

Characterization of Transient Intermediates in the Photochemistry of Cyclohexenones¹

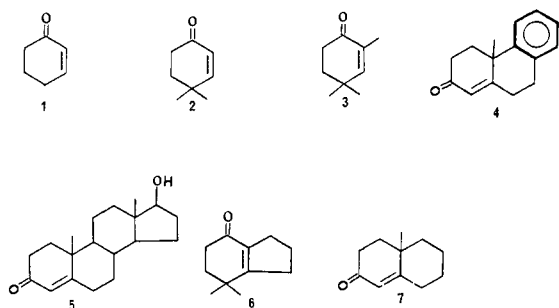
D. I. Schuster,*² R. Bonneau,³ D. A. Dunn,² J. M. Rao,² and J. Jousot-Dubien³

Department of Chemistry, New York University
New York, New York 10003
Laboratoire de Chimie Physique
Universite de Bordeaux 1
33405 Talence, France

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Laser flash photolysis has developed into a powerful technique for the direct observation and characterization of transient intermediates generated upon irradiation. However, without correlation of such data with steady-state photochemical behavior, including product identification, the mechanistic significance of such transients remains uncertain. Bonneau has observed transient absorption at 280 nm on laser flash excitation at 265 and 353 nm of a number of conjugated enones, which was ascribed to twisted triplet π, π^* excited states, whose angle of torsion around the C=C bond and consequent triplet excitation energy (estimated by triplet quenching) varied as a function of the structural constraints of the system.⁴ It has been proposed that such twisted triplet π, π^* states are obligatory reaction intermediates in the photorearrangements of 4,4-disubstituted cyclohexenones.⁵ Consequently, an attempt to integrate the flash and steady-state photochemical behavior of a series of such enones was initiated.⁶

When enones 1-6 were excited at 355 nm by using a frequency-doubled Nd-YAG laser as described previously,⁴ transient



absorption was detected at ~ 280 nm where there is a window in the enones' absorption spectra.⁷ Transient lifetimes in degassed solutions are given in Table I. Quenching of these transients by naphthalene (NA) could not be studied directly since NA absorption obscures the transients, but the rise time of NA triplet absorption at 413 nm could be easily measured as a function of NA concentration,⁸ providing quenching rate constants k_q and extrapolated enone triplet lifetimes (Table I)⁹ in good agreement with those directly measured at 280 nm. Quenching by NA of steady-state photorearrangement of enones 2, 3, and 5¹⁰ gives

Table I. Kinetic Properties of Transient Enone Species

enone	solvent	τ_{dir}^a , ns	k_q^b , $M^{-1} s^{-1}$	τ_{ext}^c , ns	flash $k_q \tau$, M^{-1}	steady-state ^d $k_q \tau$, M^{-1}
1	C_6H_{12}	25	7.5×10^8	29		
	CH_3CN	24	1.0×10^9	24		
2	<i>t</i> -BuOH	32	4.5×10^8	29		
	<i>i</i> -PrOH	21	5.5×10^8	28	15.4	15.4
	C_6H_{12}	24	3.0×10^8	25		
	CH_3CN	21				
3	C_6H_{12}	37	1.1×10^8	39	4.3	6.5^e
	<i>i</i> -PrOH	150	4.0×10^8	145	60	56
4	CH_3CN	130				
	C_6H_{12}	440				
5	CH_3CN	330				
	<i>i</i> -PrOH	1400	4.5×10^9	~ 1500		

^a Measured at 280 nm. ^b Slope of $1/\tau$ vs. [NA], 413 nm. ^c Reciprocal of intercept of $1/\tau$ vs. [NA], 413 nm. ^d Reference 10; quenching of photorearrangements by NA. ^e Value in *i*-PrOH.

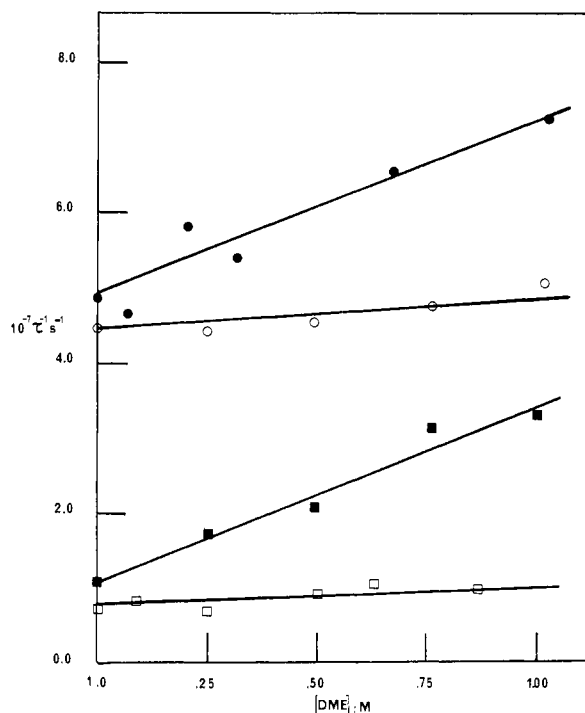


Figure 1. Plots of the reciprocal of the rise time for naphthalene triplet absorption at 413 nm vs. concentration of 1,1-dimethoxyethylene (DME) (closed symbols) and reciprocal lifetimes for enone triplet absorption at 280 nm vs. [DME] (open symbols); excitation at 355 nm. Data are for enone 2 at 0.06 M in CH_3CN (top, circles) and for enone 4 at 0.02 M in CH_3CN (bottom, squares). Concentration of naphthalene: 0.01 M (top) and 0.008 M (bottom). Values of the slopes (see ref 1 for comparison) are $2.7 \times 10^7 M^{-1} s^{-1}$ and $2.1 \times 10^7 M^{-1} s^{-1}$, respectively.

values of $k_q \tau_T$ that also are in excellent agreement with k_q and τ_T from flash data.

It therefore appeared that the 280-nm transient is the same species that is quenched by NA and is the intermediate responsible for the photorearrangement. The fact that the measured k_q values for NA quenching of 1-4 are an order of magnitude less than diffusion controlled is consistent with the proposal⁵ that these transients are relaxed enone triplet states with excitation energies approximately 61-63 kcal/mol, rather than planar spectroscopic triplets whose energies should be close to 70 kcal/mol.⁵ The data also support Bonneau's proposal⁴ that constraints to twisting around the C=C bond in enones result in higher triplet energies

(1) Part 72 of the NYU series on the photochemistry of ketones in solution. Part 71: Schuster, D. I.; Greenberg, M. M.; Nuñez, I. M.; Tucker, P. C. *J. Org. Chem.* **1983**, *48*, 2615. Part 70: Schuster, D. I.; Wang, L. *J. Am. Chem. Soc.* **1983**, *105*, 2900.

(2) New York University.

(3) University of Bordeaux.

(4) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816.

(5) For a review and background references, see: Schuster, D. I. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 167.

(6) A preliminary report of the first phase of this study was presented at the IXth IUPAC Photochemistry Symposium, Pau, France, July 1982, Abstracts p 314-315.

(7) Enone concentrations were chosen to give an OD of 0.4-1.5 at the exciting wavelength. This corresponds to concentrations of 10^{-1} - 10^{-2} M.

(8) A minimum of four different naphthalene concentrations was used in these studies.

(9) Lifetimes determined from reciprocals of the intercepts of plots of rates of growth of NA triplet absorption vs. [NA].

(10) I. M. Nuñez, Ph.D. Dissertation, New York University, 1982. Chan, C. B., Ph.D. Dissertation, New York University, 1983. Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928.

and consequently longer triplet lifetimes (greater energy gap between the triplet- and ground-state surfaces) and larger values of k_q . The observed correlation between the flash and steady-state data is indeed gratifying.

However, it is now clear that the situation is much more complicated. From steady-state experiments, we know that alkenes quench the photorearrangement of **2** through formation of [2 + 2] cycloadducts, suggesting a common precursor to these two reactions.¹¹ Amines such as triethylamine and 1,4-diazabicyclo[2.2.2]octane (Dabco) also efficiently quench the photorearrangement, with $k_q\tau_T$ values of 6.7 and 25.7 in isopropyl alcohol (IPA), respectively; presumably this occurs by photoinduced electron transfer leading in part to enone-amine adducts.¹² However, the 280-nm absorptions of **2** and **4** were not affected by up to 1.6 M cyclohexene and 1.0 M 1,1-dimethoxyethylene (DME) while DME reduces the rise time of the NA triplet absorption on excitation of **2** and **4**, as shown in Figure 1. Studies of quenching of these 280-nm transients by amines are problematic, because of the appearance of a long-lived (microsecond lifetime) amine-dependent transient absorption at 280 nm that rapidly obscures the decay of the fast transient. Using Dabco at concentrations up to 0.06 M in IPA and 0.02 M in CH₃CN, where the fast transient decay of **1**, **2**, and **4** is still measurable, we observed no effect on the enone transient lifetimes, within the precision of our measurements, which is estimated at $\pm 10\%$ from repeated flashes and alternative methods of analysis of the decay kinetics.¹³ Finally, 1,3-cyclohexadiene (CHD) up to 0.012 M did not quench the 280-nm transient decay of **2** in cyclohexane, although a long-lived transient absorption ascribed to CHD triplets was observed at 295 nm.¹⁴

Despite the agreement between the directly measured lifetimes of the 280-nm enone transients and the extrapolated lifetimes from NA quenching studies, we are forced to conclude that at least in the cases of **2** and **4** the 280-nm transient is not the species that (a) is quenched by NA and CHD, (b) reacts with alkenes and Dabco, and (c) leads to photorearrangement products. These latter processes appear to proceed via a phantom triplet species that has yet to be detected directly in flash studies but whose properties are consistent with that of a relaxed twisted triplet state. The identity of the 280-nm enone transient in these cases is unclear,¹⁵ but it is apparently not directly involved in the formation of any observed photochemical reaction product.¹⁶ In the cases of testosterone (**5**) and enone **6** (which is constrained from rearrangement),¹⁷ it is likely that these two species merge, since the 280-nm transient can be directly quenched in a linear fashion by dienes. Furthermore, other steady-state and flash data suggest that photodimerization of enones **1** and **2** as well as photoreduction

in IPA entirely bypass these transients and occur via yet another much shorter-lived triplet excited state.^{4,10,12}

Experiments in progress will hopefully clarify this unexpectedly complex situation.

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Registry No. 1, 930-68-7; 2, 1073-13-8; 3, 13395-71-6; 4, 6606-34-4; 5, 58-22-0; 6, 73013-93-1; 7, 826-56-2.

18-Electron Complexes as Ligands. Synthesis, Structure, and Stereochemical Nonrigidity of (Me₃P)(OC)₄OsW(CO)₅

F. W. B. Einstein, T. Jones, R. K. Pomeroy,* and P. Rushman

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

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We have recently described the synthesis and crystal structure of (OC)₅OsOs(CO)₃(GeCl₃)(Cl), a compound in which the 18-electron complex, Os(CO)₅, acts as a donor ligand to the second osmium atom.¹ We now report the preparation of (Me₃P)(OC)₄OsW(CO)₅, the structure of which reveals it to contain an unbridged donor-acceptor bond between different transition-metal atoms. The compound also exhibits stereochemical nonrigidity in solution, which is unusual for binuclear complexes in which the metal atoms are six-coordinate with monodentate ligands.

The reaction of W(CO)₅(THF) with Os(CO)₄(PMe₃)² in hexane affords (Me₃P)(OC)₄OsW(CO)₅ (**1**) within a few minutes; the compound was isolated by chromatography (Florisil, hexane-CH₂Cl₂ eluant) in 55% yield as air-stable, pale-yellow crystals.³ A single-crystal X-ray diffraction study⁴ shows that the 18-electron compound, Os(CO)₄(PMe₃), acts as a donor ligand to the W(CO)₅ unit via an unbridged osmium-tungsten donor-acceptor bond (Figure 1). The strong donor ligand trimethylphosphine is trans to this bond. The Os-W bond length found for **1** (3.0756 (5) Å) is somewhat longer than unbridged Os-W bonds observed in metal clusters (range 2.663 (3)-3.066 (3) Å);⁵ the bond is also longer than that determined in Re₂(CO)₁₀ (3.041 (1) Å).⁶ The inward leaning of the radial carbonyls on osmium

(11) Schuster, D. I.; Greenberg, M. M.; Nuñez, I. M.; Tucker, P. C. *J. Org. Chem.* **1983**, *48*, 2615.

(12) For kinetic studies of the effects of triethylamine on the photochemistry of **1**, see: Pienta, N. J.; McKimney, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 5501.

(13) Preliminary data using octalone **7** suggests that Dabco quenches growth of NA triplet absorption.

(14) Similar absorption was seen on sensitization of CHD by thioxanthone.

(15) As noted by one of the referees, the agreement between the measured lifetime of the 280-nm transient and the "phantom triplet" discussed in the text for so many cases (see Table I) cannot be coincidental. This suggests that there must be a kinetic relationship between the two species. One plausible suggestion is that the 280-nm species is the precursor of the quenchable triplet, forming it irreversibly, with subsequent steps being fast on this time scale. However, the fact that the 280-nm transient of **2** is not quenchable by 1,3-cyclohexadiene ($E_T = 52$ kcal/mol) would appear to be inconsistent with such a scheme. Another suggestion is that the 280-nm species is a monomeric triplet, while the quenchable "phantom" triplet is an excimeric species.¹² The following results make this proposal unlikely. First, the rate of decay and optical density of the 280-nm species of **1** and **2** are not affected by either enone concentration or solvent viscosity. Second, our results suggest that NA and DME are reacting with the same species. If this is indeed a triplet excimer in equilibrium with the monomer, as proposed by Pienta and McKimney,¹² then the lifetime of the 280-nm species should decrease with increasing concentrations of DME, which was not observed (see Figure 1). The dependence of the lifetime of both intermediates on molecular structure suggests that both species have similar (twisted) geometries.

(16) Pienta has come to a similar conclusion based on his studies of enones with amines reported in the preceding communication.

(17) Schuster, D. I.; Hussain, S. *J. Am. Chem. Soc.* **1980**, *102*, 409.

(1) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.

(2) Details of the preparation of Os(CO)₄(PMe₃) will be submitted shortly. See, however: Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1983**, *22*, 51.

(3) Compound **1**: IR (CH₂Cl₂) ν (CO) 2093 (w), 2040 (m), 2008.5 (s), 1911.5 (s), 1877.5 (m) cm⁻¹. MS, m/e 703 (w) (M⁺). Anal. Calcd for C₁₂H₉O₉PO₅W: C, 20.53; H, 1.29. Found: C, 20.50; H, 1.21.

(4) Crystal data for **1**, C₁₂H₉O₉PO₅W: $M = 702.2$; monoclinic; space group $P2_1/n$; $a = 8.832$ (1) Å, $b = 16.241$ (2) Å, $c = 12.988$ (2) Å; $\beta = 101.99$ (1)°; $V = 1822.35$ Å³, $D_c = 2.560$ g cm⁻³; $Z = 4$; μ (Mo K α) = 135.42 cm⁻¹. Structure solved by conventional methods; final agreement factors (2189 observed reflections) were $R_f = 0.019$ and $R_w = 0.023$.

(5) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161; 843. Churchill, M. R.; Bueno, C.; Wasserman, H. J. *Ibid.* **1982**, *21*, 640. Busetto, L.; Green, M.; Hessner, B.; Howard, J. A. K.; Jeffrey, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519. Park, T. J.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

(6) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.