Kinetics of Photochemical Addition of 3-Phenyl-2-cyclohexenone to Tetramethylethylene

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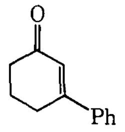
Abstract: The kinetics of photoaddition of 3-phenyl-2-cyclohexenone to tetramethylethylene are described. The direct or sensitized (Michler's ketone) addition gives a single, cis-fused cycloadduct **3**, which is assigned the structure 6-phenyl-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one. Quantum yields (Φ) of adduct formation were studied as a function of tetramethylethylene [TME] concentration in *tert*-butyl alcohol. A plot of Φ (direct) vs. $[\mathrm{TME}]^{-1}$ was linear, with slope = 8.37 ± 0.12 Einsteins and intercept = 20.8 ± 0.8 Einsteins mol^{-1}. The sensitized addition gave a similar linear plot with slope = 46.8 ± 1.5 Einsteins and intercept = 19.4 ± 2.9 Einsteins mol^{-1}. It is proposed that the enone T_1 reacts in direct and sensitized additions, and the inefficiency on sensitization is due to chemical quenching of enone T_1 by the sensitizer. The addition was quenched by di-*tert*-butyl nitroxide, and the rate constant for the enone-tetramethylethylene reaction was calculated as $1.56 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$, assuming diffusion-controlled quenching. The active excited state has a lifetime of 1.59×10^{-6} sec, which is too long for enone S_1 and is consistent with T_1. The high values for the intercepts of the TME concentration plots are taken to mean that a metastable intermediate is formed, which decomposes to ground state reactants more efficiently than it affords product. No evidence that nitroxide quenches this intermediate was found, and the nature of the intermediate is discussed. Some results with cyclopentene and norbornene are also included.

Photochemical cycloaddition of 2-cyclohexenones has been the subject of a great deal of experimental work.[2-4] The addition was applied in several syntheses,[4] and subsequently several laboratories studied the mechanism of this general reaction. Our investigations in this area have been concerned with the intermediacy of biradicals[5,6] and with excited state geometry[7] and stereochemistry of cyclobutane formation.[8]

A comparison of the structures of products from 2-cyclohexenone with those from 3-phenyl-2-cyclohexenone (**1**) in respective additions with cyclopentene, was made by Cantrell[9] and by us.[8] It was found that the stereochemistry of 3-phenyl-2-cyclohexenone addition gave only cis-fused ring junctions, while 3-methyl-2-cyclohexenone gave a major fraction of trans-fused compounds. From the mechanistic viewpoint, the 3-phenyl-2-cyclohexenone reaction is of interest for the following reasons. First, there is the question of excited state multiplicity. Although 2-cyclohexenones generally add to alkenes via the lowest triplet (T_1),[4b] it could not be assumed that 3-phenyl-2-cyclohexenone would behave similarly. In certain ketones whose lowest triplet has a π-π^* configuration, e.g., fluorenone,[10] intersystem crossing from S_1 is sufficiently slow for fluorescence to be observed. Since **1** probably has a π-π^* triplet (T_1), the singlet could not be ignored as the photochemically active species. Arnold, Chapman, and coworkers have in fact reported that various cinnamate derivatives add to tetramethylethylene via S_1.[11]

The second interesting question concerns the effects of phenylsubstitution on the behavior of 1,4 biradicals which have been invoked—for good reasons—in 2-cyclohexenone additions.[3-5] A biradical such as **2** would, of course be stabilized by the aryl substitution, and its reactions could differ markedly from the alicyclic examples which have been described.



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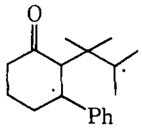

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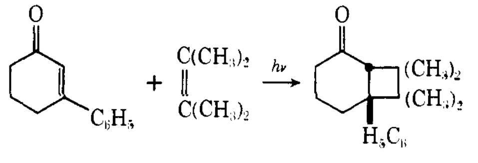
In this paper, we describe the kinetics of photoaddition of **1** and tetramethylethylene, from the viewpoint of the excited state, and other intermediates involved. The behavior of **1** is compared with that of cyclohexenones lacking the phenyl group.

Results

Addition of 3-Phenyl-2-cyclohexenone and Tetramethylethylene. Irradiation of 3-phenyl-2-cyclohexenone and tetramethylethylene at 300-400 nm (Pyrex filter) in *tert*-butyl alcohol gave a single mixed addition product **3** and the known dimer **4** of the enone.[12] The formation of the photodimer could be suppressed using high concentrations of tetramethylethylene. Thus, the yield of the dimer was about 50% when a 10-fold excess of the olefin was used, but was negligible when the olefin was in 60-fold excess. The photodimer **4** and mp 200-201° (lit.[12] 204-205°) and had spectral properties identical with those reported.



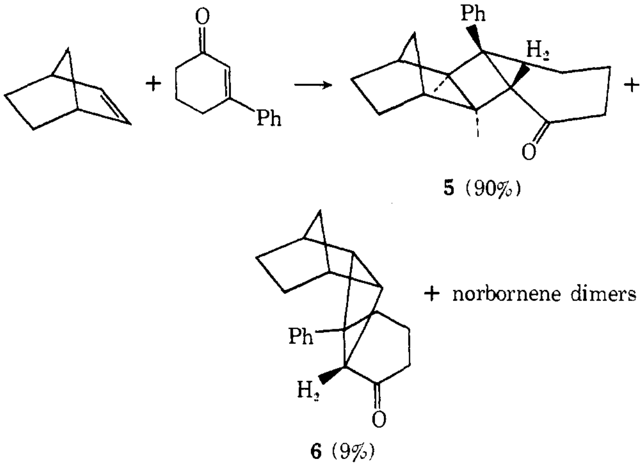
3 + dimer 4

The mixed addition product **3** was isolated by column chromatography, distillation, and vacuum sublimation as a waxy solid, mp 57-60°. The spectral data are consistent with structure **3** and are given in the Experimental Section. The compound was unchanged by treatment with basic alumina, showing that the six-four ring fusion is cis.[2a] The same adduct was formed if Michler's ketone or 2-acetonaphthone was used as sensitizer.

Addition of 3-Phenyl-2-cyclohexenone and Norbornene. This irradiation afforded two mixed addition products together with the known photodimers of norbornene.[13] The mixed adducts **5** and **6** are assigned as the exo and endo isomers, respectively, of 8-phenyltetracyclo$[8.2.1.0.^{2,9}0.^{3,8}]$tridecan-4-one[14] and are shown in Chart I.

The gross structures were established from the infrared absorption at 5.88 μ (cis-fused cyclohexanone ring) and

Chart I



from the mass spectra which showed parent ions at *m/e* 266 and base peaks at *m/e* 173, the latter corresponding to cleavage of the cyclobutane ring. The major product **5** mp 87-88.5°, is tentatively assigned the exo structure, which is in accordance with the well-known preference of norbornene to undergo exo addition in ground state[15] and photochemical[13,16] reactions.

Details of the NMR spectra are given in the Experimental Section. Of particular note, however, is a one proton doublet which appeared at 2.84 ppm (J = 3.6 Hz) in the spectrum of **5** and at 2.87 ppm (J = 3.0 Hz) in **6**. This resonance is believed to be due to the cyclobutane proton (H_2), adjacent to the phenyl-substituted carbon and the carbonyl group, on account of its chemical shift. The coupling constants of 3.6 and 3.0 Hz are consistent with trans coupling[17] of vicinal protons in a model system where J_{12} = 3.5 Hz. Thus, the structures **5** and **6** are tentatively assigned to these adducts on the basis of the available structural evidence, and by analogy with similar reactions.[2,8,12]

Also formed in this reaction were the photodimers of norbornene.[13] The major dimer obtained by preparative vapor phase chromatography was a waxy solid, mp 36-38°. Its mass spectrum showed the molecular ion peak at *m/e* 188, and the nuclear magnetic resonance spectrum was identical with that described for the exo-trans-endo dimer.[13b] An authentic sample of the latter was prepared by the irradiation of norbornene using acetone as sensitizer.

Addition of 3-Phenyl-2-cyclohexenone and Norbornadiene. Irradiation of enone **1** and norbornadiene gave three 1:1 adducts, which were assigned structures of cis-fused cyclobutanes. Of these adducts, the major two were isolated as crystalline solids, mp 104.5-106.5° (45%), **7**, and 75-83° (35%), **8**. The minor adduct (20%), **9**, was an oil, purified by preparative VPC. The stereochemistry of these compounds is not known with certainty, although we did determine that adduct **8** gave **5** on catalytic hydrogenation. We are certain, however, that no α-nortricyclyl- or α-norbornenylcyclohexenones, which are formed in 3-methylcyclohexenone-norbornadiene addition,[5] are produced.

Kinetics. Quantum Yields of Addition. Dependence on Olefin Concentration. For this quantitative work, tetramethylethylene (TME) was generally used because it gives a single product in the photoaddition and has a vapor pressure which allowed work at room temperatures. Some quantum yields were measured for the cyclopentene addition. The relative quantum yields of photoaddition of 3-phenyl-2-cyclohexenone and tetramethylethylene for various concentrations of the olefin were determined, and the details are described in the Experimental Section. These were converted to absolute quantum yields since this had been measured for one of the tetramethylethylene concentrations. For the latter, an optical bench and ferrioxalate actinometry were used. The data are given in Table I. A plot of reciprocal quantum yield vs. reciprocal TME concentration gave a straight line (Figure 1).

Table I. Effect of TME Concentration[a] on the Quantum Yield of Photoaddition

	[TME], M	$[TME]^{-1}$, M^{-1}	Amount of 3, mg	Relative[a] Φ	Absolute Φ × 10^3	$Φ^{-1}$
Run 1	0.05	20	6.60	0.244	5.42	184.50
	0.10	10	11.61	0.430	9.55	104.70
	0.20	5	18.41	0.672	14.92	67.00
	0.33	3	26.95	1.000	22.20	45.05
Run 2	0.33	3	16.24	1.000	22.20	45.05
	0.50	2	19.84	1.220	27.08	36.55
	1.00	1	27.33	1.682	37.34	26.78
	2.00	0.5	27.33	1.685	37.41	26.74

[a] Enone was 0.005 M, in *tert*-butyl alcohol.

Table II. Quantum Yields of Sensitized Photoaddition of 3-Phenyl-2-cyclohexenone and TME[a]

Sensitizer	Concn of sensitizer, M	Light absorbed, mEinsteins	Amount of 3 mg	mmol	Quantum yield, Φ
Michler's ketone	0.0024	30.56	49.0	0.193	0.0062
Michler's ketone	0.0024	30.40	46.4	0.181	0.0060
2-Acetonaphthone	0.05	26.84	39.9	0.156	0.0058
Biacetyl[b]	0.10	66.00	Traces		0.0

[a] Enone was 0.005 M; TME was 0.33 M, in *tert*-butyl alcohol. [b] Additional products, probably sensitizer–olefin adducts, were observed.

Table III. Effect of TME Concentration on the Quantum Yield of Sensitized Photoaddition[a]

	[TME], M	$[TME]^{-1}$, M	Amount of 3, mg	Relative[b] Φ	Absolute[c] Φ × 10^3	$Φ^{-1}$
Run 1	0.15	6.67	5.41	0.502	3.01	332.2
	0.20	5	7.28	0.675	4.05	246.9
	0.25	4	8.87	0.823	4.94	202.4
	0.33	3	10.78	1.000	6.00	166.7
Run 2	0.33	3	4.20	1.000	6.00	166.7
	0.50	2	5.84	1.390	8.35	119.7
	1.00	1	12.05	2.870	17.22	58.1

[a] Enone was 0.005 M; MK was 0.0024 M. The sensitizer (Michler's ketone, MK) absorbed more than 98% of the incident light. The same amount of light was absorbed in each sample in the same run. [b] The relative quantum yields are given with respect to that for 0.33 M tetramethylethylene. [c] A value of 6.0 × 10^{-3} for 0.33 M tetramethylethylene was used for calculating the absolute quantum yields (see Table IV).

The photoaddition of 3-phenyl-2-cyclohexenone to cyclopentene and to TME was found to be sensitized by triplet energy donors such as 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) and by 2-acetonaphthone. In all sensitized runs, the concentrations were so chosen that essentially all the light was absorbed by the sensitizer, and energy transfer to the enone should be quantitative.

A concentration study of the sensitized enone-TME addition was also carried out. The procedure paralleled that used in the study of the direct irradiation; viz., by simultaneously irradiating solutions of identical absorption properties and different TME concentrations, relative quantum yields were obtained; these were converted to absolute quantum yields by measuring this for a particular TME concentration. These results are shown in Tables II and III. A plot of reciprocal quantum yield vs. reciprocal TME concentration was linear and is shown in Figure 2. Note that this plot has a different slope from Figure 1. The inference

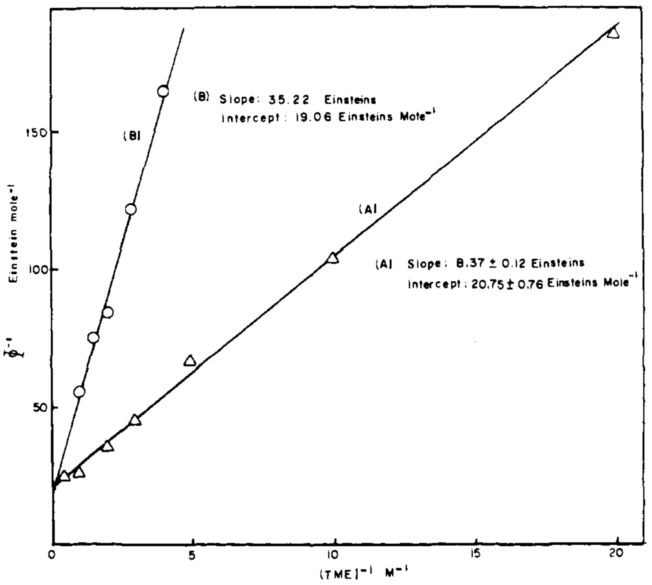


Figure 1. (A) Dependence of quantum yield of 3-phenyl-2-cyclohexenone-TME addition on TME concentration. (B) Same as (A) with 10^{-3} *M* DBN present. Solvent was *tert*-butyl alcohol.

was that different excited states were involved in the two reactions and, to obtain further evidence on this point, quenching studies were undertaken.

Quenching Experiments. Our next purpose was to find the effect of singlet and triplet quenchers on the quantum yield of photoaddition. Amines are known to act as efficient quenchers of excited singlet states.[18] Triethylamine was used, and a decrease in the rate of cycloaddition was observed in presence of the amine. Quantitative studies, however, could not be carried out since side products were observed in these runs.

Di-*tert*-butyl nitroxide (DBN), which is known to quench many singlets and triplets at diffusion-controlled rates,[19,20] was the next alternative. This compound was found to be a very satisfactory and effective quencher for the addition. A Stern-Volmer plot (Φ_0/Φ vs. DBN concentration) was linear; the plot is shown in Figure 3, and the data used are given in Table III. From the slope of this plot and the slopes and intercepts of the dilution plot (Figure 1A), the rate constant for radiationless decay was calculated (see below) to be 0.63×10^6 sec^{-1}, which corresponds to a lifetime of 1.59×10^{-6} sec.

This value is too long for the enone S_1 (see Discussion) and is of the right order for a T_1 state.[21] Thus, contrary to our suggestion,[6] and in agreement with that of Cantrell,[9] apparently the direct and sensitized reactions both involve the enone T_1.

To check for possible quenching of a complex by DBN, a dilution plot was determined in presence of 1.0×10^{-3} *M* DBN quencher. The data are shown in Figure 1. We note that the two plots in Figure 1 have the same intercept but different slopes.

Sensitized Dimerization of Norbornene. It is known that norbornene dimerizes when sensitized by sensitizers having triplet energies above 72 kcal/mol.[22] It was mentioned earlier that the dimers were formed as side products in the enone-norbornene photolysis.

A considerable effort was expended to determine whether these dimers were formed by sensitization by 3-phenyl-2-cyclohexenone (which would have implicated a T_2 state since T_1 is too low in energy),[13,22] or whether they merely result from sensitization by the mixed addition products **5** and **6**. In a control experiment, using adduct **3** as sensitizer, the norbornene dimers did form. Also, in an irradiation of enone and norbornene, with a Pyrex filter, the norbornene dimers were present when only 50% of the enone had reacted. However, in an irradiation of enone and norbornene in

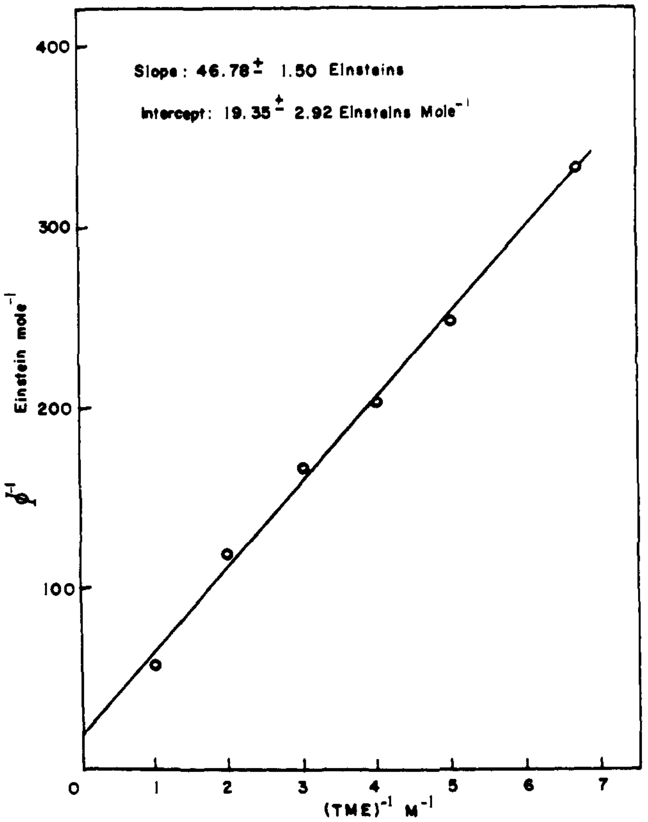


Figure 2. Dependence of quantum yield of Michler's ketone sensitized addition of **1** and TME on concentration of TME.

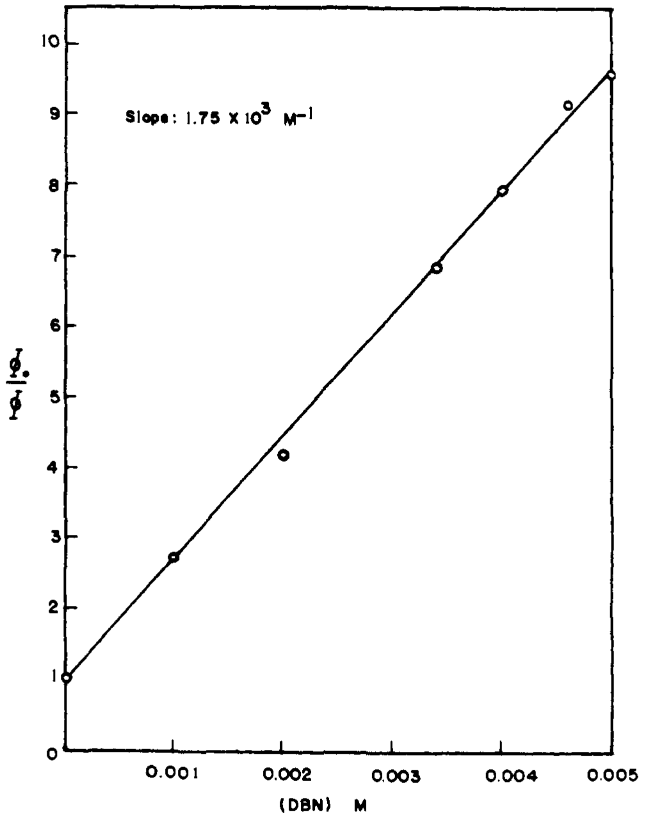


Figure 3. Stern-Volmer plot for quenching of addition of **1** and TME. Solvent was *tert*-butyl alcohol.

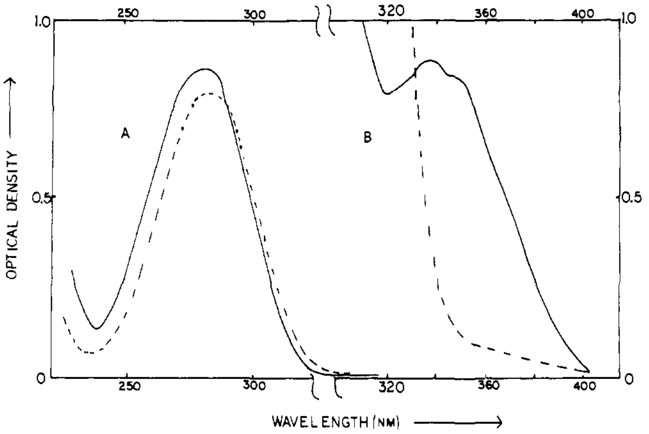


Figure 4. Absorption spectra of 3-phenyl-2-cyclohexenone (—) and its oxime (- - -): (A) 4 × 10^{-5} *M* in ethanol, showing π-π^* bands; (B) 10^{-2} *M* in cyclohexane, showing enone n-π^* band, absent from oxime spectrum.

the "Wisconsin Black Box", using chemical and glass filters to ensure no light was absorbed by the adducts **5** and **6**, no norbornene dimers were found. Sensitization by the mixed adducts **5** and **6** therefore appears to be responsible for the dimerization reaction.

Discussion

Excitation Processes and Possible Reactive States. The absorption spectrum of 3-phenyl-2-cyclohexenone in ethanol (the solvent generally used was ethanol, methanol, or *tert*-butyl alcohol) shows a band with λ_{max} 285 nm (log ϵ 4.3) whose long-wavelength tail extends to 375 nm. In hexane, this enone shows two bands, with λ_{max} 270 nm (log ϵ 4.3) and 340 (2.0). The spectrum of 3-phenyl-2-cyclopentenone is similar. Since π-π^* transitions in carbonyl compounds generally are red shifted, while the n-π^* bands are blue shifted, as the medium polarity is increased,[23] the above spectra are understandable. Thus, the single band in ethanol should be the π-π^* band, with the n-π^* band obscured by the long-wavelength tail. This assignment receives confirmation from the spectrum of the oxime of the enone,[24] which had λ_{max} (EtOH) 284 nm (log ϵ 4.34) virtually identical with the enone spectrum. The oxime also showed one band in hexane, λ_{max} 277 nm (log ϵ 4.3), which identifies the intense band as the π-π^* transition in the enone, and the weak, long-wavelength band, absent from the oxime spectrum, as a n-π^* transition.[24] The above spectra are shown in Figure 4.

We note that this interpretation of the absorption spectra of the enone is consistent with the spectra of 2-cyclohexenones, which have the π-π^* and n-π^* bands at about 220 nm (log ϵ 4.31) and at 376 nm (O-O band), respectively.[25] The extra conjugation of 3-phenyl-2-cyclohexenone red-shifts the π-π^* band much more than the n-π^* band, and it is interesting that the latter has almost the same energy in simple 2-cyclohexenones[25] as in the 3-phenyl derivative.

Therefore, it is most probable that the lowest singlet, S_1, of this enone is a π-π^* state, in the polar media which we used. The intensity of the S_0-S_1 (π-π^*) band is that of a highly allowed transition, and the calculated radiative lifetime of the S_1 (π-π^*) state is 2.7 nsec.[26] The actual lifetime of S_1 (π-π^*) must be much shorter than this since we were unable[27] to observe fluorescence from the purest samples of 3-phenyl-2-cyclohexenone. Thus, in alcohol solvents, reactions involving S_1 would necessarily have high rate constants.

In the sensitized reactions, there is little doubt that the lowest triplet T_1 of the enone undergoes addition. In our experiments, essentially all the light was absorbed by the sensitizer, Michler's ketone or 2-acetonaphthone, which have E_T of 61 and 59.5 kcal/mol, respectively.[28] Weak phosphorescence from the enone in ether-ethanol at 77° indicates E_T of 54-55 kcal/mol, and energy transfer should be exothermic. Further, both these sensitizers have high intersystem crossing efficiencies,[29] long triplet lifetimes,[30] and seemed ideal for investigating the enone T_1 reactivity.

Olefin Concentration Plots in the Direct and Sensitized Additions. The plots shown in Figures 1 and 2 have different slopes, and this suggests that different excited states of the enone are involved in the two reactions, direct and sensitized. This can be seen by considering the simple kinetic scheme for the bimolecular reaction (see Scheme I).

Scheme I

$$\mathrm{K} \longrightarrow \mathrm{K}^* \qquad aI \qquad (1)$$

$$\mathrm{K}^* \longrightarrow \mathrm{K} \qquad k_d[\mathrm{K}^*] \qquad (2)$$

$$\mathrm{K}^* + \mathrm{TME} \longrightarrow \mathrm{COMPLEX} \qquad k_c[\mathrm{K}^*][\mathrm{TME}] \qquad (3)$$

$$\mathrm{COMPLEX} \longrightarrow \mathrm{ADDUCT}\ \mathbf{3} \qquad k_r[\mathrm{COMPLEX}] \qquad (4)$$

$$\mathrm{COMPLEX} \longrightarrow \mathrm{K} + \mathrm{TME} \qquad k_{diss}[\mathrm{COMPLEX}] \qquad (5)$$

K is the enone ground state, K* the active excited state, formed with efficiency *a*, and COMPLEX is a metastable intermediate which can collapse to product **3** or dissociate to ground state enone and TME. Such a scheme is applicable to many photoadditions, including 2-cyclohexenone reactions.[4b]

The quantum yield of formation of **3** (Φ) is given by eq 6.

$$1/\Phi = [(k_r + k_{diss})/ak_r](1 + k_d/k_c[\mathrm{TME}]) \qquad (6)$$

Both plots show good linear relationships between $1/\Phi$ and 1/[TME], which means that just one excited state is involved in each case. Both reactions have the same quantum yield at infinite olefin concentration, as shown by the identical intercepts in the two plots. Therefore the different slopes appear to be due to different values of k_d/k_c, and this implies different excited states in the direct and sensitized additions. The first possibility which we considered[6] was that enone S_1 was involved in the direct and T_1 in the sensitized addition. Since S_1 should have a short lifetime (see above), one experiment was to try to determine the lifetime of the excited state involved in the direct irradiation by quenching.

Figure 3 shows the results of a Stern-Volmer study, using di-*tert*-butyl nitroxide (DBN) as quencher. Although this quencher does not quench all excited states at the diffusion-controlled rate,[20] quenching of benzophenone and fluorenone triplets,[20] and fluorenone singlets,[19] is diffusion controlled. Also, DBN and naphthalene quench a cyclohexenone triplet at the same rate in *tert*-butyl alcohol.[31] We therefore assumed that k_q (eq 7) was the diffusion-controlled rate constant.

$$\mathrm{K}^* + \mathrm{DBN} \longrightarrow \mathrm{K} + \mathrm{DBN} \quad \text{rate: } k_q[\mathrm{K}^*][\mathrm{DBN}] \qquad (7)$$

The usual Stern-Volmer kinetics give eq 8 for the relationship between quantum yield (Φ) and TME and DBN concentrations.[32]

$$\frac{1}{\Phi} = \frac{(k_r + k_{diss})}{ak_r}\left(1 + \frac{k_d}{k_c[\mathrm{TME}]} + \frac{k_q[\mathrm{DBN}]}{k_c[\mathrm{TME}]}\right) \qquad (8)$$

From the intercept of Figure 1A and the slopes of Figures 1A and 3, the rate constants k_c and k_d can be calculated, if it is assumed that $k_q = 2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ for *tert*-butyl alcohol at 27°.[31] The values derived are: $k_c = 1.56 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$; $k_d = 0.63 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$; and τ (excited state lifetime) is therefore 1.59 × 10^{-6} sec. The absolute values of k_r and k_{diss} cannot be derived from the present data but, since the intercept of Figure 1 is given by $(k_r + k_{diss})/ak_r = 20.7$, and if $a = 1$, then $k_{diss} = 19.75k_r$.

The first point of note is the low value of k_d; taking $k_d = \tau^{-1}$, $\tau = 1.59 \times 10^{-6}$ sec. Comparing the above lifetime of 1.59 × 10^{-6} sec with the limiting, radiative lifetime for the enone $S_{\pi-\pi^*}$ of 2.7 nsec (see above), it appears that the enone S_1 (π-π^*) cannot be the reactive excited state. This conclusion is supported by the failure of the enone to sensitize fluorescence of biacetyl, although singlet-singlet energy transfer should be exothermic.[33] The enone was 0.01 *M*. and biacetyl 0.33 *M*. in ethanol. The enone absorbed all the incident light at 350 nm, and no fluorescence from the biacetyl at 464 nm[34] was observed.

Thus, while we note that certain aromatic ketones do have active S_1 states in solution,[35] the data discussed so far for 3-phenyl-2-cyclohexenone are reminiscent of benzophenone or 2-cyclohexenones,[2] where intersystem crossing is rapid resulting in triplet reactions. A further point in support of enone T_1 as addendum is the ability of biacetyl to *sensitize* the addition to cyclopentene (see Experimental Section) with a quantum yield of 0.14 at 0.84 *M* cyclopentene, in methanol.[36] The biacetyl is apparently acting as a triplet sensitizer here since the enone quenches the phosphorescence of biacetyl, while hardly affecting the fluorescence.

Finally, we note that the long lifetime (low k_d) derived from the DBN quenching experiments for the enone is consistent with a reactive T_1 state. The value of k_d is lower than for 2-cyclohexenones in general, which have values in the range 10^7-10^8 sec^{-1}, while 3-phenyl-2-cyclohexenone has $k_d = 0.63 \times 10^6$ sec^{-1}. The latter is actually in the range of many aromatic compounds[37] which is consistent with the π-π^* type phosphorescence emission and corresponding low T_1 energy (54 kcal/mol) of this enone.

Reasons for Inefficiency in the Sensitized Reaction. The lower efficiency of the sensitized reaction compared with that of the direct irradiation was previously explained by invoking different excited states in the two reactions.[6] However, it appears that the enone T_1 is involved in both cases. It has also been suggested that the difference between the two reactions could be due to the different lifetimes of the enone T_1 and sensitizer triplet.[38] This explanation is probably incorrect, for inefficiency in the sensitized case due to sensitizer lifetime could not affect the slope of the dilution plot (Figures 1 and 2) without affecting the intercept; yet the intercepts in the two plots are equal.[39]

Two processes can, however, be invoked to explain the observed kinetics. The first is reverse energy transfer from the enone T_1 to sensitizer[40] (Michler's ketone), as follows:

$$\text{sensitizer } T_1 + \text{Enone} \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} \text{Sensitizer} + \text{Enone } T_1 \tag{9}$$

$$\text{enone } T_1 + \text{TME} \longrightarrow \text{COMPLEX} \tag{4}$$

From equations 4 and 9, it can be seen that, if k_{-s} is significant, then reverse transfer will compete with the reaction of enone T_1 with TME, except at infinite TME concentration. Thus, the different slopes but equal intercepts in Figures 1 and 2 can be readily understood.

The relationship between quantum yield and olefin (TME) concentration in the reversibly sensitized reaction is given by eq 10.

$$\frac{1}{\Phi} = \frac{1}{P}\left[\left(1 + \frac{k_d}{k_0[\text{TME}]}\right)\left(1 + \frac{k_d'}{k_s[\text{E}]} + \frac{k_d' k_{-s}[\text{S}]}{k_r k_s[\text{E}][\text{TME}]}\right)\right] \tag{10}$$

Here P is the fraction of complexes giving product **3**, k_d' is the decay rate constant of the sensitizer triplet, and [E], [TME], and [S] represent the concentrations of enone, olefin, and sensitizer, respectively; the other parameters are defined in eq 1-9. For the sensitized process, the ratio of slope/intercept (Figure 2) is found to be 2.41 and is given by:

$$\frac{\text{slope}}{\text{intercept}} = \frac{k_d}{k_c} + \frac{k_d' k_{-s}[\text{S}]}{k_c k_s[\text{E}]} = 2.41$$

The ratio slope/intercept for the direct irradiation (Figure 1) is $k_d/k_c = 0.41$. Therefore,

$$\frac{k_d' k_{-s}[\text{S}]}{k_c k_s[\text{E}]} = 2$$

and substituting values for k_c, k_d', [S], and [E], we can estimate the ratio $k_{-s}/k_s \sim 1$-10 (depending on the value used for sensitizer lifetime). Such a large ratio for k_{-s}/k_s is not consistent with the triplet energies of sensitizer (60-61 kcal/mol for Michler's ketone) and enone (55 kcal/mol). The latter could be lower than the actual value for enone T_1 energy, if the O-O band in the phosphorescence is not observed. However, this energy is probably correct since biacetyl sensitizes the reaction, apparently via the triplet.

The second process which could give the observed kinetics is chemical quenching of the enone T_1 by the ground state sensitizer,[41] as shown in equation 11.

$$\begin{aligned} &\text{Enone } T_t + \text{Sensitizer} \xrightarrow{k_{\text{CHEM}}} (\text{CHEM}) \\ &(\text{CHEM}) \longrightarrow \text{Enone} + \text{Sensitizer} \end{aligned} \tag{11}$$

This bimolecular process, which could lead to an exciplex (CHEM) or an ion pair, would compete with olefin for the enone triplet and would become insignificant at infinite olefin concentration. From the difference in slopes of the plots in Figures 1 and 2, k_{CHEM} can be calculated for each sensitizer used. The value for Michler's ketone is 1.3 × 10^9 M^{-1} sec^{-1} and, for 2-acetonaphthone, it is 6.4 × 10^7 M^{-1} sec^{-1}. These rate constants are comparable to values in the literature for similar processes.[41] Thus, we propose that chemical quenching of the enone triplet by the sensitizer is responsible for the lower quantum yields in the sensitized addition, in that it is consistent with the rate constants and excitation energies involved.

In an attempt to establish the correctness, or otherwise, of the above scheme, the quantum yield of adduct formation with TME in the sensitized addition, was measured as a function of sensitizer (Michler's ketone) concentration. Relative quantum yields were measured in the Rayonet apparatus, with irradiation at 350 nm. The solutions absorbed strongly so that all the incident light was absorbed, regardless of the sensitizer concentration, and a negligible fraction of light was absorbed by the enone.

If the above scheme is correct, eq 8a should relate the quantum yield of addition (Φ) and the sensitizer (MK) (now also acting as a *quencher*) concentration.

$$\frac{1}{\Phi} = \frac{(k_r + k_{diss})}{ak_r}\left(1 + \frac{k_d}{k_c[\text{TME}]} + \frac{k_{\text{CHEM}}[\text{MK}]}{k_c[\text{TME}]}\right) \tag{8a}$$

The results of this study are shown in Table IV and Figure 5.

The linear relationship between Φ^{-1} and [MK] is in excellent agreement with eq 8a. Further, the intercept of this plot (Figure 5) corresponds to the quantum yield at zero quencher ([MK]) concentration, at the [TME] concentration used (0.33 *M*). From the measurement of quantum yields in the direct irradiation, the latter was found to be

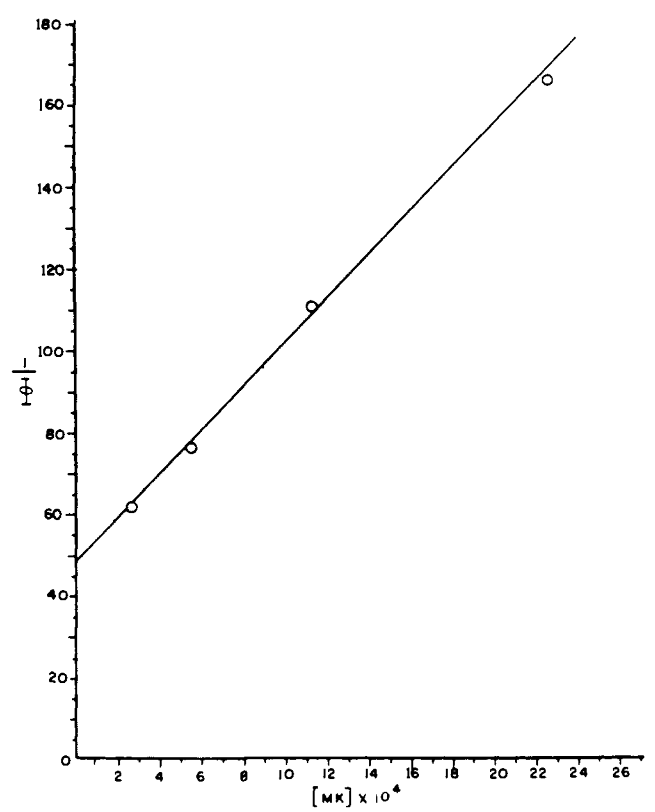


Figure 5. Dependence of enone-TME addition on Michler's ketone concentration in sensitized reaction. Intercept = 48.2 Einsteins M^{-1}; slope = 5.33×10^4 Einsteins.

Table IV. Dependence of Sensitized Quantum Yield[a] on Michler's Ketone Concentration

Sample	[MK], $M \times 10^3$	Quantum yield (Φ), absolute	Φ^{-1}
1	2.246	0.006	166
2	1.123	0.009	111
3	0.562	0.013	77
4	0.281	0.016	63

[a] Yields are for the enone–TME addition in *tert*-butyl alcohol. TME concentration was 0.33 M, for which the absolute quantum yield was known for 2.246×10^{-3} M MK (sample 1), see Table II. Enone was 0.005 M.

0.022 (Table I), and the intercept of Figure 5 gives 0.021. From the slope in Figure 5 (5.33×10^4 M^{-1}), using $k_c = 2.24 \times 10^6$ M^{-1} sec^{-1}, $k_{CHEM} = 1.27 \times 10^9$ M^{-1} sec^{-1}, which is in close agreement with the value derived from the slopes of the dilution plots in Figures 1 and 2, i.e., 1.3×10^9 M^{-1} sec^{-1}. Thus, the quantum yield dependence on [MK] concentration is qualitatively and quantitatively in full agreement with the above scheme, in which the Michler's ketone acts as a *sensitizer and as a quencher*.

One important point remains to be explained. That is, if the quenching of enone triplet by MK is diffusion controlled, and if the initial sensitization of enone by MK triplet is also diffusion controlled (see above), then the reaction should be very inefficient even at infinite TME concentration. This, of course, is because each enone triplet, formed by collisional sensitization, would immediately be quenched by the proximal ground state MK molecule, according to eq 11.

It is possible, however, that the sensitization by Michler's ketone (as proposed in eq 9), occurs in fact over a greater distance than the usual collisional triplet-triplet sensitization requires. For example, the highly allowed transitions in the absorption spectra of MK (ϵ 3.3×10^4) and of the enone (ϵ 1.9×10^4) and the fact that these bands overlap might allow sensitization by singlet-singlet energy transfer via a Forster mechanism.[42] Further work is needed, however, to pinpoint the reason for the efficient sensitization by Michler's ketone in this reaction.

Finally, we note that quenching of the enone triplet by the amino compound (Michler's ketone) does have precedent in the work of Cohen and Guttenplan[41c] and, indeed, some of the quenchers (amines) used by these authors did quench benzophenone and fluorenone triplets at high rates.

The Metastable Intermediate. Exciplex or Biradical? Schemes involving triplet exciplexes and 1,4 biradicals have been advanced to explain the products and kinetics of 2-cyclohexenone-olefin photoadditions.[3-5] Thus, there are good reasons for considering these intermediates[43] in a mechanism for the present addition. First, we note that the limiting quantum yield (Φ_{lim}), from the intercept of Figure 1, has the value[44] of 0.05, which signifies that an important energy-wasting process involves the olefin. Further, since the direct and sensitized reactions have the same Φ_{lim}, the energy-wasting process is presumably the same in both cases. We also note that the limiting quantum yield is unaffected by 10^{-3} M DBN, which means that, if a triplet exciplex is involved, its lifetime must be shorter than 0.5×10^{-7} sec.[47,48] Finally, the rate constant[49] for the enone T_1-TME reaction (process 3 in Scheme I), as derived from the DBN quenching study, is 1.56×10^6 M^{-1} sec^{-1}. This rate constant is comparable with the corresponding values for 2-cyclohexenone additions,[4b] which are in the range 10^7–10^8 M^{-1} sec^{-1}, and suggests that the same primary step is involved in all cases—formation of a triplet complex.

As with the 2-cyclohexenone additions generally,[3-6] there is evidence that 3-phenyl-2-cyclohexenone additions also involve biradical intermediates, e.g., **2.** For example, the dimerization of **1** affords the head-to-head dimer only,[12] as would be expected on the grounds of radical stability. In contrast, 2-cyclohexenone gives both regioisomers on dimerization.[50] In the present study, it was found that irradiation of 3-phenyl-2-cyclohexenone and *cis*-but-2-ene gave a much higher yield of *trans*-but-2-ene than of the addition products. The details are given in the Experimental Section, and the experiment was not performed quantitatively, but the yield of *trans*-but-2-ene is estimated to be about 300 times the adduct yield. This result strongly suggests that the species which determines the limiting quantum yields in the addition of **1** and olefins may indeed be a 1,4 biradical, such as **2.**[51]

Summary and Conclusions

3-Phenyl-2-cyclohexenone resembles 2-cyclohexenones in general[4b] in that it adds to olefins via T_1. Michler's ketone sensitization of 3-phenyl-2-cyclohexenone-TME addition gave a dilution plot with a larger slope than the plot for the direct addition. The difference is explained by chemical quenching of the enone T_1 by Michler's ketone. This explanation is different from earlier schemes proposed to explain inefficiency on sensitization by compounds with π-π^* triplets[40] and should be borne in mind as a possible "complication in photosensitized reactions". The above addition is proposed to involve a triplet olefin exciplex, and a 1,4 biradical, both of which may react to give product or decay to give ground state reactants.[52] These processes could account for the high intercept in the dilution plots.

Experimental Section

Materials. All solvents and reagents for photoaddition reactions were distilled before use. Cyclopentene (Aldrich Reagent) was distilled under nitrogen, bp 44-45°C, and was used immediately. Bicyclo[2.2.1]hept-2-ene (norbornene, Aldrich Reagent) was used without further purification. Tetramethylethylene (Columbia Organic Chemicals) was distilled through a 12-in. Vigreux column under nitrogen, bp 72-73°C. It was redistilled through a 12-in. column packed with glass helices. *cis*- and *trans*-but-2-enes were obtained from Matheson Coleman and Bell of Canada, Ltd. 4,4-Bis(dimethylamino)benzophenone, Michler's ketone (Matheson Coleman and Bell), crystallized twice from benzene was pale yellow, mp 173-173.5°C. 2-Acetonaphthone (Eastman Organic Chemicals) was crystallized from absolute ethanol, mp 53-53.5°C. Benzophenone, once crystallized from ethyl alcohol, had mp 48-49°C. Biacetyl (Matheson Coleman and Bell, chromatoquality reagent) distilled many times through a 6-in. Vigreux column, bp 88-89°C, was used immediately. Naphthalene (Baker Analyzed Reagent) was crystallized from ethanol, mp 80-81°C. *tert*-Butyl alcohol was Baker Analyzed Reagent, bp 82-83°C. Methanol was Mallinckrodt Analytical Reagent, bp 64.5-65°C. Benzene used for column chromatography was Mallinckrodt Analytical Reagent.

3-Ethoxycyclohex-2-enone was prepared by the method of Gannon and House;[53] the boiling point was 49-52°C (0.075-0.1 mm/Hg) [lit.[53] 66-68.5°C (0.4 mm/Hg)]. From this, 3-phenylcyclohex-2-enone was prepared by the method of Woods and Tucker,[54] and Allen and Converse;[55] the pale yellow solid was distilled [135-145°C (1 mm/Hg)], and the material was chromatographed on silica gel and finally was crystallized from ethanol-light petroleum, bp 30-60° and had mp 63.5-64°. Di-*tert*-butyl nitroxide was prepared by the method of Hoffmann et al.[56] and had bp 52-54°C (10 mm/Hg) [lit.[56] 60°C (11 mm/Hg)]. Potassium ferrioxalate [$K_3Fe(C_2O_4)_3$], used in the actinometry, was prepared by the method of Parker and Hatchard.[57]

Chromatography. Silica gel, Grace, Grade 923 (100-200 mesh) or MN silica gel G (Macherey, Nagel and Co.) was used for column chromatography. Thin layer chromatography was conducted using silica gel coated sheets with fluorescent indicator (Eastman Organic Chemicals) or MN silica gel G with fluorescent indicator (Macherey, Nagel and Co.) coated on glass plates. Analytical vapor phase chromatography (VPC) was performed on a Varian-Aerograph Model 204-B dual column instrument, having flame ionization detectors. Peak areas were determined using Varian Model 476 electronic digital integrator. The following columns were used using helium as the carrier gas at 30 ml/min: column A, 5 ft × ⅛ in. 4% QF 1 on 60-70 Diatoport; column B, 3 ft × ⅛ in. 10% FFAP on 60-70 Chromosorb W. Preparative VPC was conducted on a Varian-Aerograph Model 200 dual control instrument with thermal conductivity detectors. The following columns were used with a helium flow of 60-70 ml/min: column C, 10 ft × 0.25 in. 31% SE 550 on Firebrick; column D, 4 ft × ⅜ in. 20% FFAP on 45-60 Chromosorb W. Melting points were determined on a Reichert hot stage and are uncorrected. Elemental analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Spectra. Nuclear magnetic resonance spectra were recorded with a Varian T-60, A-60, or HA-100 instrument; spectrograde carbon tetrachloride was the usual solvent with tetramethylsilane as the internal standard. Chemical shifts are given in parts per million (ppm) downfield from the standard.

Infrared spectra were run on a Beckman IR-5 or a Perkin-Elmer Model 337 instrument. Spectrograde carbon tetrachloride (Fisher "spectroanalyzed" grade) was the usual solvent. Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer; 95% ethyl alcohol or methyl alcohol was the usual solvent, unless specified. Mass spectra were run on a Hitachi Perkin-Elmer MRU6A instrument. Emission spectra were recorded with an Aminco-Bowman spectrofluorometer. Optical density measurements for quantum yield determinations were performed using a Bausch & Lomb precision spectrophotometer.

Photoaddition of 3-Phenylcyclohex-2-enone and Tetramethylethylene. A solution of 3-phenylcyclohex-2-enone (3.44 g, 0.02 mol) and tetramethylethylene (16.0 g, 0.19 mol) in *tert*-butyl alcohol (375 ml) and methanol (25 ml) was irradiated with a Hanovia Type L 450-W medium-pressure mercury arc lamp, fitted with a Pyrex sleeve, placed in a water-cooled quartz immersion apparatus. The photolysis solution was deoxygenated by bubbling argon through the solution before photolysis; a slight positive pressure of argon was maintained during irradiation.

The reaction was about 95% complete in 5 hr as estimated by VPC analysis (column A, 185°C). The analysis showed the formation of a single product with a retention time of 4 min. The solvent and the excess olefin were distilled, and white granular crystals were obtained, as well as a viscous oil. The residue was dissolved in ethyl alcohol and cooled in a Dry Ice-acetone mixture, and the crystals were filtered and dried (1.75 g). This was identified as the photodimer of 3-phenyl-2-cyclohexenone and had mp 200-201° (lit.[12] 204-205°), from ether-light petroleum.

The filtrate was concentrated and chromatographed on a 3 × 23 cm column of silica gel in benzene, and 200-ml fractions were collected. Fractions 1-5 were eluted with benzene; 6-10 with 0.5% ethyl acetate in benzene; 11-20 with 1.0%; 21-25 with 2.0%; 26 and 27 with 4.0%; and 28-30 with 8.0% ethyl acetate in benzene. Fractions 8-10 contained the photoadduct **3**. These fractions were combined and evaporated to give a yellow oil which was distilled in a short-path distillation set-up [bath temp 170-180°C (0.3 mm/Hg)]. The colorless distillate solidified to a waxy solid on keeping at −20°. After two sublimations at 1-mm pressure, the solid had mp 57-60°C. The VPC analysis (column A, 185°C) showed a single peak with retention time of 4 min. The infrared, NMR, and mass spectra confirmed the structure of the adduct. Anal. Calcd for $C_{18}H_{24}O$: C, 84.38; H, 9.38. Found: C, 84.47; H, 9.50.

Attempted Equilibration of Adduct 3. The photoadduct (0.050 g, 0.002 mol) was stirred with basic alumina (3.0 g) in ether (30 ml) for 40 hr at room temperature. The alumina was removed by filtration, and the solution was concentrated to give an oil (0.050 g). The NMR, infrared, mass spectral, and VPC analyses showed that there was no change after this treatment, confirming the cis 4-6 ring fusion in **3**.

Photostability of 3. The photoadduct (0.1 g, 0.0004 mol) in *tert*-butyl alcohol (70 ml) and methanol (5 ml) was irradiated through Pyrex with the Hanovia lamp for 4 hr. The spectra of the material were identical with those of a sample of **3**, before irradiation.

Photolysis of 3-Phenyl-2-cyclohexenone and Norbornene. Irradiation of 3-phenyl-2-cyclohexenone (0.301 g, 0.00175 mol) and norbornene (6.578 g, 0.070 mol) in *tert*-butyl alcohol (65 ml) and methanol (5 ml) with the Hanovia 450-W lamp for 2 hr in a Pyrex tube resulted in 96% reaction of 3-phenyl-2-cyclohexenone, as determined by VPC analysis on column 3 (245°). The VPC indicated three products, whose retention time and ratio were: 4.3 min, 1%; 5.0 min, 90% (**5**); and 7.5 min, 9% (**6**). After distillation of the solvent, chromatography of the photolysis mixture (580 mg) on a 3 × 27 cm column of silica gel, slurry packed in and eluted with benzene, yielded a mixture of two norbornene dimers in the first 2 × 100 ml fractions. Following two additional 100-ml fractions using benzene, the column was eluted with 400 ml of ether giving quantitative recovery. Fractions were monitored for the dimers by VPC on 10 ft × ⅛ in. of 10% Carbowax on 60-70 Chromosorb W at 185°. From the fractions eluted with ether, the major adduct (**5**) crystallized. Recrystallization from ether-light petroleum gave colorless plates, mp 87-88.5°. The infrared had absorption at 3.40, 5.88 (cis-fused cyclohexanone), 13.18, and 14.24 μ (monosubstituted benzene). The NMR showed a single proton resonance at 2.84 ppm (doublet) and complex aromatic resonance at 7.10 ppm. A molecular ion of *m/e* 266 (46), base peak *m/e* 173 (100), and strong peak *m/e* 144 (67) were exhibited in the mass spectrum. Anal. Calcd for $C_{19}H_{22}O$: C, 85.65; H, 8.32. Found: C, 85.58; H, 8.39. This adduct is tentatively assigned the structure 8β-phenyl-2β,8α,1α-tetracyclo[8.2.1.$0^{2,9}$.$O^{3,8}$]tridecan-4-one (**5**).[13]

From preparative VPC of the photolysis mixture on 5 ft × ⅜ in. of 20% FS 1265 on 45-60 Chromosorb W at 245°, compound **6** was obtained (retention time, 29 min). The infrared showed absorption at 3.41 and 14.25 μ (monosubstituted benzene). Complex aromatic (5 H) resonance at 7.17 ppm, single proton at 2.87 ppm, and two proton peak at 1.00 ppm characterized the NMR spectrum. Anal. Calcd for $C_{19}H_{22}O$: C, 85.65; H, 8.32. Found: C, 85.57; H, 8.40.

Photoaddition of 3-Phenyl-2-cyclohexenone and Norbornadiene. Irradiation of 3-phenyl-2-cyclohexenone (2.279 g, 0.0132 mol) and norbornadiene (Aldrich reagent, distilled before use) (26.86 g, 0.292 mol) in *tert*-butyl alcohol (375 ml) and methanol (20 ml) for 10 hr (Hanovia 450-W lamp, Pyrex filter) resulted in reaction of 98% of 3-phenyl-2-cyclohexenone, as determined by VPC (column B, 245°C). The VPC analysis showed that three major products were formed, with retention times: 6.5 min, **8**; 9.0 min, **9**; 11.5 min, **7**. They were in the ratio: 34:20:46.

After solvent distillation, 1.848 g of the residue was chromatographed on a 4 × 83 cm column of silica gel, slurry packed in benzene, and 200-ml fractions were collected. The column was eluted by successively increasing the percentage of ethyl acetate in benzene: 3.6 l. of 1%; 3.0 l. of 1.5%; 1.8 l. of 2%; 1.0 l. of 6%; 0.6 l. of 10%; and 1.2 l. of 20%. Fractions were monitored by infrared and VPC. Fraction 22 consisted mainly of **7** (526 mg), fractions 27-42 were mainly **8** (248 mg), and no fraction contained **9** as the major component. Recovery from the column was 1.655 g (90%).

Fraction 22 from chromatography was dissolved in ether-light petroleum, bp 30-60°C, from which crystalline **7** (180 mg) was obtained, mp 104.5-106.5°C. The infrared showed absorption at 5.85 (carbonyl), 13.31, and 14.15 μ (monosubstituted benzene). In the NMR spectrum, resonance at 6.87 ppm (5 H, aromatic protons) and 6.16 ppm (2 H, vinylic protons) was observed.

The mass spectrum had a molecular ion *m/e* 264 (73), base peak *m/e* 143 (100), and peak *m/e* 121 (53). The infrared and NMR spectra of compound **7** were shown to be unchanged after the following attempted equilibration. A solution of the adduct (35.0 mg) in 20 ml of ether was stirred with basic alumina (2.0 g) for 8 hr. This indicated that **7** has a cis-fused cyclohexanone ring. This component was formed in approximately 45% yield. Anal. Calcd for $C_{19}H_{20}O$: C, 86.30; H, 7.63%. Found: C, 86.40; H, 7.63%. This adduct **7** is tentatively assigned the cis-syn-cis-endo geometry, on the basis of NMR experiments.

Component **8** was separated from fractions 27-42 of the chromatography by VPC on column D at 245°, on which it had a retention time of 21 min. Crystallization from ether-light petroleum, bp 30-60°C, gave crystals, mp 75-83°C. The infrared showed bands at 3.41, 5.88 (cis-fused 6-4 ring system), 13.20, and 14.24 μ (monosubstituted benzene). Also NMR resonance at 7.12 ppm (5 H, aromatic protons), 5.92 ppm (2 H, vinylic proton triplet), and 0.98 ppm (2 H, endocyclic protons) indicated a cyclobutane adduct. This product was formed in approximately 34% yield as indicated by VPC and column chromatography and is tentatively assigned the cis-anti-cis-exo geometry. Anal. Calcd for $C_{19}H_{20}O$: C, 86.30; H, 7.63. Found: C, 86.36; H, 7.74.

Hydrogenation of 8. A solution of **8** (50 mg, 0.189 mmol) in 95% ethanol (75 ml) was hydrogenated at 55 psi with palladium, 5% on charcoal [Englehard Industries, Inc. P (6.4 mg)] for 24 hr at 20°. The catalyst was filtered, and the solution on evaporation gave crystals, mp 86-88°, identical with the major product **5** from the norbornene addition, according to mixture melting point and NMR and infrared spectra. Anal. Calcd for $C_{19}H_{22}O$: C, 85.65; H, 8.32. Found: C, 85.45; H, 8.39.

Norbornene Dimerization in the Photoaddition of 3-Phenylcyclohex-2-enone and Norbornene. A solution of 3-phenylcyclohex-2-enone (1.0 g, 0.0058 mol), and norbornene (18 g, 0.19 mol) in *tert*-butyl alcohol (55 ml) and methanol (5 ml) was irradiated in a Rayonet photochemical reactor containing 16 RPR 3500 Å lamps. About 85% of the enone disappeared in 13 hr. The residue (~2 g) was chromatographed on a 3 × 15 cm column of silica gel slurry packed in benzene. Two 200-ml fractions were collected with benzene as the eluant. The norbornene dimers (0.075 g) came off in those fractions. VPC analysis (column B, 105°C) showed two peaks in the ratio 9:1 (retention times, 2.5 and 3.5 min). Endo-trans-exo dimer was collected by preparative VPC (column D, 180°C). The dimer was a waxy solid with mp 36-38°C (lit.[12a] 38-39°C). The mass spectrum showed a molecular ion peak at *m/e* 188.

Effect of Filtering the Incident Light on the Formation of the Norbornene Dimers. The beam from the "Wisconsin Black Box" (see above) was filtered through Pyrex and focused into a cylindrical cell, 26 ml in volume, using a mirror and lens collimating system. The light was further filtered by a Corning 0-54 glass filter (cut-off at 300 nm). The cell contained enone (5.3×10^{-2} *M*) and norbornene (2.02 *M*) in *tert*-butyl alcohol (26 ml). The above filter system ensured that no light was absorbed by adducts **5** and **6**.

Irradiation for 6 hr gave 55% conversion of enone to adducts **5** and **6** (VPC assay). However, the amount of norbornene dimers formed was almost undetectable by VPC, and we conclude that the latter are formed in the earlier experiments via sensitization by the mixed addition products **5** and **6**.

Irradiation of 3-Phenylcyclohex-2-enone and *cis*-But-2-ene. Cis-Trans Isomerization of Butene. A solution of 3-phenylcyclohex-2-enone (1.0 g, 0.0058 mol) in 99% ethyl alcohol (300 ml) in a photolysis vessel was deoxygenated by bubbling argon for 30 min. The solution was cooled to −15 to −12°C with ice-salt mixture. *cis*-But-2-ene (15 g, 0.27 mol) was added to the solution, and the mixture was irradiated for 2.5 hr. About 10 ml of this photolysis solution was withdrawn and injected into an evacuated flask and allowed to come to room temperature. The vapors in the flask were then drawn into a gas syringe and analyzed by VPC (column C, 45°C), which showed the presence of about 9% of *trans*-but-2-ene. The reaction corresponded to about 2% conversion of enone, as estimated by VPC (column A, 190°C).

Table V. Triplet Sensitization of Enone-Olefin Additions

Run[a]	Olefin, *M*	Sensitizer, (concn, *M*)	Irradiation time, hr	% reaction
1[b]	TME (0.33)		1	76
1	TME (0.33)	Michler's ketone (0.0025)	1	22
1	TME (0.33)	2-Acetonaphthone	1	20
2[b]	Cyclopentene		3	95
2	Cyclopentene (0.5)	Michler's ketone (0.005)	3	20

[a] Samples in the same run were irradiated simultaneously. The Rayonet apparatus with 350-nm lamps was used. [b] Enone was 0.005 *M* in run 1, 0.015 *M* in run 2.

Triplet sensitized photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene. A solution of 3-phenylcyclohex-2-enone (0.129 g, 0.0075 mol) and tetramethylethylene (4.2 g, 0.05 mol) in *tert*-butyl alcohol (total volume 75 ml) was equally divided in three Pyrex tubes. To one 25 ml of 0.005 *M* Michler's ketone in *tert*-butyl alcohol was added; to another was added 25 ml of 0.1 *M* 2-acetonaphthone. The volume in the third tube was taken to 50 ml with *tert*-butyl alcohol. The solutions were deoxygenated with argon, mounted on a rotating turntable, and irradiated with 350-nm lamps (16) in a rayonet photochemical reactor for 1 hr. The extent of conversion of the enone was determined by VPC (column A, 185°C). The results are given in Table V.

Isolation and Identification of 3 from the Sensitized Photoaddition. A solution of 3-phenylcyclohex-2-enone (0.2 g, 0.00116 mol), tetramethylethylene (7.5 g, 0.089 mol), and Michler's ketone (0.075 g, 0.00028 mol) in *tert*-butyl alcohol (50 ml) was irradiated as described previously. The reaction was 95% complete in 8 hr. The photolysis mixture was concentrated, and residue was chromatographed as described for the direct irradiation. VPC, NMR, infrared, and mass spectroscopic analyses confirmed the product to be identical with the adduct **3** from the direct reaction.

A similar experiment was conducted with the enone (0.2 g, 0.00116 mol), tetramethylethylene (7.5 g, 0.089 mol), and 2-acetonaphthone (2.015 g, 0.0119 mol), and the same product was obtained.

Determination of Absolute Quantum Yields. An apparatus similar to the "Wisconsin Black Box" was used.[58] The light source was a Phillips SP 500-W high-pressure mercury arc lamp giving directed radiation, placed at the focus (12 cm) of a quartz lens 11 cm in diameter. This water-cooled lamp is an economical source of uv radiation. The appropriate wavelength band of the mercury arc spectrum was isolated by various combinations of filter solutions; these were contained in a cell divided into three compartments each 11.7 cm in diameter and 5 cm in path length (capacity 575 ml) and were cooled internally with a cooling coil. The compartments had quartz windows, and neoprene gaskets were used to give liquid-tight seals. The filter solutions used were different for various quantum yield determinations, and hence the details are given separately for each case. For quantum yield measurements, a cell 11.5 cm in diameter with two compartments each 5 cm in length also with quartz windows was used. Viton[59] gaskets were used to give the seal. The compartments had provision for bubbling argon for deoxygenation and one had a thermistor probe for controlling temperature. The temperature of the photolysis solution was controlled by a Yellow Springs Instruments Model 63 Thermistemp temperature controller. Hot or cold water was circulated through internal coils, as needed to provide heating or cooling, respectively.

The amount of the enone-olefin adducts was determined by VPC using appropriate internal standards. The calibration of the VPC was done periodically using known ratios of the internal standard and the adduct.

Actinometry was performed with the potassium ferrioxalate system. The concentration of potassium ferrioxalate used depended on the wavelength, and the recommendations of Hatchard and Parker[57] were followed.

Each quantum yield determination required three irradiations: the first and third had actinometer in both cells; the second had reaction solution in cell 1 (nearest lamp) and actinometer in cell 2. The first and the third irradiations, which generally differed by less than 5%, were averaged to calculate the light output per unit time of the lamp, which was used to determine the total amount of light incident on the reaction solution. The amount of light transmitted by the latter was calculated from the change in the actinometer solution in cell 2 during the second irradiation. Fresh actinometer solutions were used for each irradiation. Both the reaction and actinometer solutions were stirred mechanically during irradiation.

Quantum Yield of Photoaddition of 3-Phenylcyclohex-2-enone and Olefins. The filter used in these determinations had maximum transmittance of 35% at 330 nm and 0% at 285 and 375 nm. Some transmittance (ca. 0.3% T) was observed at 430 mμ. The filter consisted of (1) a Pyrex plate 3 mm thick nearest lamp, (2) 5 cm path length of a solution of $CoSO_4{\cdot}7H_2O$ (160 g) and $NiSO_4{\cdot}6H_2O$ (60 g) per liter of 3 *N* H_2SO_4, (3) 5 cm of a solution of $SnCl_2{\cdot}2H_2O$ (1.6 per liter of 15% HCl, and (4) 5 cm of distilled water. The $SnCl_2$ solution was freshly prepared before each run. Quantum yields were measured for 3-phenyl-2-cyclohexenone (0.005 *M*) and TME (0.33 *M*) in *tert*-butyl alcohol. Benzophenone was used as internal standard (added after irradiation) for VPC assay (column A, 185°) of formation of **3**.

In a typical run, the enone-TME solution was irradiated for 200 min at 27°, and 13.9 mEinsteins of light was absorbed, and 0.3084 mmol of **3** was formed, giving a quantum yield of 0.022 mol Einstein^{-1}. In the 3-phenyl-2-cyclohexenone-cyclopentene addition, the adducts were assayed by VPC (column B, 195°) using *p*-bromobenzophenone as internal standard. The adducts were recovered quantitatively by isolation techniques described previously.[7] In a typical run, enone (0.580 g, 3.37 mmol) and cyclopentene (32.7 g, 0.495 mmol) in methanol (total volume, 575 ml) were irradiated for 180 min, 15.5 mEinsteins of light was absorbed, and 0.102 g (0.425 mmol) of adduct was formed. This quantum yield is 0.027 mol Einstein^{-1}. The quantum yield of decomposition of ferrioxalate at this wavelength was taken as 1.23.

Quantum Yields of Sensitized Reactions. The same filter was used with Michler's ketone and 2-acetonaphthone sensitizers and had transmittance maximum at 350 nm (26%) and zero transmittance at 325 nm. Some light (~0.5%) was transmitted from 390-425 nm. The filter consisted of (1) a Pyrex plate, 3 mm thick, nearest lamp, (2) 5 cm of $CoSO_4{\cdot}7H_2O$ (160 g) and $NiSO_4{\cdot}6H_2O$ (12 g) per liter of 0.1 *N* H_2SO_4, (3) 5 cms of saturated $SnCl_2{\cdot}2H_2O$ in 15% HCl (at 20°), and (4) distilled water, 5 cm. Light absorbed by the enone was <2% with Michler's ketone. Assay was by VPC as in the direct reaction. In a typical run, enone (0.005 *M*), TME (0.33 *M*), and Michler's ketone (0.0024 *M*) in *tert*-butyl alcohol were irradiated for 312 min; 30.5 mEinsteins of light was absorbed, and 1.93×10^{-4} mol of **3** was formed, giving a quantum yield of 6.2×10^{-3}. Results of other runs are given in Table II.

Sensitization by biacetyl was also studied, with cyclopentene as substrate. Irradiation was at 430 nm, and the filter was (1) the 3 mm Pyrex plate, (2) 5 cm path of 8.8 g of $CuSO_4{\cdot}5H_2O$ per liter of 2.7 *M* aqueous NH_3, (3) 5 cm path of 150 g of $NaNO_2$ per liter of H_2O, and (4) 5 cm path of distilled water. The filter had maximum transmittance at 430 nm (70%) and zero transmittance at 405 and 505 nm. The potassium ferrioxalate actinometer solution was 0.05 *M*, and its quantum yield of decomposition was taken to be 1.03 at this wavelength. In 180 min of irradiation, a solution of biacetyl (0.174 *M*), enone (0.00575 *M*), and cyclopentene (0.835 *M*) absorbed 56.6 mEinsteins and gave 0.196 g (0.82 mmol) of adducts, giving a quantum yield of 0.014. A similar experiment with TME gave a very low yield of **3**, with several unidentified side-products.

Determination of Relative Quantum Yields. Relative quantum yields of photoaddition as a function of TME concentration were measured using a Rayonet photochemical reactor with 16 RPR 350-nm lamps, and a turntable arrangement by which the sample tubes could be rotated during irradiation. Pyrex tubes (23 × 2.5 cm) were used for photolysis. Exactly 50-ml solutions were taken in each tube, such that each solution was 0.005 *M* in enone, and different concentrations (0.05, 0.10, 0.20, 0.33, 1.00, and 2.00 *M*) in tetramethylethylene. The solutions were then deoxygenated by three cycles of freeze-pump-thaw, and the tubes were sealed under nitrogen. The time of irradiation was so chosen as to give a suitable range of conversion. The amount of photoadduct **3** in each tube was determined by VPC, using benzophenone as the internal standard. Since all the tubes were of the same dimensions and contained exactly the same volume of solution, and the concentration of the enone was the same in all, it was assumed that the light absorbed in each tube was the same so that the amount of product was proportional to the quantum yield.

The absolute quantum yields could be determined using the previously measured value of 0.022 for 0.005 *M* enone and 0.33 *M* tetramethylethylene. Experiments using Michler's ketone as sensitizer or di-*tert*-butyl nitroxide as quencher were similarly conducted.

Emission Spectroscopy. The phosphorescence spectrum of 3-phenyl-2-cyclohexenone was recorded at 77 K in a glass of ethanol: ether (2:1). The spectrum showed maxima at 515 and 550 nm.

Quenching of Biacetyl Phosphorescence. Excitation of biacetyl in deoxygenated ethanol at ambient temperature, using 436-nm radiation, gives the well-known fluorescence and phosphorescence of biacetyl at 470 and 520 nm, respectively. Addition of 0.32, 0.16, and 0.08 *M* 3-phenyl-2-cyclohexenone reduced the biacetyl fluorescence intensity to some extent but totally quenched the phosphorescence at 520 nm.

Attempted Sensitization of Biacetyl Fluorescence by 3-Phenyl-2-cyclohexenone. A solution of the enone (0.01 *M*) and biacetyl (0.3 *M*) in methanol was excited at 354 nm, and the fluorescence of biacetyl was monitored at 464 nm. No fluorescence was observed.

Oxime of 3-Phenyl-2-cyclohexenone. This was prepared by the general procedure using pyridine described in Shriner, Fuson, and Curtin,[60] and had mp 123-126°, (lit.[54] 113.5-118°). The material was most conveniently purified by chromatography on a short silica gel column, using benzene as eluant. Anal. Calcd for $C_{12}H_{13}ON$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.86; H, 6.95; N, 7.53.

Acknowledgments. We thank Mr. W. Dyba for help with the preparative work and Dr. C. Manning for assistance with the experiment in which Michler's ketone concentration was varied. We also acknowledge a referee, who stressed that the latter experiment should be performed. We gratefully acknowledge financial support from the National Research Council of Canada.

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where τ is the radiative lifetime, $\bar{\nu}$ the frequency (cm^{-1}) and ϵ the extinction coefficient at the maximum, and $\Delta\bar{\nu}_{1/2}$ the band width at half maximum intensity. See M. Orchin and H. H. Jaffe, "Symmetry, Orbitals and Spectra", Wiley-Interscience, New York, N.Y., 1971, p 306.

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(37) For example, T_1 lifetimes of biphenyl and naphthalene are 3.04×10^{-5} and 7.35×10^{-5} sec, respectively [F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963)]; T_1 lifetime of fluorenone is reported as 4.5×10^{-6} sec [S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968)].

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(42) For a discussion of Forster theory, see J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970, p 568, and references cited.

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(49) We recognize that the exciplex is probably formed reversibly, and that a more detailed kinetic analysis could be used (see, for example, ref 43b). However, the simple analysis used here is sufficient to support our conclusions.

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