# The Photocycloaddition of Fluorenone to Dimethyl-N-(cyclohexyl)ketenimine. Evidence for both Singlet and Triplet Reactions

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Abstract: The photocycloaddition of fluorenone to dimethyl-N-(cyclohexyl)ketenimine at room temperature in benzene solution was studied. Quenching experiments with di-*t*-butylnitroxide (DTBN), coupled with a study of the quenching of the fluorenone fluorescence by DTBN and the ketenimine, allowed a separation of the reaction into parts involving the singlet and triplet states of fluorenone. The singlet reaction is believed to proceed by way of complex formation with the ketenimine. A kinetic analysis indicates a limiting quantum yield of ~0.6. A similarly derived rate constant for the cycloaddition between fluorenone triplet and the ketenimine is almost within an order of magnitude of the diffusion limit. An additional deactivation process between the complex and ketenimine is proposed to account for the dramatic decrease in the quantum yield for the singlet reaction at the higher ketenimine concentrations.

The photocycloadditions of aldehydes and ketones to olefins to give oxetanes (the Paterno–Büchi reaction)[2] generally proceed by way of a low-lying n–π^* triplet state in the carbonyl compound.[3] Recently, however, Yang and coworkers have shown that the reactive state in the cycloaddition of anthraldehyde to 2,3-dimethyl-2-butene is an upper singlet or, more likely, an upper triplet n–π^* state[4] while Turro and coworkers suggest that acetone reacts with *trans*-1,2-dicyanoethylene through a singlet-state complex.[5] The Paterno–Büchi reaction has been extended to allenes[6] and ketenimines (1).[7] With the latter, photoadducts of both the α and β orientation have been observed.[7–9]
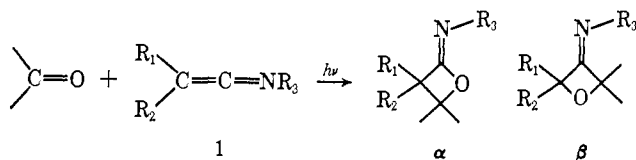
We have shown that in the benzophenone–ketenimine reaction: (i) the reactive state of the ketone is the triplet, (ii) the cycloaddition step is within an order of magnitude of diffusion control, and (iii) energy transfer from

benzophenone triplet to ground-state ketenimine competes with the cycloaddition step as aryl groups are substituted into the ketenimine structure.[8] With three aryl groups in the structure (1, $R_1 = R_2 = R_3 = C_6H_5$), energy transfer occurs to the exclusion of cycloaddition.

In contrast, fluorenone readily reacts with aryl as well as alkyl ketenimines.[9b] Preliminary work on the photocycloaddition of fluorenone to dimethyl-N-(cyclohexyl)-ketenimine (1, $R_1 = R_2 = CH_3$, $R_3 = C_6H_{12}$) showed that (i) an adduct of the α orientation is formed,[9b] (ii) the cycloaddition to some extent involved the triplet state of fluorenone, (iii) the cycloaddition step proceeded at a rate close to the diffusion limit, and (iv) at higher concentrations of ketenimine, the quantum efficiency of adduct formation dramatically decreased.[9a]

We now wish to report on further studies on this system which allow a refinement of our preliminary kinetic data and which indicate that adduct formation results from a *fluorenone singlet*– as well as *fluorenone triplet*–*ketenimine interaction.*

Results

Dimethyl-N-(cyclohexyl)ketenimine (2) was prepared as previously described.[8] Degassed and sealed Pyrex ampoules containing benzene solutions of 0.60 or 1.0 M fluorenone, variable concentrations of 2, and with and without variable concentrations of di-*t*-butylnitroxide (DTBN)[10,11] were irradiated along with actinometer tubes (benzophenone–benzhydrol[13,14]) in a rotat-

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(2) G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **78**, 876 (1956).

(3) (a) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (b) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964).

(4) (a) N. C. Yang, R. Loeschen, and D. Mitchell, *J. Am. Chem. Soc.*, **89**, 5465 (1967); (b) N. C. Yang and R. L. Loeschen, *Tetrahedron Letters*, 2571 (1968).

(5) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Am. Chem. Soc.*, **90**, 3274 (1968).

(6) (a) D. R. Arnold and A. H. Glick, *Chem. Commun.*, 813 (1966); (b) H. Gotthardt, R. Steinmetz, and G. S. Hammond, *ibid.*, 480 (1967).

(7) L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1887 (1964).

(8) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 598 (1967).

(9) (a) L. A. Singer and G. A. Davis, *ibid.*, **89**, 158 (1967); (b) *ibid.*, **89**, 941 (1967).

(10) A. K. Hoffman, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 639 (1964).

(11) We assume that DTBN quenches the triplet state of fluorenone at a diffusion-controlled rate. Previously, we noted that DTBN and naphthalene quench the benzophenone triplet with the same efficiency (G. A. Davis, unpublished results). The naphthalene quenching reaction is believed to be a diffusion-controlled process.[12]

(12) W. M. Moore and M. Keetchum, *ibid.*, **84**, 1368 (1962).

(13) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

(14) Although the isolated yield of adduct is 74%,[9b] infrared analysis of the crude reaction mixture with an adduct calibration curve indicates a 96% yield.

Table I. Quenching of the Fluorenone-Dimethyl-N-(cyclohexyl)ketenimine Reaction by DTBN[a]

| 0.010 M ketenimine | | | 0.020 M ketenimine | | | 0.050 M ketenimine | | | 0.13 M ketenimine | | |
[DTBN], M	Φ	Φ_cor	[DTBN], M	Φ	Φ_cor	[DTBN], M	Φ	Φ_cor	[DTBN], M	Φ	Φ_cor
0.00	0.53	0.53	0.00	0.69	0.69	0.00	0.46	0.46	0.00	0.29	0.29
0.0060	0.14	0.19	0.031	0.063	0.16	0.017	0.11	0.18	0.053	0.041	0.091
0.0082	0.11	0.16	0.042	0.044	0.14	0.044	0.057	0.16	0.099	0.021	0.074
0.012	0.079	0.13	0.066	0.029	0.13	0.051	0.055	0.17	0.143	0.016	0.074
0.024	0.042	0.099	0.13	0.017	0.13	0.075	0.036	0.14	0.199	0.012	0.070
0.043	0.029	0.10	0.15	0.015	0.13	0.10	0.030	0.15			
0.088	0.013	0.078	0.17	0.014	0.14	0.14	0.022	0.14			
0.12	0.0095	0.075	0.20	0.012	0.13	0.16	0.019	0.14			
0.14	0.0078	0.070	0.22	0.010	0.12	0.21	0.015	0.14			
0.16	0.0071	0.072				0.23	0.013	0.13			
0.18	0.0062	0.070									
0.20	0.0056	0.069									

[a] Limits of error in quantum yields are $\leq \pm 10\%$.

ing photochemical assembly. The light from a 450-W Hanovia lamp was filtered through Corning 7-39 filters. Essentially all the light was taken up by fluorenone under the concentration conditions used. The rates of disappearance of **2** were followed by infrared spectroscopy to 20-25% reaction. These were converted to quantum yields by reference to the actinometer samples which were irradiated at the same time. The rate of disappearance of **2** represents the rate of appearance of the fluorenone-**2** α-adduct[9] since the adduct yield essentially is quantitative.[14]

The quantum yields for adduct formation at various ketenimine concentrations with and without added 0.0030 M DTBN are plotted as reciprocals in Figure 1. The data clearly show (i) the over-all quenching effect of added DTBN on the quantum efficiency of adduct formation and (ii) a sharp decrease in the quantum efficiency of adduct formation at the higher ketenimine concentrations.
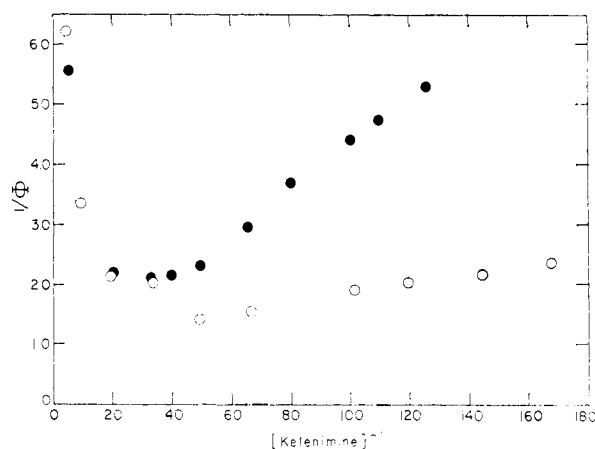

Figure 1. Dependency of the reciprocal of the quantum yield for adduct formation on the reciprocal of the ketenimine concentration: O, no DTBN; ●, with 0.0030 M DTBN.

Table II. Quenching of the Fluorenone Emission in Benzene Solution at Room Temperature by DTBN and Dimethyl-N-(cyclohexyl)ketenimine[a]

[DTBN], M	Φ_0/Φ[b]	[Ketenimine], M	Φ_0/Φ[b]
0.00	1.00	0.00	1.00
0.010	1.55	0.024	1.32
0.020	2.10	0.044	1.50
0.024	2.65	0.058	1.75
0.030	2.80	0.079	2.00
0.067	5.40	0.10	2.30
0.081	6.17		
0.13	7.58		

[a] Degassed and sealed square Pyrex precision bore cells containing 0.10 M fluorenone with and without quenches were used. The exciting light was a narrow band centered at 4000 Å and the emission was monitored at 5000 Å. [b] Represent an average of the data from all four faces of a given cell. Limits of error ±5%.

The quantum yields for adduct formation at constant ketenimine concentrations (0.010, 0.020, and 0.050 M) and varying amounts of DTBN are given in Table I. The over-all quenching effect by the added DTBN is shown by the ratios of the quantum yields for the unquenched to the quantum yields for the quenched reactions (Φ_0/Φ) at ~0.20 M DTBN for 0.010, 0.020, and 0.050 M **2** which are 94, 62, and 40, respectively.

Emission Studies

Previously, we noted that the fluorescence[15] from fluorenone in benzene solution at room temperature is quenched by **2**.[9a] More recent work indicates that DTBN also quenched this emission. These data are given in Table II and are displayed in Figure 2.

Discussion

In our preliminary work, we ascribed the DTBN quenching of the fluorenone-**2** reaction to a diffusion-controlled deactivation of the fluorenone triplet by the DTBN.[9a] Our most recent work suggests that the following features also must be incorporated into the kinetic scheme.

The quenching of the fluorenone fluorescence by DTBN (Figure 2) clearly requires the inclusion of a singlet as well as triplet quenching step by DTBN. The quenching of the fluorenone fluorescence by the ketenimine indicates an interaction between the fluorenone singlet and **2** while the kinetic data (as analyzed below) suggests that this interaction leads to adduct. Further, there is no evidence for a complex between ground-state

(15) K. Yoshihara and D. R. Kearns, J. Chem. Phys., **45**, 1991 (1966), present evidence that the principal emission from fluorenone at room temperature and at 77°K is fluorescence.
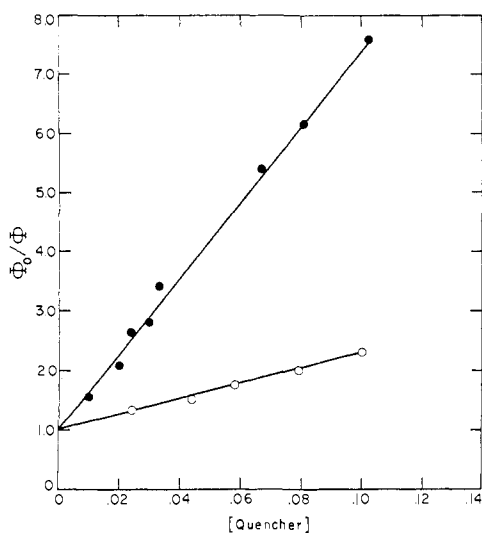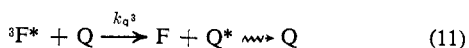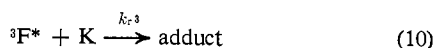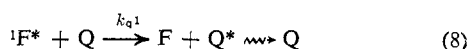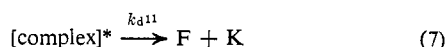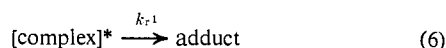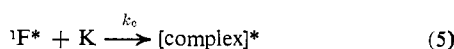
Figure 2. Stern–Volmer plot of the quenching of the fluorenone emission in benzene solution at room temperature: ●, by DTBN, slope = 64.5 M^{-1}; O, by dimethyl-N-(cyclohexyl)ketenimine, slope = 13.0 M^{-1}.

fluorenone and **2** from absorption spectra measurements. Also, classical singlet–singlet energy transfer cannot account for the fluorescence quenching by **2** because of the unfavorable disposition of the energy levels in the potential donor and acceptor.[16] Thus, we propose a fluorenone singlet–**2** complex to explain our observations. Quenching of the fluorescence of aromatic hydrocarbons by dienes[17] and amines[18] has been observed and similarly ascribed to such complex formation. The following scheme accommodates our observations on the fluorenone–**2** reaction.

$$F \xrightarrow{h\nu} {}^1F^* \tag{1}$$

$${}^1F^* \xrightarrow{k_e} F + h\nu' \tag{2}$$

$${}^1F^* \xrightarrow{k_{d^1}} F \tag{3}$$

$${}^1F^* \xrightarrow{k_x} {}^3F^* \tag{4}$$

$${}^1F^* + K \xrightarrow{k_c} [\text{complex}]^* \tag{5}$$

$$[\text{complex}]^* \xrightarrow{k_{r^1}} \text{adduct} \tag{6}$$

$$[\text{complex}]^* \xrightarrow{k_{d^{11}}} F + K \tag{7}$$

$${}^1F^* + Q \xrightarrow{k_{q^1}} F + Q^* \rightsquigarrow Q \tag{8}$$

$${}^3F^* \xrightarrow{k_{d^3}} F \tag{9}$$

$${}^3F^* + K \xrightarrow{k_{r^3}} \text{adduct} \tag{10}$$

$${}^3F^* + Q \xrightarrow{k_{q^3}} F + Q^* \rightsquigarrow Q \tag{11}$$

(16) Fluorenone has an absorption band at ~400 mμ while the lowest energy absorption band in the ketenimine is at ~290 mμ. Thus, singlet–singlet energy transfer from fluorenone to **2** would be a highly endothermic and unfavorable process. See N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Inc., New York, N. Y., 1965, p 96.

(17) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966).

(18) H. Leonhardt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 74.

In this scheme (1) is excitation of fluorenone to its singlet state, (2) and (3) are radiative and unimolecular nonradiative decay of this state, (4) is intersystem crossing of the singlet to the triplet, (5) is complex formation of the fluorenone singlet with ground-state ketenimine, (6) is collapse of the complex to adduct, (7) is deactivation of the complex leading eventually to ground-state fluorenone and ketenimine, (8) is quenching of the fluorenone singlet by DTBN, (9) is unimolecular nonradiative deactivation of the fluorenone triplet, (10) is adduct formation by way of the fluorenone triplet, and (11) is quenching of the fluorenone triplet by DTBN.

Kinetic analysis of steps 1–8 using the steady-state approximation leads to the following expression for the quantum yield for adduct formation resulting from the fluorenone singlet–ketenimine interaction.

$$1/\Phi_{\text{singlet}} = 1/n + [k_{d^1} + k_e + k_x + k_{q^1}(Q)]/[nk_c(K)] \tag{12}$$

where $n = k_{r^1}/[k_{r^1} + k_{d^{11}}]$ and describes the fraction of complexed molecules that collapse to adduct.

The corresponding expression for the quantum yield for adduct formation resulting from the fluorenone triplet–ketenimine reaction is

$$1/\Phi_{\text{triplet}} = 1/a + [k_{d^3} + k_{q^3}(Q)]/[ak_{r^3}(K)] \tag{13}$$

where $a = k_x/[k_x + k_{d^1} + k_e + k_{q^1}(Q) + k_c(K)]$ and represents the fluorenone singlet to triplet intersystem crossing efficiency. In the absence of added DTBN or ketenimine, $a_0 = k_x/[k_x + k_{d^1} + k_e] \approx 0.93$.[19]

Sorting Out the Singlet and Triplet Reactions

The quantum yields for adduct formation given in Table I and plotted in Figure 1 contain contributions from both the singlet and triplet reactions ($\Phi = \Phi_{\text{singlet}} + \Phi_{\text{triplet}}$). The extent of the fluorenone singlet–ketenimine interaction at the different ketenimine concentrations is available from the emission data if we assume that the fluorescence-quenching step is the complex-formation step. The DTBN quenching data presented in Table II were obtained at ketenimine concentrations of 0.010, 0.020, and 0.050 M ketenimine so that in each case the observed reaction is made up of singlet and triplet components.

Generally, a mixture of singlet- and triplet-state reactions can be sorted out by use of a quencher of the triplet state alone. A plot of the ratio of the quantum yield in the absence of added quencher to the quantum yield in the presence of added quencher (Φ_0/Φ) against quencher concentration will show downward curvature. In our case, because of the facile quenching of the singlet state of fluorescence by the quencher (Figure 2), the quenching data do not lend themselves to such a treatment. Instead, we approximate the former approach by correcting the observed quantum yields for the DTBN singlet quenching step in the following way.

The Stern–Volmer expression for emission quenching by DTBN is

$$\Phi_0/\Phi = 1 + [k_{q^1}(Q)]/[k_e + k_{d^1} + k_x] = 1 + 64.5 \, M^{-1} \, (Q) \tag{14}$$

(19) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

and that for the ketenimine is

$$\Phi_0/\Phi = 1 + [k_c(K)]/[k_e + k_{d^1} + k_x] =$$
$$1 + 13.0 \ M^{-1} (K) \quad (15)$$

The expected Stern–Volmer expression for the quenching of the fluorenone emission by DTBN in the presence of any concentration of ketenimine is

$$\Phi_0/\Phi = 1 + [k_{q^1}(Q)]/[k_x + k_e + k_{d^1} + k_c(K)] =$$
$$1 + [64.5 \ M^{-1} (Q)]/(1 + 13.0 \ M^{-1} (K)] \quad (16)$$

Thus, the extent of singlet quenching by DTBN in the presence of the ketenimine can be calculated.[20] Accordingly, the experimental quantum yields were corrected by multiplying them by the appropriate factor derived from eq 16. The corrected values are given in Table II. The effect of this correction on both the singlet and triplet components of the total quantum yield is shown below. The correction factor is shown in eq 17.

$$(F) = [k_x + k_{d^1} + k_e + k_{q^1}(Q) + k_c(K)]/$$
$$[k_x + k_{d^1} + k_e + k_c(K)] \quad (17)$$

(i) Correction of Expression for Quantum Yield of the Singlet Reaction

$$(\Phi_{singlet})(F) = [[nk_c(K)]/\{[k_x + k_{d^1} + k_e + k_{q^1}(Q) + k_c(K)]\}](F) = [nk_c(K)]/[k_x + k_{d^1} + k_e + k_c(K)]$$

Thus

$$1/\Phi_{singlet \ (cor)} = 1/n + [k_x + k_{d^1} + k_e]/[nk_c(K)] \quad (18)$$

(ii) Correction of Expression for Quantum Yield of the Triplet Reaction

$$(\Phi_{triplet})(F) = [[k_x k_r(K)]/\{[k_x + k_{d^1} + k_e + k_{q^1} + k_c(K)][k_r(K) + k_{d^3} + k_{q^3}(Q)]\}](F) =$$
$$[k_x k_r(K)]/\{[k_x + k_{d^1} + k_e + k_c(K)] + [k_r(K) + k_{d^3} + k_{q^3}(Q)]\}$$

Thus

$$1/\Phi_{triplet \ (cor)} = 1/a' + [k_{d^3} + k_{q^3}(Q)]/[a'k_r(K)] \quad (19)$$

where $a' = k_x/[k_x + k_{d^1} + k_e + k_c(K)]$.

The corrected quantum yields in Table II are plotted in Figure 3. The rises in the plots between 0.0 and 0.1 M DTBN represent the DTBN quenching of the triplet reaction while the plateaus reveal the quantum yields for the singlet reactions at their respective ketenimine concentrations. Note that the expression for the corrected quantum yields for the singlet reaction (eq 18) contains no DTBN term. Figure 4 shows a plot of these values (which are the reciprocals of the quantum yields for the singlet reaction in the absence of DTBN) against the reciprocal of ketenimine concentration. The intercept of this plot is $1/n$ and the slope is $[k_x + k_{d^1} + k_e]/[nk_c]$. The line shown in the figure has an intercept (1.6) and slope (0.12 M) which give $[k_x + k_{d^1} + k_e]/k_c = {}^1/_{13} \ M$ which is the value obtained in the emission

(20) This treatment assumes that the DTBN quenching step is the same in the presence and absence of the ketenimine. We observed that for a benzene solution containing 0.10 M fluorenone, 0.020 M ketenimine, and with and without 0.022 M DTBN, $\Phi_0/\Phi = 2.17$ which agrees very well with the value of 2.14 expected by eq 16.
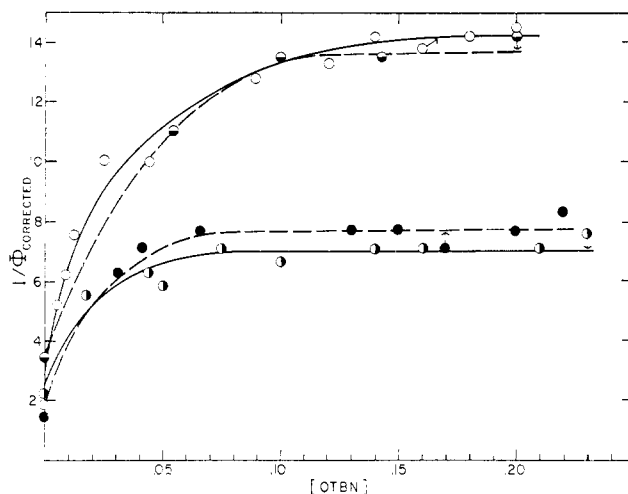

Figure 3. Dependency of the corrected quantum yield for adduct formation on quencher concentration at ○, 0.010 M; ●, 0.020 M; ◑, 0.050 M; ◒, 0.13 M ketenimine.
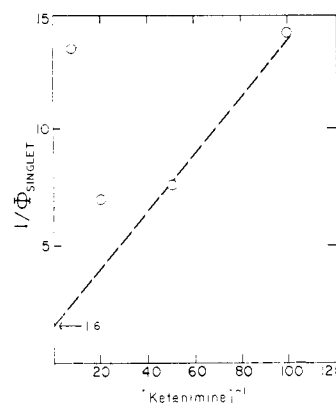

Figure 4. Dependency of the reciprocal of the derived quantum yield for the fluorenone singlet–ketenimine reaction on the reciprocal of the ketenimine concentration; intercept = 1.6, slope = 0.12 M.

study (Figure 2). The upward deviation at the higher ketenimine concentrations will be discussed later. The intercept of 1.6 suggests that the fluorenone singlet–ketenimine complex proceeds on to adduct with high efficiency (*ca.* 60%).

The Fluorenone Triplet–Ketenimine Reaction

The quantum yields for the unquenched fluorenone triplet–ketenimine reaction were evaluated by subtracting the quantum yields for the singlet reaction, as obtained from the dashed line in Figure 4, from the experimental quantum yields for the unquenched run. The quantum yields for the triplet reaction in the presence of 0.0030 M DTBN similarly were calculated except that the experimental quantum yields were corrected for the DTBN singlet deactivation step according to eq 16. This correction is necessary because the quantum yield for the singlet reaction that we are subtracting from the experimental one is for the unquenched reaction. These values are given in Table III and are plotted in Figure 5.

Table III. Calculated Quantum Yields for the Fluorenone Triplet–Dimethyl-N-(cyclohexyl)ketenimine Reaction

[Ketenimine], M	$\phi_{exptl}{}^{a}$	$\phi_{cor}{}^{c}$	$\phi_{singlet}{}^{b}$	$\phi_{triplet}$
No DTBN				
0.0060	0.42		0.044	0.35
0.0069	0.46		0.050	0.41
0.0083	0.50		0.060	0.40
0.010	0.53		0.071	0.46
0.015	0.64		0.10	0.54
0.020	0.69		0.13	0.56
0.0030 M DTBN				
0.0080	0.19	0.22	0.058	0.16
0.0090	0.21	0.25	0.066	0.18
0.010	0.23	0.27	0.071	0.20
0.013	0.27	0.31	0.093	0.22
0.015	0.34	0.39	0.10	0.29
0.020	0.43	0.49	0.13	0.36

[a] Experimentally observed value, limits of error $\leq \pm 10\%$. [b] Obtained from Figure 4. [c] Corrected for singlet quenching by DTBN according to eq 16.

Figure 5. Dependency of the derived quantum yield for the fluorenone triplet–ketenimine reaction on the reciprocal of the ketenimine concentration: O, no DTBN, slope $= 0.010$ M; ●, 0.0030 M DTBN, slope $= 0.040$ M.

The line drawn through the points was chosen so as to give an intercept of 1.08.[19] The slopes of the unquenched and quenched reactions are 0.010 M and 0.040 M which, when analyzed by eq 13, give $k_r = 9.4 \times 10^{-2} k_q$ and $k_d = 1.02 \times 10^{-3} k_q$. Table IV contains several recently determined rate constants for photocycloaddition reactions.

The data compiled in Table IV indicate that these cycloadditions involving the triplet state of aromatic aldehydes and ketones and olefinic substrates occur at close to the diffusion limit ($k_{diffusion} \approx 5 \times 10^9$ l. mol^{-1} sec^{-1}). Also, the triplet energy of the carbonyl compound does not seem to be an important factor since triplet fluorenone ($E_T \approx 53$ kcal/mol) and triplet benzophenone ($E_T \approx 69$ kcal/mol) cycloadd to dimethyl-N-(cyclohexyl)ketenimine with almost the same facility.

Figure 6. Theoretical quantum yield profiles for the fluorenone-dimethyl-N-(cyclohexyl)ketenimine reaction: ---, for the fluorenone singlet and triplet reactions; ——, for the total reaction.

Table IV. Rate Constants of Photocycloadditions of Aromatic Carbonyl Triplets to Olefinic Substrates

Carbonyl compd	$E_{T},{}^{a}$ kcal/mol	Substrate	Quencher	$k_r{}^{b}$	Ref
Fluorenone	53[c,d]	$(CH_3)_2C{=}C{=}NC_6H_{12}$	DTBN	$0.094 k_q$	This work
Benzophenone	69[e]	$(CH_3)_2C{=}C{=}NC_6H_{12}$	DTBN or naphthalene	$0.5 k_q$	e
Benzophenone	69[e]	$(CH_3)_2C{=}C{=}NC_6H_5$	DTBN	$0.3 k_q$	e
Benzaldehyde	72	$(CH_3)_2C{=}C(CH_3)_2$	Piperylene or DTBN	$0.2 k_q$	4a

[a] Triplet energy of carbonyl compound. [b] Expressed in terms of the bimolecular rate constant for quenching of the triplet state of the carbonyl compound by the quencher, $k_q \approx k_{diffusion}$. [c] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 4537 (1964). [d] N. C. Yang, *Pure Appl. Chem.*, 9, 591 (1964). [e] L. A. Singer and G. A. Davis, unpublished results.

Obviously, there are many unanswered questions that require further kinetic studies.

Lifetime of the Fluorenone Singlet State

The lifetime of the singlet state of fluorenone can be estimated from the emission data in Figure 2. If we assume that the fluorescence quenching by DTBN is diffusion controlled ($k_{q^1} \approx 5 \times 10^9$ l. mol^{-1} sec^{-1}), then by eq 14, $[k_e + k_{d^1} + k_x] \approx 7.8 \times 10^7$ sec^{-1} and $\tau = 1.3 \times 10^{-8}$ sec.[21] Since $k_x/[k_e + k_{d^1} + k_x] \approx 0.93$,[19] $k_x \approx 7.2$

(21) This estimate agrees well with the value of $\tau \approx 2 \times 10^{-8}$ sec at 77°K in alcohol as measured by Dr. Reid Kellog and reported in footnote 17 of ref 15. The similarity of the two values measured at such widely different temperatures reflects the major role of k_x (which is temperature independent) in determining the lifetime of the fluorenone singlet state.
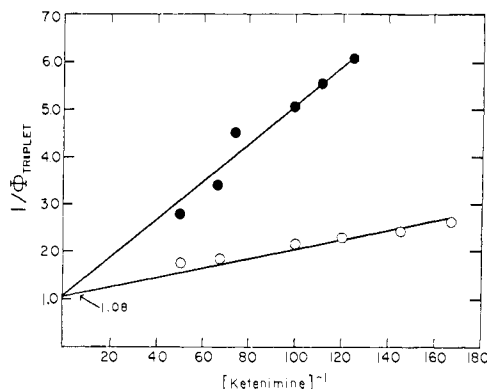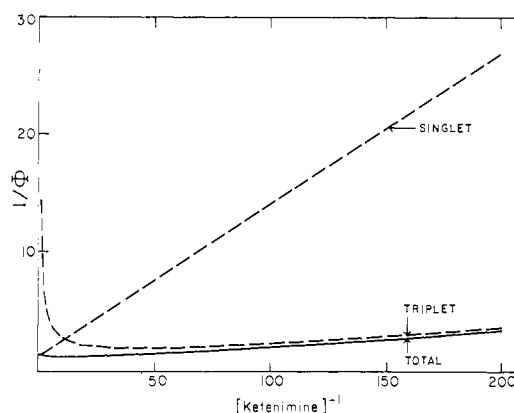
$\times 10^7$ sec^{-1}. The absence of kinetic evidence for the involvement of the benzophenone singlet in the photocycloaddition with ketenimines[8,22] may simply be related to the faster intersystem crossing rate constant in that ketone which is estimated to be $>5 \times 10^9$ sec^{-1}.[13]

The Question of an Additional Deactivation Process at High Ketenimine Concentrations

The dramatic decrease in the quantum yield for adduct formation at the higher ketenimine concentrations is still not explained by the present work. The derived parameters for the singlet and triplet reactions lead to

(22) See footnote e, Table IV.

the partial and total quantum yield profiles shown in Figure 6. The decrease in the quantum yield for the triplet reaction relates to the continual decrease in the intersystem crossing efficiency of fluorenone as the bimolecular complex formation reaction becomes more efficient at higher ketenimine concentrations (eq 13), while the quantum yield for the singlet reaction is expected to linearly increase toward the limiting value of ~0.60. Thus, the quantum yield for the total reaction $(1/\Phi_{total} = 1/[\Phi_{singlet} + \Phi_{triplet}])$ *should not decrease* at the higher ketenimine concentrations.

At this time, we can only speculate on an additional deactivation process that is second order in ketenimine and which may be described by step 5a. When incorporated into eq 12, the kinetic expression for the quantum yield of the singlet reaction becomes

$$1/\Phi_{singlet} = 1/n' + [k_{d^1} + k_e + k_x + k_{q^1}(Q)]/[n'k_c(K)]$$

where $n' = k_{r^1}/[k_{r^1} + k_{d^{11}} + k_K(K)]$ and would lead to a decrease in the quantum yield for the singlet reaction at higher ketenimine concentration as is observed in Figure 4. If step 5a proceeds at the diffusion limit,

$$[\text{complex}]^* + K \xrightarrow{k_K} F + 2K \qquad (5a)$$
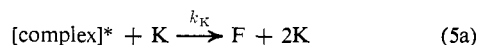
k_{r^1} must be approximately an order of magnitude less than the diffusion limit in order for this deactivation step to be significant. Further work directed toward clarifying this picture is in progress.

Experimental Section

Materials. Dimethyl-N-(cyclohexyl)ketenimine was prepared as previously described.[8] Di-*t*-butylnitroxide was prepared as described by Hoffman and coworkers.[10] The material, purified by distillation through a spinning-band column, gave an extinction coefficient at 465 mμ in excellent agreement with that reported. Benzene (Mallinckrodt, thiophene free) was distilled through a 2-ft glass column packed with glass beads and a center cut was collected. Benzophenone (Matheson Coleman and Bell), fluorenone (Aldrich), and benzhydrol (Eastman) were recrystallized from ether–petroleum ether (bp 30–60°) prior to use.

Kinetic Measurements. All kinetic measurements were made at room temperature on a rotating photochemical assembly as previously described:[8] The light from a 450-W Hanovia lamp was filtered through Corning 7-39 filters. Actinometry was by the benzophenone–benzhydrol system (0.10 M benzophenone–1.0 M benzhydrol, $\Phi = 0.97$).[13]

Emission Spectra. The instrument employed a xenon light source monochromated to the desired exciting wavelength with an American Instrument Co., Inc. monochromator, Model 4-8400. An identical monochromator, placed at 90° and motorized for continuous scan, picked up the emitted light. The photocurrent from an IP-21 phototube was displayed on an American Instrument Co., Inc. Microphotometer, Model 10-213, and the data were collected with a pen recorder.

All emission spectra were taken at room temperature by irradiating degassed and sealed precision bore square Pyrex ampoules. The Stern–Volmer plots of the quenching of the fluorenone emission by DTBN and the ketenimines in benzene were done on solutions containing 0.1 M fluorenone. The exciting light was a narrow band centered at 4000 Å. The pen response near the emission peak was noted after ascertaining that no change in peak shape or position occurred at different concentrations of quencher. Periodic measurements on a standard indicated excellent reproducibility of the pen response throughout the experiments.

Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud. Optical Resolution and Thermal Rearrangement Studies[1,2]

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Abstract: *trans*-15,16-Dimethyldihydropyrene (1) undergoes a thermal rearrangement at around 200° giving *trans*-13,15-dimethyldihydropyrene (2). The structure of 2 has been established from its spectral and chemical properties. The preparation and optical resolution of 4-carboxy-*trans*-15,16-dimethyldihydropyrene (18) has been accomplished. When 18 was subjected to a thermal rearrangement and the reaction was stopped at approximately 50% of completion, the unrearranged 18 showed no loss of optical activity, demonstrating that there is no interchange of the interior methyl groups occurring prior to the thermal rearrangement of a methyl group out to the exterior.

Previously, we have described the preparations of *trans*-15,16-dimethyldihydropyrene (1)[3] and have reported on certain of its chemical properties.[4] One of

the properties of 1 not discussed in the previous report, though, is the instability of 1 toward heat. When 1 is placed in an evacuated melting point tube, the deep emerald green crystals melt without decomposition at 119–120°. But, if the temperature is raised, a rapid transition occurs at around 200–210° in which the green color of the solution turns a pale yellow. The ultraviolet absorption spectrum of the product closely resembles that of pyrene and our first assumption was that the interior methyl groups had simply been ex-

(1) We express our appreciation to the National Science Foundation for their support of this work.
(2) For the preceding communication in this series, see V. Boekelheide and T. Miyasaka. *J. Am. Chem. Soc.*, **89**, 1709 (1967).
(3) V. Boekelheide and J. B. Phillips, *ibid.*, **89**, 1695 (1967).
(4) J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *ibid.*, **89**, 1704 (1967).