The Photo-addition of 3-Phenylcyclohex-2-enone and Tetramethylethylene. Evidence for Singlet and Triplet Pathways leading to a Common Intermediate

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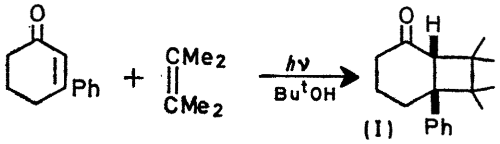
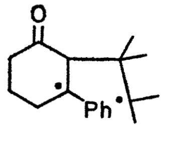
Summary The photo-addition of 3-phenylcyclohex-2-enone and tetramethylethylene occurs from S_1 on direct irradiation, and from T_1 on sensitization, to afford the same cyclobutane adduct.

THE photo-cycloadditions of alicyclic enones[1,2] have been intensively studied in recent years, from the viewpoint of synthesis[3] and mechanism. Although the dimerization of cinnamic acid[4] is probably the oldest photochemical cycloaddition, photochemical studies of the cinnamate system[5-7] have generally been concerned with structures of products, rather than mechanism. We have investigated the addition of 3-phenylcyclohex-2-enone and tetramethylethylene, and report our results on the multiplicity of this addition.



(I)



(II)

The reaction proceeds cleanly, though inefficiently, to afford the cyclobutane adduct, (I).† Adduct (I) is formed

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† The adduct was a waxy solid, m.p. 48—57° which analysed correctly. It was characterized by infra-red, n.m.r., and mass spectrometry.

on direct irradiation of the enone, and on sensitization using Michler's ketone or 2-acetonaphthone. This agrees qualitatively with the report of Cantrell *et al.* that 3-phenylcyclohex-2-enone and cyclopentene react on sensitization using xanthone.[6] However, a quantitative study, in which quantum yields for formation of (I) were measured as a function of tetramethylethylene (TME) concentration, showed that the direct and sensitized reactions proceed *via* different excited states. The results are given as plots of (Quantum yield)$^{-1}$ *versus* (TME concentration)$^{-1}$ shown in the Figure.

The steps shown in the Scheme comprise a kinetic model for the system. K* is the reactive excited state of the ketone (K), which can be intercepted by TME to form a metastable intermediate complex. The latter can collapse to product (I) (step 4) or to reactants (step 5).

				Rate
(1)	K	$\xrightarrow{h\nu}$	K*	aI
(2)	K*	$\longrightarrow$	K	k_d[K*]
(3)	K* + TME	$\longrightarrow$	(K–TME) COMPLEX	k_c[TME] [K*]
(4)	(K–TME)	$\longrightarrow$	(I)	k_r[K–TME]
(5)	(K–TME)	$\longrightarrow$	K + TME	k_{diss}[K–TME]

SCHEME. *Kinetic processes involved in addition of 3-phenylcyclohex-2-enone and tetramethylethylene* (TME). *K* is the reactive excited state of the ketone formed with efficiency* a, *I is the light intensity.*

The following equation is easily derived using the steady-state approximation:

$$1/\Phi = [(k_r + k_{diss})/ak_r] \times (1 + k_d/k_c[\mathrm{TME}])$$

Φ is the quantum yield for formation of (I). Since the intercepts of the plots in the Figure are equal, and the slopes are different, it is certain that K* is different in the direct and sensitized reactions. In the sensitized reaction, K* is undoubtedly T_1 of the enone, since Michler's ketone has unit intersystem crossing efficiency[8] and $E_t = 61$ kcal/mole[9] while the enone has $E_t = 54$ kcal/mole.‡ It is most likely, therefore, that the state reacting in the direct irradiation is the singlet excited state, S_1, of the enone, and that the tetramethylethylene intercepts it before intersystem crossing occurs. If this were not the case, the plot from the direct irradiation should show curvature, due to a less efficient triplet component in the reaction.

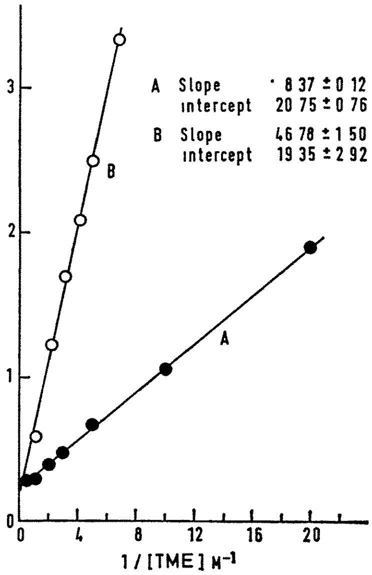

FIGURE. *Plots of* (*quantum yield*)$^{-1}$ versus [TME]$^{-1}$. A, *direct*, B, *sensitized irradiation. Slopes are in Einsteins, intercepts in Einsteins* M^{-1}. *t-Butyl alcohol was the solvent, and the enone was* 5×10^{-3} M. *The sensitizer* (*Michler's ketone*) *was* 2.4×10^{-3} M *and absorbed* $>99\%$ *of the total light absorbed.*

Although singlet processes of certain aromatic carbonyl compounds are known,[10] the present case is of interest in that the enone reacts exclusively from S_1 on direct irradiation, but T_1 will react when generated by sensitization.

It is obvious that the sensitized formation of (I) could not be used to draw conclusions on the mechanism of the direct irradiation, without a quantitative comparison.

It is interesting that the plots in the Figure have the same intercept.§ This intercept gives the quantum yield at infinite olefin concentration, about 0.05. Thus, k_{diss} is greater than k_r and this is a major source of inefficiency in the reaction. The fact that the intercepts are equal suggests that both reactions, sensitized and unsensitized, have a common intermediate. This might be an exciplex,[2] or the 1,4-biradical[2] (II) in which the spin correlation of the enone singlet and triplet excited states has been lost.

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‡ This was calculated from the weak phosphorescence observed at 77 K from this enone, in a glass of ether—ethanol, 1:2. The phosphorescence excitation matched the absorption spectrum of the enone.

§ In both reactions $a = 1$.

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