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Mechanistic Alternatives in Photocycloaddition of Cyclohexenones to Alkenes[1-3]

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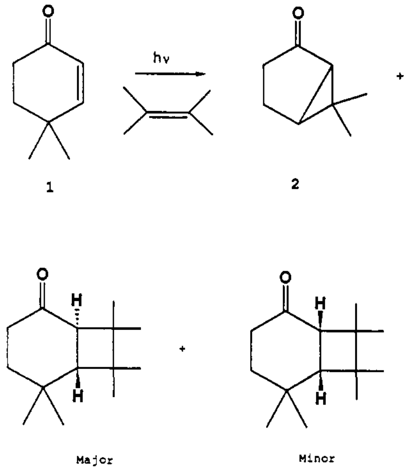
We have previously reported[5] that alkenes linearly quench the photorearrangment of enone **1** to the bicyclic ketone **2** (lumiketone) concomitant with formation of [2 + 2] cycloadducts, implicating a common intermediate on the two reaction pathways.

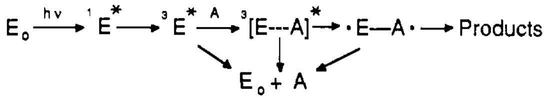


1 2

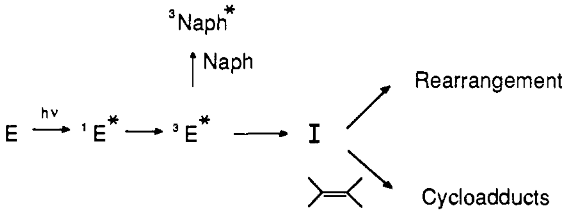
Major Minor

For 2,3-dimethyl-2-butene (TME) in acetonitrile (AN), the quenching slope $k_a\tau$ is 0.48 M^{-1}, where k_a is the rate constant for interaction of TME with an intermediate of lifetime τ derived from enone **1**.[6] Data for several other alkenes is given in Table I. The generally accepted mechanism of enone photoannelation shown in Scheme I, based on the original postulates of Corey[7] as elaborated by de Mayo,[8] involves interaction of an enone (E) triplet excited state with the alkene (A) to give an exciplex, which then proceeds to one or more 1,4-diradicals and thence to products; each of these intermediates could revert back to starting materials. The formation of trans- as well as cis-fused adducts to cyclohexenones[7,9] suggested[5,8c] that the first step involves interaction of twisted enone triplets with the alkenes, consistent with the proposal that such twisted species are intermediates in cyclohexenone photorearrangements.[10] Indeed, naphthalene quenches formation of **2** and the stereoisomeric cycloadducts of **1** with TME in 2-propanol (IPA) to exactly the same extent, confirming that these products arise from a common enone triplet.[11]

Scheme I



Scheme II



Transient absorption observed on laser flash excitation of several conjugated cyclic enones has been ascribed to twisted triplet excited states,[12,13] whose lifetimes vary inversely with the structural rigidity of the C=C bond. The reported triplet lifetime of **1** in AN at room temperature is 25 ± 1 ns;[13] our new measurements[14] give $\tau_T = 27 \pm 2$ ns in AN, 33 ns in IPA, and 24 ns in isooctane, and lifetimes increased only slightly in isooctane when the temperature was lowered to 188 K. If this enone triplet were the species intercepted by TME, k_a would have to be $\sim(2.0 \pm 0.5) \times 10^7$ M^{-1} s^{-1}, in which case reaction of this triplet with high concentrations of TME would be competitive with the unimolecular triplet decay rate of $\sim 4 \times 10^7$ s^{-1}. However, at concentrations up to 3.8 M, TME has no effect on the optical density nor on the rate of decay of the transient from **1** absorbing at 280 nm, consistent with our previous experiments using cyclohexene and 1,1-dimethoxyethylene (DME).[13] Also, in neat cyclopentene, τ_T is 23 ns, indistinguishable from that in isooctane. In addition, TME has no effect on the rate of growth of methylnaphthalene (MN) triplets at 420 nm on excitation of **1** and MN at 337 nm; e.g., $k_q^{MN} = (2.6 \pm 0.6) \times 10^8$ M^{-1} s^{-1} in AN and in AN containing 30% freshly distilled TME (v/v). Extrapolated lifetimes of ^{3}**1*** from plots of k_{growth} vs. [MN] were 26 and 29 ns in AN and in AN containing 30% TME. After reexamination of our earlier data,[13] we conclude that DME also has no effect on triplet energy transfer from ^{3}**1*** to naphthalene (NA).[16] Contrary to our previous conclusions,[13] one enone triplet (or less likely two thermally equilibrated triplets) is sufficient to rationalize all our kinetic data.

Table I illustrates the clear mismatch between values of $k_A\tau$ based on product quenching studies and values of k_q and τ_T determined from flash experiments, using four alkenes in three solvents. Quantum yields for cycloadduct formation given in Table

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[3] Presented at: (a) 21st Mechanisms Conference, Austin, TX, June 1986; (b) Symposium on "Flash Photolysis and its Applications" in honor of Sir George Porter, London, July 1986; (c) XI IUPAC Symposium on Photochemistry, Lisbon, July 1986.

[4] (a) New York University. (b) National Research Council.

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[6] Adducts of TME and enone 1 have been previously characterized: Nelson, P. J.; Ostrem, D.; Lassila, J. D.; Chapman, O. L. *J. Org. Chem.* **1969**, *34*, 811. Our product assignments are in complete agreement.

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[8] (a) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. (b) Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559. (c) See also: Bowman, R. M.; Calvo, C.; McCullough, J. J.; Rasmussen, P. W.; Snyder, F. F. *J. Org. Chem.* **1972**, *37*, 2084.

[9] For reviews, see: Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123. Weedon, A. C. In *Synthetic Organic Photochemistry*, Horspool, W. M., Ed.; Plenum: New York, 1984.

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[11] Data from our studies and the literature[10b] indicate enone singlet excited states have no role in these reactions. Absorption spectra suggest enone-alkene ground-state complexes are not formed at high alkene concentrations.

[12] Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816.

[13] Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Rao, J. M.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706.

[14] These experiments used the pulses (337.1 nm, ~8 ns, 6 mJ/pulse) from a nitrogen laser for excitation. Further details are reported elsewhere.[15]

[15] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

[16] The error in the studies reported in ref 13 was due to problems in estimation of the top of the curve for growth of triplet naphthalene absorption at 420 nm. The growth portions of these curves are in fact superimposable at all DME concentrations.

Table I. Comparison of Product Quenching and Flash Data for the Reaction of **1** with Alkenes

solvent	quencher[a]	$k_a\tau$,[b] M^{-1}	k_q,[c] $M^{-1}\ s^{-1}$	τ_T,[c] ns	$k_q\tau_T$	ϕ[d]
AN	TME	0.48	$<2 \times 10^6$	27	<0.05	0.041 (0.25)
IPA	TME	0.45	$<2 \times 10^6$	33	<0.06	
AN	CP	0.43	$\leq 1.4 \times 10^6$	27	≤0.05	0.032 (0.34)
IPA	CP		$\sim 1 \times 10^7$	33	~0.3[e]	
isooctane	CP		$<1 \times 10^6$	24	≤0.02	
AN	DME	1.2	$<1 \times 10^6$	27	<0.03	(0.44)
IPA	DME		$<3 \times 10^6$	33	<0.08	
AN	CH	0.13	$<2 \times 10^6$[f]	27	<0.05	
IPA	CH	0.39[g]	$<2 \times 10^6$[f]	33	<0.06	

[a] TME = tetramethylethylene; CP = cyclopentene; DME = 1,1-dimethoxyethylene; CH = cyclohexene. [b] From product quenching studies. [c] From flash studies. [d] Quantum efficiencies for cycloaddition at 313 nm of 0.2 M enone at 1.0 M alkene and neat alkene (in parentheses). [e] The apparent quenching observed in this case may be due to solvent effects. [f] From ref 13 and: Dunn, D. A. Ph.D. Dissertation, New York University, 1985. [g] Reference 5.

I are similar in magnitude to those previously reported[8,17] for photoaddition of alkenes to cyclohexenones. The unavoidable conclusion is that the species intercepted by alkenes on photoexcitation of **1** is not the reactive enone triplet, i.e., that at least for these systems the Corey–de Mayo photoannelation mechanism does not apply.

In the correct form of the mechanism, shown in Scheme II, the enone π,π^* triplet is a precursor of a reactive intermediate I, which proceeds to lumiketone or reverts to starting material. In the absence of alkene, the reversion predominates, since rearrangement efficiencies are typically on the order of 0.01,[10b,18] while photocycloaddition efficiencies are as high as 0.44 in neat alkene. The Corey–de Mayo mechanism would require a substantial reduction in τ_T at high alkene concentrations, which is not observed in the flash experiments nor in steady-state quenching by naphthalene of photocycloaddition of TME to **1** in IPA. Finally, relative reactivities of 17 alkenes as quenchers of rearrangement of **1** show no correlation with ionization potentials,[19] as would have been expected for formation of an enone–alkene exciplex.[20] Rather, alkene reactivity seems to be governed mainly by steric parameters.

We suggest that I may be a ground-state *trans*-cyclohexenone analogous to well-characterized trans isomers of cycloheptenone,[21] cyclooctenone,[22] and 1-phenylcyclohexene.[23] Corey failed to detect such a species by IR spectroscopy upon irradiation of 2-cyclohexenone in a hydrocarbon matrix at −190 °C.[21a] A *trans*-cyclohexenone was implicated by Hart in the photoaddition of methanol to Pummerer's ketone,[24] a process which occurs in very low yields in the case of **1**.[25] The suggestion that I is on the ground-state rather than the triplet-state potential surface is supported by the low value of log A (8.01 ± 0.15) measured for decay of $^3\mathbf{1}^*$ in isooctane ($E_a = 0.52 \pm 0.16$ kcal/mol), inconsistent with adiabatic isomerization of $^3\mathbf{1}^*$ but compatible with intersystem crossing to the ground-state surface.

A corollary of our findings (see Scheme I) is that the photorearrangement of **1** to **2** appears to occur on the ground-state potential surface rather than directly from an enone triplet as long held.[5,8c,10,26] This would provide an explanation for the high stereospecificity and very low quantum efficiency of this reaction,[10] as well as the formation of products attributed many years ago to a "polar-state" intermediate.[27]

As a mechanistic alternative, the Corey–de Mayo mechanism (Scheme I) may hold for cyclopentenones, geometrically constrained cyclohexenones, and perhaps even cyclohexenone itself. Experiments are in progress to examine this possibility.

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Registry No. 1, 1073-13-8; TME, 563-79-1; CP, 142-29-0; DME, 922-69-0; CH, 110-83-8.

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(19) Corey's concluson[7] that alkene reactivity correlated with electron-donating ability was based on relative product yields in competitive irradiations, which clearly depends on many factors in a multistep mechanism.

(20) For a discussion of exciplexes and primary references, see: Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233.

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Flash Pyrolysis of 1,4-Bis(5-tetrazolyl)benzene. Entry to the C_8H_6 Energy Surface[1,2]

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Twenty years ago Murray and Kaplan,[4] building upon earlier work[5] on polyphenyl bis-diazo compounds, irradiated 1,4-bis(diazomethyl)benzene in benzene and obtained a 2% yield of a diadduct to solvent. They did not claim dicarbene (**1**) as an intermediate, recognizing that a sequence of events in which monocarbenes were the active ingredients was likely. In the succeeding years there have been a number of other reactions in which polycarbenes were possible, if usually unlikely, intermediates.[6] Most impressive has been the recent work in which polycarbenes containing ever growing and quite remarkable

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(2) Portions of this work are taken from the A. B. Theses of J. L. F. and M. E. M., Princeton University, 1978 and 1976.

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