Outcalt, Fiona Geiser, Stephen K. Gee, Wayne Brabender, Lario Yerino, Jr., Tod T. Conrad, and Gregg A. Tharp

Contribution from the Department of Chemistry, University of Cincinnati,
Cincinnati, Ohio 45221. *Received March 16, 1981*

Abstract: The output of an argon ion laser has been used to generate reactive intermediates through the excitation of a carbonyl compound (*p*-benzoquinone or benzophenone) in the presence of an olefin. These reactive intermediates can be trapped either with oxygen to form 1,2,4-trioxanes or with sulfur dioxide to form cyclic sulfones. Several lines of evidence are presented that indicate that these reactive intermediates frequently are not the preoxetane biradicals but instead are charge-transfer exciplex species. Trioxane chemistry has been studied under a variety of conditions and found to be characterized by a fragmentation of the trioxane ring into three carbonyl compounds: the carbonyl compound involved in the formation of the trioxane ring and the two carbonyl compounds formally derived from the oxidative cleavage of the original olefin. The photolability of vitamin K analogues has been established to arise from the initial formation of an intramolecular trioxane with visible light and the fragmentation of this trioxane into the three carbonyl constituents with ultraviolet light.

During the past few years, photochemists have become increasingly aware of the influence of various chemical agents upon the fate of biradical or biradicaloid species. Biradical trapping agents that have been studied in detail to date include molecular oxygen[2] and other paramagnetic species including nitroxyl radicals[3] and nitric oxide,[4] radical scavengers such as di-*tert*-butyl selenoketone[5] and sulfur dioxide,[6] electron acceptors such as paraquat

Scheme I



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(1) This paper is dedicated to the memory of Robert Burns Woodward, deceased July 8, 1979.

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