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# Photocycloaddition of 4,4-Dimethylcyclohexenone to 1,1-Diphenylethylene. Evidence for a Triplet Exciplex Intermediate

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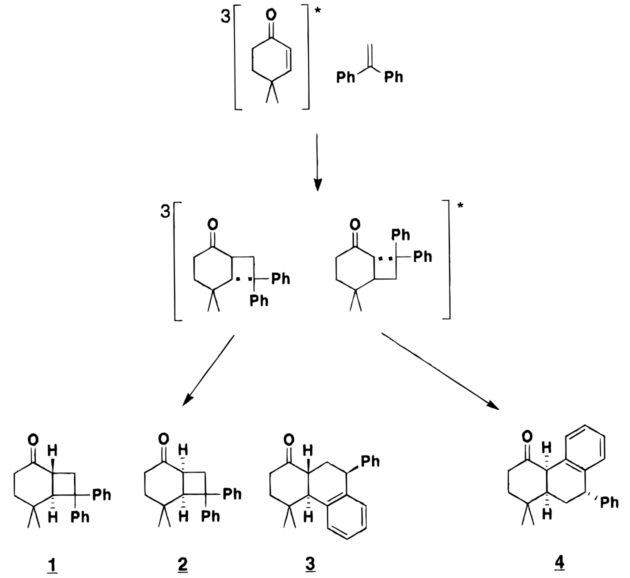
We here report the photocycloaddition of 1,1-diphenylethylene (DPE) to 4,4-dimethylcyclohexenone (DMC) and attendant observations indicating the presence of a triplet exciplex intermediate. While the existence of singlet exciplexes and excimers is unquestionable,[1−6] our direct knowledge of triplet excimers and exciplexes is sparse. While at least some (intramolecular) triplet excimers seem on secure ground,[7−11] the intermolecular case has been the subject of vigorous debate. Corey[12] suggested an "oriented $\pi$-complex" intermediate in triplet state photoannelations of cyclohexenones. Loutfy and de Mayo rationalized their own data using this hypothesis.[13−15] Caldwell suggested triplet exciplexes in the Paterno−Buchi reaction,[16−18] supported by work of Wagner[19] and Winnik,[20] although the latter indicated limits on the possibility. Wilson and Halpern[21−23] have also reported triplet exciplexes formed between aliphatic ketones and benzene derivatives.

Recently, the invocation of triplet exciplexes in photocycloadditions has fallen out of favor. Evidence for triplet exciplexes in photocycloadditions has been indirect, and none has been observed directly in a cycloaddition system. Schuster has questioned the need for these intermediates in cyclohexenone photoannelation,[24−27] and Peters[28,29] has interpreted the quenching of ketone triplets by electron rich alkenes as direct formation of a biradical. Biradical-trapping studies[30−33] have led Weedon to conclude that exciplexes are not a requirement in explaining the regiochemical outcome of enone−alkene photoannelations.

**Scheme 1**



Irradiation of a solution of DMC (55 mM) and DPE (110 mM) in cyclohexane yields four major products (**1**−**4**; Scheme 1) which were characterized by NMR and, for compounds **1**, **3**, and **4**, X-ray crystallography. Compounds **1** and **2** are the expected head-to-tail cyclobutanes. Compounds **3** and **4** formally arise from an α-ortho ring closure followed by a 1,3-hydrogen shift, previously observed in alkene triplet state photoadditions.[34] The *trans*-cyclobutane **1** is readily isomerized to the thermodynamically more stable *cis*-fused isomer upon stirring in methanolic potassium hydroxide. Only compound **4** arises from the head-to-head 1,4-biradical. Both biradical orientations were expected.[30−33] GC analysis suggests cyclobutanes resulting from simple ring closure of the head-to-head biradical are a minor component of the reaction mixture, if present at all. 1,4-Ring closure therefore appears to compete inefficiently with possible reversion to starting materials, while the 1,6-ring closure, with temporary loss of aromaticity in one of the phenyl substituents, remains competitive.

Laser flash photolysis of DMC (70 mM) in cyclohexane yields the expected enone triplet; $\lambda_{\max}$ 280 nm, $\tau$ 24 ns.[35−37] The enone triplet is quenched by oxygen with a rate constant $k_q^{ox} = 4.6 \times 10^9$ L mol$^{-1}$ s$^{-1}$. This value is slightly lower than a previously reported rate constant.[37] Similarly, the DPE triplet state ($\lambda_{\max}$ 335 nm, $\tau$ 34 ns, $k_q^{ox}$ 6.3 × $10^9$ L mol$^{-1}$ s$^{-1}$)[38] was characterized upon photolysis of a thioxanthone solution ($OD_{355} = 1.0$) containing DPE (0.1 M) in cyclohexane. The DPE triplet lifetime is essentially independent of the DPE concentration up to 1.0 M and is unaffected by the presence of DMC for the concentrations employed.

Photolysis of DMC ($OD_{355} = 1.5$) in the presence of DPE leads to the rapid generation of a new transient species. Direct observation of the DMC triplet decay in the presence of DPE

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is not possible due to the much larger extinction coefficient of the new transient in the relevant wavelength range. Analysis of the rate of grow-in of the transient signal as a function of the DPE concentration, monitored at 345 nm, employing a 355 nm, 200 ps excitation pulse suggests a rate constant for quenching of the enone triplet of $2.4 \times 10^8$ L mol$^{-1}$ s$^{-1}$. The quenching process was also studied under nanosecond excitation, by extrapolation of the transient optical density to time zero again as a function of [DPE]. Analysis using the equation

$$\Phi/\Phi_\infty = k_q\tau[\text{DPE}]/(1 + k_q\tau\,[\text{DPE}])$$

where $\tau$ is the enone triplet lifetime, $\Phi$ is the measured yield of the observed transient, and $\Phi_\infty$ is its yield at infinite DPE concentration leads to a quenching rate constant of $k_q = 3.9 \times 10^8$ L mol$^{-1}$ s$^{-1}$. This rate constant is in line with that expected for a typical reactive interaction of an alkene with an enone triplet.[25] While the transient spectrum for the new species is essentially identical to that of the DPE triplet, its decay is consistently measured as a clean single exponential with a lifetime of 50 ns. This is *not* consistent with its assignment as the DPE triplet.[39]

We had initially expected that the interaction of the DMC triplet with DPE would yield either observable 1,4-biradical intermediates or a mixture of these biradicals with some proportion of DPE triplets resulting from competing energy transfer. Kinetic observations appear to rule out both of these simple schemes and suggest the production of an alternative spectroscopically observable intermediate. The following experiments provide strong support for this conclusion and further information on the nature of this species.

Production of singlet oxygen by the enone−alkene system was examined in aerated cyclohexane. $S_\Delta$ values[40] for DMC ($\text{OD}_{355} = 1.0$; $\Phi_T = 1.0$) and DPE (sensitized by *p*-methoxyacetophenone, $\text{OD}_{355} = 1.0$) were determined to be 0.53 and 0.19, respectively. The $\Phi_\Delta$[40] for a solution of DMC ($\text{OD}_{355} = 1.0$) and DPE (0.4 M) can be predicted from the enone and DPE triplet lifetimes, the rate at which the enone triplet is quenched by DPE ($3 \times 10^8$ L mol$^{-1}$ s$^{-1}$[41] ), the relevant oxygen quenching rates ($^3$Enone* = $4.6 \times 10^9$ L mol$^{-1}$ s$^{-1}$; $^3$DPE* = $6.3 \times 10^9$ L mol$^{-1}$ s$^{-1}$), and the $S_\Delta$ for the oxygen quenching events. If the interaction between the enone triplet and DPE produced biradicals exclusively, the enone triplet would be the only singlet oxygen source in the system and the predicted $\Phi_\Delta$ would be 0.033. At the other extreme, if the DPE triplet were produced by energy transfer with unit efficiency, the predicted $\Phi_\Delta$ would rise to 0.077. The observed value for this system is 0.080 which is within experimental error of the energy transfer limit. In the absence of kinetic absorption studies, the singlet oxygen data would suggest that chemical reaction is a very minor component of the enone−alkene interaction and that we are generating DPE triplets with almost unit efficiency. This conclusion is completely inconsistent with the observed transient lifetime of 50 ns. However, we are clearly producing significantly higher yields of singlet oxygen than one would predict for a system in which the enone triplet is the only singlet oxygen source. The 50 ns transient therefore appears to be a source of singlet oxygen which therefore retains at least 23 kcal mol$^{-1}$ of electronic excitation and triplet multiplicity. The measured rate constant for quenching of the 50 ns transient by oxygen, $k_q^{\text{ox}}$, is $5.9 \times 10^9$ L mol$^{-1}$ s$^{-1}$.

The novel transient is also quenched by azulene. Addition of azulene (1.73 mM) to a solution of DMC ($\text{OD}_{355} = 1.0$) in cyclohexane leads to rapid generation of the azulene triplet state, characterized by its transient absorption spectrum.[42] The amplitude of the azulene triplet decay at 370 nm was extrapolated to time zero, and the experiment then repeated under identical conditions following addition of DPE (0.88 M) to the solution. This analysis yielded a value for $\Phi_{3\text{Az}*}(\text{DPE})/\Phi_{3\text{Az}*}$, the ratio of the azulene triplet yields in the presence and absence of DPE, of 0.47. This ratio can also be predicted from a knowledge of the fraction of enone triplets quenched by azulene in both experiments and the assumption that only the enone triplet can produce triplet azulene. The DPE triplet, which rapidly relaxes, is not quenched by azulene. Azulene itself does not intersystem cross upon 355 nm excitation. Quenching of the enone triplet by DPE with a measured rate constant of $3 \times 10^8$ L mol$^{-1}$ s$^{-1}$ leads to a predicted $\Phi_{3\text{Az}*}(\text{DPE})/\Phi_{3\text{Az}*}$ ratio of 0.16. The observed value is significantly higher, indicating that the enone triplet is not, in fact, the only source of azulene triplets in this system. This experiment reinforces the conclusion that the 50 ns transient is not the DPE triplet but some other species, capable of transferring triplet excitation to azulene and molecular oxygen, which retains significant electronic excitation and triplet multiplicity.

We considered that reversible energy transfer between the DMC triplet and DPE might complicate our experiments. However, rapid relaxation of the DPE triplet should preclude such reversibility. Energy transfer to produce the relaxed DPE triplet is exothermic by around 11.5 Kcal (DMC − $E_{\text{T(rel)}}$ 63.6 ± 0.7; DPE − $E_{\text{T(spec)}}$ 60.8, $E_{\text{T(rel)}}$ 52.1 ± 1.8 kcal mol$^{-1}$)[36,38] and would therefore not be reversible on the 50 ns time scale. Biradical intermediates would be expected to be significantly more stable than the DPE triplet and are not expected to be formed reversibly. We conclude that reversibility is an issue only if the unknown intermediate is an exciplex lying reasonably close in energy to the enone triplet.

In conclusion, quenching of the DMC triplet by DPE leads to the production of a transient with an absorption maximum at 335 nm. Its lifetime of 50 ns is inconsistent with its assignment as either the DPE triplet or the triplet 1,4-biradical leading to the cyclobutane products. The species is electronically excited and retains triplet multiplicity. We assign the transient as a triplet exciplex intermediate resulting from interaction of DPE with the enone triplet state. The involvement of a triplet exciplex intermediate along the reaction coordinate, formed prior to or in competition with triplet biradicals and able to revert to ground state starting materials, would presumably constitute a further energy-wasting step in the reaction[18,43] in addition to biradical reversion and would account for the low quantum yield for product formation observed. Experiments to determine the nature and role of these species in photocycloaddition processes are in progress.

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(39) We considered that the 50 ns transient might be a 1,4-biradical. The head-to-tail biradical was investigated by 266 nm laser flash photolysis of **1**. Its lifetime is 78 ns with an absorption spectrum similar to those of the DPE triplet and the new transient. Its lifetime is insensitive to the presence of isoprene up to a concentration of 0.3 M, consistent with its assignment as a biradical. Photolysis of **1** may produce the alternative head-to-head biradical. We have no quantitatitive information on the fragmentation of **1** under 266 nm photolysis but were aided by the fact that the head-to-head biradical is not spectroscopically observable. We considered further that the observed 50 ns decay might be a mixture of the 34 ns DPE triplet and a 78 ns biradical. Exhaustive multiple-component kinetic analyses lead us to reject this.

(40) $S_\Delta$ and $\Phi_\Delta$ refer to the fraction of oxygen quenching events leading to the production of singlet oxygen and the overall singlet oxygen quantum yield, respectively. For further information consult ref 44.

(41) The rate constant for quenching of the enone triplet by DPE is approximated to $3 \times 10^8$ L mol$^{-1}$ s$^{-1}$ for these calculations given our two measured values of 2.4 and $3.9 \times 10^8$ L mol$^{-1}$ s$^{-1}$.

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