

# Photochemistry of Unsaturated Ketones in Solution.

## 51. Photophysical and Photochemical Studies of Michler's Ketone<sup>1</sup>

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**Abstract:** Various aspects of the photochemical behavior of Michler's ketone (MK) in solution have been clarified through steady-state and flash excitation experiments. The triplet yield for MK is strongly solvent dependent, from values near unity in hydrocarbon solvents to very small values in alcoholic media. The primary product in dilute cyclohexane solutions has been isolated and identified as Michler's pinacol; the same product is formed very inefficiently in dilute 2-propanol and is destroyed on further irradiation at 254 nm. The quantum efficiency for MK disappearance at 366 nm has been determined to be 0.42 in cyclohexane and  $<2 \times 10^{-3}$  in 2-propanol. Flash absorption studies are complicated by the formation and decay of several radical transients in addition to the MK triplet, but decay of the latter could be conveniently studied by flash emission studies and single photon counting. From the dependence of the triplet lifetime on MK concentration, self-quenching rate constants and limiting triplet lifetimes have been determined. The data provide values of the rate constant  $k_a$  for hydrogen abstraction by MK triplet from cyclohexane ( $1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) and 2-propanol ( $\leq 2.4 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$ ). These values can be made consistent with the Porter-Suppan proposal of a lowest  $n, \pi^*$  triplet of reduced electrophilic reactivity in cyclohexane and a lowest CT triplet in 2-propanol, although the possibility of reaction via thermally populated upper  $n, \pi^*$  triplets in either or both solvents cannot be excluded. An alternative proposal, which also accommodates previous low-temperature absorption and emission studies, is that MK in protic media is complexed with the solvent by H bonding to the carbonyl, reducing both the rate constant for intersystem crossing and for H abstraction by the triplet. Arguments and data are presented relating to the possible formation of triplet excimers in this system.

### Introduction

As part of our studies of the photophysical and photochemical processes occurring on excitation of benzophenone and substituted benzophenones in various media, we have studied in considerable detail the photochemistry of 4,4'-bis(dimethylamino)benzophenone, commonly known as Michler's ketone (MK). The literature on the solvent dependency of the reactivity of this ketone contains conflicting reports. The earliest report by Porter and Suppan<sup>2</sup> gives the quantum yield for MK disappearance on excitation at 3650 Å as 0.6 in cyclohexane and 0.00 in 2-propanol. Subsequent reports<sup>3</sup> contended that excited MK was "unreactive" in cyclohexane. Suppan<sup>4</sup> reinvestigated this question and added a new wrinkle. He found a pronounced dependence of the quantum yield for ketone disappearance not only on the solvent, but also on the wavelength of irradiation. In 2-propanol, he reported the quantum yield to be  $10^{-4}$  at both 2537 and 3650 Å. In cyclohexane, however, the reported quantum yields were 0.4 at 2537 Å and 0.03 at 3650 Å.<sup>4</sup>

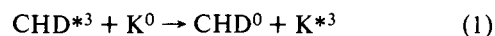
We wished to settle this controversy, as well as determine the fate of photoexcited MK in cyclohexane, a notable deficiency in the previous literature. It had generally been assumed that photoreduction was occurring, but pinacols were never actually isolated and characterized in the earlier work.

A second area of controversy existed. Porter and Suppan<sup>2</sup> claimed that the energies and electronic configurations of the lowest lying triplet states of the aminobenzophenones were strongly solvent dependent, and that the sequence of triplet states was subject to inversion in polar vs. nonpolar solvents. This suggestion was made to rationalize marked reactivity differences as well as spectral shifts in different solvents.<sup>2</sup> This postulate was contested by Koch and Jones<sup>5</sup> on the basis of the similarity which they observed in deuterium exchange reactions between MK and ethanethiol-*S-d* in both polar (acetonitrile) and nonpolar (benzene) solvents, and by Cohen et al.<sup>6</sup> on the basis of the marked difference in quantum yields for intersystem crossing of *p*-aminobenzophenone in alcohols vs. nonpolar solvents. We believed these problems could be clar-

ified by determining both the yields and lifetimes of MK triplets as a function of solvent. Surprisingly, no flash photolytic studies of MK were reported prior to the inception of our investigation.

### Results

**Triplet Yield Determinations.** In all prior references to the pronounced solvent dependency of the reactivity of Michler's ketone, it had been tacitly assumed that the yield of MK triplets was unity or nearly so in all solvents. A yield of 1.00 had been previously determined in benzene.<sup>8</sup> Indeed, based on this measurement and also its high UV extinction coefficient, MK is frequently encountered as a triplet sensitizer in photochemical studies. However, the observance by Cohen et al.<sup>6</sup> of a near-zero triplet yield for *p*-aminobenzophenone in alcohol and more recent work by Favaro<sup>7</sup> raised considerable doubts as to the validity of this assumption. Consequently, we determined the intersystem crossing quantum yields for MK in typical polar and nonpolar solvents to see if the trends observed for *p*-aminobenzophenone also hold true for MK.<sup>6,7</sup> The method chosen was an adaptation of the standard triplet counting method of Hammond and Lamola,<sup>8</sup> utilizing 1,3-cyclohexadiene as the triplet quencher and cyclohexadiene dimer yields (in degassed MK solutions relative to the dimer yield in parallel irradiations of benzophenone) as the measure of production of triplets. The results obtained are summarized in Tables I-IV. Runs 3 and 4 of Table II were conducted to determine if reverse energy transfer of the type (eq 1) found by Favaro<sup>7</sup> to be significant for *p*-hydroxy- and *p*-aminobenzophenone



is a factor to be considered here as well. As can be seen from Table II, reverse energy transfer does not appear to be significant for MK in 2-propanol.

We have also confirmed Cohen's conclusion that the failure of *p*-aminobenzophenone (PAB) to be photoreduced in polar solvents results from the essentially complete absence of in-

**Table I.** Quantum Yields for Intersystem Crossing ( $\Phi_{ST}$ ) for Michler's Ketone in Benzene<sup>a</sup>

Run	Initial OD (M) <sub>366</sub>	Initial OD (B) <sub>366</sub>	$\Phi_{ST}^b$
1	0.906	0.786	0.86 ± 0.07
2	0.757	0.845	1.13 ± 0.09
3	0.606	0.873	1.11 ± 0.09
4	0.926	0.913	0.98 ± 0.08
5	0.863	0.833	0.97 ± 0.08
		Av	1.01 ± 0.08

<sup>a</sup> All samples were irradiated for 15 min. M, Michler's ketone; B, benzophenone. <sup>b</sup> [CHD] = 0.1 M.

**Table II.** Quantum Yields for Intersystem Crossing ( $\Phi_{ST}$ ) for Michler's Ketone in 2-Propanol

Run	Initial OD (M) <sub>366</sub>	Initial OD (B) <sub>366</sub>	Irrad time, min	$\Phi_{ST}^a$
1	0.731	0.547	15	0.23 ± 0.02
2	0.865	0.575	15	0.26 ± 0.03
3	0.350	0.471	45	0.30 ± 0.03
4	0.368	0.570	75	0.19 ± 0.02
			Av	0.24 ± 0.04

<sup>a</sup> [CHD] = 1.25 M.

**Table III.** Quantum Yields for Intersystem Crossing ( $\Phi_{ST}$ ) for Michler's Ketone in Ethanol

Run	Initial OD (M) <sub>366</sub>	Initial OD (B) <sub>366</sub>	$\Phi_{ST}^{a,b}$
1	0.250	0.238	0.08 ± 0.008
2	0.227	0.166	0.08 ± 0.008
		Av	0.08 ± 0.008

<sup>a</sup> [CHD] = 1.5 M. <sup>b</sup> Samples irradiated for 30 min.

tersystem crossing. We conducted a single experiment on PAB in ethanol with 1.0 M 1,3-cyclohexadiene<sup>9</sup> as quencher. Upon GLC analysis, no cyclohexadiene dimers were detected in the PAB photolysate, indicating the complete absence of intersystem crossing for PAB in ethanol.

**Quantum Yield Studies.** Absolute quantum yields for Michler's ketone disappearance were determined in cyclohexane and 2-propanol at two wavelengths (254 and 366 nm) with potassium ferrioxalate as the actinometer (Table V).<sup>10</sup> The quantum yield for MK disappearance in cyclohexane was found to be critically dependent on the presence of oxygen. Consistently higher quantum yields were obtained using rigorous degassing procedures. Additionally, the quantum yield for ketone disappearance at 254 nm in cyclohexane was found to be dependent on the extent of MK conversion (Table VI). We believe that a photoproduct formed during the irradiation effectively competes with MK for light absorption and consequently leads to lower quantum yields than those measured at very small conversions. These observations run contrary to the "induction period" observed by Suppan<sup>11</sup> for MK in cyclohexane, most reasonably attributable to residual oxygen in his samples. Our data (Table V) generally corroborate the original report of Porter and Suppan<sup>2</sup> that MK is "reactive" in cyclohexane and "unreactive" in 2-propanol.

**Triplet Lifetimes.**<sup>12</sup> Initially, we attempted to determine the triplet lifetime of MK in a solvent where the classical mechanism for photoreduction<sup>2</sup> would be inoperative. Absorption flash photolysis studies in benzene over a concentration range

**Table IV.** Quantum Yields for Intersystem Crossing ( $\Phi_{ST}$ ) for Michler's Ketone in Cyclohexane

Run	Initial OD (M) <sub>366</sub>	Initial OD (B) <sub>366</sub>	$\Phi_{ST}^{a,b}$
1	0.052	0.119	0.93 ± 0.09
2	0.055	0.150	0.89 ± 0.09
		Av	0.91 ± 0.10

<sup>a</sup> [CHD] = 1.25 M. <sup>b</sup> Samples irradiated for 30 min.

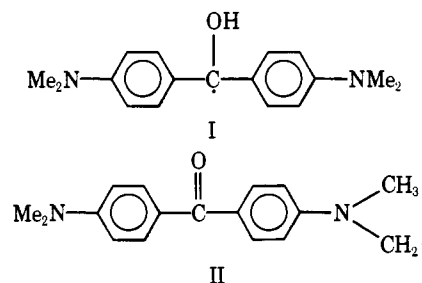
**Table V.** Quantum Yields for Michler's Ketone Disappearance at 254 and 366 nm

Solvent	Quantum yield		Ref
	254 nm	366 nm	
2-Propanol	0.00	0.00	2
2-Propanol	$1 \times 10^{-4}$	$1 \times 10^{-4}$	4
2-Propanol	$<2 \times 10^{-3}$	$<2 \times 10^{-3}$	This work
Cyclohexane		0.6	2
Cyclohexane	0.4	0.03	4
Cyclohexane	0.35 ± 0.06	0.38 ± 0.06	11
Cyclohexane	0.5	0.41, 0.43	This work
Ethanol		$<10^{-4}$	11

**Table VI.** Quantum Yields for Michler's Ketone Disappearance in Cyclohexane at 254 nm as a Function of Percent Conversion

% conversion	$\Phi_{-MK}$
4	0.51
28	0.30
48	0.23
51	0.22
53	0.10

of  $10^{-3}$  to  $10^{-5}$  M demonstrated strong transient absorption but the decay of the absorption was not cleanly first or second order. We attribute this behavior to competitive absorption in the visible region by radicals such as I and II



in addition to MK triplets.<sup>13,14</sup> However, using very dilute MK solutions ( $10^{-5}$  M) and monitoring wavelengths between 500 and 550 nm in benzene and at 535 nm in carbon tetrachloride, a weak long-lived transient was observed which decayed by clean first-order kinetics,  $k_d = 1.7 \times 10^3 \text{ s}^{-1}$  in  $\text{C}_6\text{H}_6$  and  $1.8 \times 10^2 \text{ s}^{-1}$  in  $\text{CCl}_4$ .

Absorption flash photolysis studies of  $1-4 \times 10^{-4}$  M MK solutions in cyclohexane yielded strong transient absorption which again did not obey either first- or second-order kinetics. After several flashes, an unidentified precipitate began to form in these solutions.

No transient absorption was observed in 2-propanol over the range 425–600 nm. This result was surprising in that our initial expectation based on the Porter–Suppan formulation<sup>2</sup> was that triplet MK should be relatively long lived in this polar solvent.

**Table VII.** Limiting Triplet Lifetimes ( $\tau_{lim}$ ) of Michler's Ketone as a Function of Solvent

Solvent	$\tau_{lim}$ , $\mu$ s	Technique	Ref
CCl <sub>4</sub>	30	<i>a</i>	<i>c</i>
C <sub>6</sub> H <sub>6</sub>	27	<i>a</i>	<i>c</i>
	19	<i>b</i>	This work
	25	<i>a</i>	<i>d</i>
	27	<i>a</i>	<i>c</i>
(CH <sub>3</sub> ) <sub>2</sub> CHOH	70	Not specified	<i>e</i>
	43	<i>f</i>	<i>f</i>

<sup>a</sup> Emission flash photolysis. <sup>b</sup> Time-correlated single photon counting. <sup>c</sup> This work. Calculated from  $1/\tau_{obsd} = 1/\tau_{lim} + k_{sq}[\text{MK}]$ . <sup>d</sup> Reference 15. <sup>e</sup> Reference 13. <sup>f</sup> Measured using a submicrosecond pulse technique by M. Topp and D. Axelrod, University of Pennsylvania. The previously reported<sup>12</sup> value of  $\tau_{lim} = 3.0 \mu$ s using single photon counting was in error, apparently because of deterioration of the sample.

We turned next to flash emission studies where the triplet decay could be monitored without the complication of the competing decay of intermediate radicals, such as I or II. Indeed, it was found that the phosphorescence decay was clearly first order in several solvents. However, in three solvents (benzene, carbon tetrachloride, and 2-propanol) in which the MK concentration was varied the first-order decay rate constant was linearly dependent on the concentration of MK, thus providing evidence for direct interaction of MK triplets with ground-state molecules, as had been suggested earlier<sup>5</sup> but not actually established. Using the general relationship:

$$1/\tau_{obsd} = 1/\tau_{lim} + k_{sq}[\text{MK}] \quad (2)$$

limiting triplet lifetimes,  $\tau_{lim}$  (Table VII), and rate constants for self-quenching,  $k_{sq}$  (Table VIII), were obtained in these solvents. Singer and co-workers<sup>15</sup> recently reported laser flash photolysis measurements of  $\tau_{lim}$  and  $k_{sq}$  for MK in benzene in excellent agreement with our measured values (see Tables VII and VIII). It is worth noting that Cohen and Cohen<sup>16</sup> observed self-quenching in the photoreduction of *p*-aminobenzophenone some time ago.

The presence of an adventitious quencher in the Michler's ketone sample would, of course, give a result kinetically indistinguishable from the self-quenching phenomenon. In order to account for the increased decay rates observed upon increasing MK concentration, a minimum of 1% of an impurity in MK on a molar basis would be required, if quenching were diffusion controlled. At less than diffusion-controlled quenching rates, even larger amounts of impurity would be required to explain our observations. Although we cannot rigorously exclude the presence of such an impurity, it is exceedingly doubtful if this much of an adventitious quencher remains after our exacting purification procedure. The agreement between the measured parameters for MK in benzene and those measured in Singer's laboratory<sup>15</sup> supports the contention that these are indeed true photophysical constants.

Since the self-quenching process entails the approach of an MK triplet to a ground-state molecule, one might expect for this bimolecular reaction a dependency of  $k_{sq}$  on the viscosity of the medium. For MK, the self-quenching rate constant does indeed parallel the calculated rate constant for diffusion (Table VIII).

**Steady-State Irradiations.** The results of Cohen<sup>16</sup> and Suppan<sup>4</sup> for reduction of *p*-aminobenzophenone in cyclohexane indicate that pinacols derived from ketyl radicals are formed, but as previously indicated only indirect and contradictory data were available with respect to MK photoreduction prior to this study. We have attempted with only limited suc-

**Table VIII.** Rate Constants for Michler's Ketone Self-Quenching Compared with Rate Constants for Diffusion in Several Solvents

Solvent	$k_{diff}$ at 20 °C, <sup>a</sup> l. mol <sup>-1</sup> s <sup>-1</sup>	$k_{sq}$ , <sup>b</sup> l. mol <sup>-1</sup> s <sup>-1</sup>
Benzene	$1.00 \times 10^{10}$	$1.25 \pm 0.22 \times 10^8$ <sup>c</sup> $2.5 \pm 0.3 \times 10^8$ <sup>d</sup>
Carbon tetrachloride	$0.67 \times 10^{10}$	$7.61 \pm 0.87 \times 10^7$
2-Propanol	$0.27 \times 10^{10}$	$1.96 \pm 0.41 \times 10^7$ <sup>e</sup>

<sup>a</sup> J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 627. <sup>b</sup> This work. Calculated from  $1/\tau_{obsd} = 1/\tau_{lim} + k_{sq}[\text{MK}]$ . <sup>c</sup> This value agrees reasonably well with the value of  $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  calculated from a Stern-Volmer treatment of a deuterium exchange reaction between perprotio MK and EtSD reported in ref 5. <sup>d</sup> Reference 15. <sup>e</sup> Reference 13 gives  $8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  as the lower limit for the rate constant of quenching of MK by Ph<sub>2</sub>CO in this solvent.

cess to determine the products upon photolysis (at both 254 and 350 nm) of very dilute solutions of MK ( $10^{-4}$ – $10^{-5}$  M) in cyclohexane and 2-propanol. This limited concentration range was selected to minimize reactions which are the consequence of the facile self-quenching decay pathway for MK triplets.<sup>5</sup> Analysis by GLC for photoproducts derived from MK was difficult if not impossible due to the low concentrations of materials available and long GLC retention times. Where attempts at isolation of photoproducts succeeded, characterization was accomplished by comparison of spectra with those of authentic samples.

**Irradiations in 2-Propanol.** As can be seen in Table V, reaction in this solvent is extremely inefficient ( $\Phi_{-MK} < 0.002$ ). However, upon prolonged photolysis (several days) at 350 nm of a nondegassed  $1.8 \times 10^{-4}$  M solution, the original UV absorbance of MK at 355 nm disappears and a new absorption,  $\lambda_{max}$  265 nm, appears. The UV spectrum is identical with that of a solution of Michler's pinacol in 2-propanol, and, indeed, upon evaporating the solvent from the photolysate, material was obtained with an infrared spectrum similar to that of the pinacol synthesized independently. Additionally, GLC analysis of the photolysate showed (by co-injection) that 2,3-dimethyl-2,3-butanediol was also formed.

Photolysis at 254 nm ( $1.9 \times 10^{-4}$  M MK, nondegassed) was slightly more efficient. After 21 h irradiation there was negligible UV absorption above 220 nm. The photolysis was repeated and aliquots were withdrawn periodically. Analysis of these aliquots by ultraviolet spectroscopy indicated an initial increase in absorption between 260–300 nm (with a corresponding decrease in absorption by MK at 350–370 nm) and ultimately the disappearance of all absorption above 220 nm. As before, GLC analysis of the photolysate indicated the presence of 2,3-dimethyl-2,3-dihydroxybutane. We found that authentic Michler's pinacol underwent rapid decomposition in 2-propanol upon photolysis at this wavelength. Thus, circumstantial evidence is available that MK is inefficiently photoreduced upon irradiation at 254 nm in 2-propanol, probably to form Michler's pinacol, which is itself photochemically labile at this wavelength.

**Irradiations in Cyclohexane.** Cohen and Siddiqui<sup>17</sup> had shown that column chromatography on alumina of the pinacol derived from *p*-aminobenzophenone led to considerable conversion on the column to the corresponding pinacolone and starting ketone. We obtained similar results upon chromatography of Michler's pinacol and confirmed the rearrangement to the corresponding pinacolone by comparison with an authentic sample. Chromatography on Woehlm neutral alumina of photolysates after MK irradiations in cyclohexane at both 254 and 350 nm showed that Michler's pinacol (based on pinacolone detected) is indeed the major photoproduct in cy-

clohexane. A similar conclusion was reached by Suppan<sup>11</sup> based on the UV absorption spectrum ( $\lambda_{\max}$  265 nm,  $\epsilon$  15 000) of crude photoproduct.

**Concentration Dependence of MK Phosphorescence.** In our earlier communication,<sup>12</sup> we had tentatively ascribed the weak, long-lived transient observed in absorption flash photolysis studies in benzene and carbon tetrachloride (see below) to the product of the self-quenching interaction of  $^3\text{M}^*$  and  $\text{MK}^0$ , which we dubbed a "triplet excimer". [Cognizant of the distinction made by Singer and co-workers<sup>15</sup> between an "excimer" and an "exciplex" in terms of the mode of interaction of two like molecules, one in an excited state and one in a ground state, we will continue to use the term "excimer" in the balance of the present discussion.] Self-quenching of any triplet should be manifested by reduction in monomer phosphorescence intensity in solution as ground-state concentration is increased. Experiments in benzene on a Hitachi-Perkin-Elmer fluorescence spectrophotometer demonstrated dramatic quenching of MK phosphorescence ( $\lambda_{\max}$  430–435 nm) upon increasing the ketone concentration from  $10^{-5}$  to  $10^{-3}$  M. If a new emissive species such as an excimer were formed, one might hope to observe a new phosphorescence band in increasing intensity concomitant with the decrease in monomer phosphorescence. While such an effect was observed with some samples of "purified" MK, experiments with rigorously re-purified MK showed no new emission. This, of course, does not in itself imply that triplet excimers are definitely not formed in this system; it does require that such a species, if indeed formed in benzene, must either (a) be quite short lived or (b) have a very small radiative transition probability, or possibly possesses both characteristics.

## Discussion

In order to assess the original suggestion of Porter and Suppan<sup>2</sup> that an inversion occurs in the ordering of triplet states for MK and *p*-aminobenzophenone in polar ( $^3\text{CT}$  lowest) compared with nonpolar ( $^3\text{n},\pi^*$  lowest) solvents, it is instructive to calculate the rate constants  $k_a$  for hydrogen abstraction by MK from cyclohexane and 2-propanol. Contrary to the claims of Walling and Pitts and co-workers,<sup>3</sup> there can be no doubt that photoexcited MK is indeed reactive in cyclohexane, and the reaction which occurs is photoreduction of the ketone to the corresponding pinacol. The rate constant  $k_a$  can be obtained from eq 3, using the values of  $\Phi_{\text{dis}}$ ,  $\Phi_{\text{ST}}$ , and  $\tau_{\text{lim}}$  determined at 366 nm in this study (0.42, 0.91, and  $43 \times 10^{-6}$  s, respectively):

$$\Phi_{\text{dis}} = \Phi_{\text{ST}} k_a [\text{RH}] \tau_{\text{lim}} \quad (3)$$

$$k_a^{\text{cyclohexane}} = 1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

This value of  $k_a$  is a factor of 720 less than the value of  $7.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for hydrogen abstraction from cyclohexane by benzophenone triplet,<sup>18</sup> the prototype ketone  $\text{n},\pi^*$  triplet state. An upper-limit estimate for  $k_a$  for MK in 2-propanol at 366 nm can be made based on the limiting quantum yield for ketone disappearance ( $< 2 \times 10^{-3}$ ), and the values determined for  $\Phi_{\text{ST}}$  (0.24) and  $\tau_{\text{lim}}$  ( $27 \times 10^{-6}$  s), using eq 3:

$$k_a^{\text{2-propanol}} \leq 2.4 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$$

This value is at least five orders of magnitude less than the corresponding value for benzophenone triplet in 2-propanol,<sup>19</sup>  $1.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Thus, we are forced to conclude that the lowest triplet state of MK in 2-propanol has little if any inherent reactivity toward hydrogen abstraction.

The results can be made consistent with the Porter–Suppan<sup>2</sup> formulation with perhaps some modifications. Thus, the assignment of the lowest triplet in 2-propanol (and presumably other protic solvents) as a  $^3\text{CT}$  state can account for the chemical inertness of the state as well as the effects of alcoholic

solvents on electronic absorption and emission spectra of MK as originally observed by Porter and Suppan.<sup>2,4</sup> (It should be noted, however, that solvent effects on phosphorescence lifetimes of amino ketones in glasses at 77 K have been recently found<sup>20</sup> to be much more complex and problematic than was recognized in the earlier<sup>2</sup> studies.) The inefficient photoreduction observed on prolonged irradiation of MK in 2-propanol may represent either the residual reactivity of the lowest triplet or reaction via reactive upper  $\text{n},\pi^*$  triplets accessible by thermal activation of the lowest (unreactive) triplets. A case of the latter mechanism has been made by Wagner<sup>21</sup> for several analogous systems. The data in cyclohexane are accommodated by an interpretation in which  $\text{T}_1$  is an  $\text{n},\pi^*$  triplet whose reactivity toward hydrogen abstraction has been sharply reduced relative to benzophenone, which is understandable since electron donation by the dimethylamino groups would reduce the electrophilicity at oxygen. Alternatively, a significant amount of  $\pi,\pi^*$  character may be mixed into the lowest  $^3\text{n},\pi^*$  state by configuration interaction, in which case a clear distinction between  $\text{n},\pi^*$  and  $\pi,\pi^*$  triplets becomes lost. These conclusions are similar to those reached independently by Suppan<sup>11</sup> based on his estimates of natural phosphorescence lifetimes and emission quantum yields for MK in polar and nonpolar solvents.

However, one cannot exclude the possibility that the lowest triplet in cyclohexane is also of the  $\pi,\pi^*$  type (perhaps with reduced CT character) with reaction occurring after thermal population of an upper  $\text{n},\pi^*$  triplet. Since the energy gap between the  $\text{n},\pi^*$  and CT (or  $\pi,\pi^*$ ) triplets would be smaller in hydrocarbon compared with alcoholic solvents, because of the well-known stabilization of the former and destabilization of the latter relative to the ground state,<sup>2</sup> the  $\text{n},\pi^*$  triplet would be more readily populated *even if there was no inversion in the ordering of the triplet states*. Enhanced thermal accessibility of the  $\text{n},\pi^*$  triplet could easily account for the observed change in  $k_a$ . This question might be resolved by determination of the activation parameters for H abstraction by MK in various solvents from studies of the temperature dependence of the relevant quantum yields and the triplet lifetimes, but this has not yet been done.

An important observation in this study was the finding that the triplet yield for MK in alcoholic solvents is quite small (0.08 in ethanol, 0.24 in 2-propanol) compared with hydrocarbon solvents (1.00 in benzene, 0.91 in cyclohexane), in agreement with the findings of Cohen et al.<sup>6</sup> for *p*-aminobenzophenone. These findings have obvious implications with respect to the use of the ketones as photosensitizers. They also indicate that one cannot assume that triplet yields determined in one solvent are appropriate in another solvent, particularly one of different polarity.<sup>22</sup>

Figure 1 shows the energy levels of *p*-aminobenzophenone in 2-propanol and cyclohexane as originally given by Porter and Suppan.<sup>2</sup> From the ordering given in Figure 1, one would expect that the intersystem crossing quantum yields in the absence of a competitive singlet reaction should be about the same in both solvents, which is not the case. A more likely ordering of the lower electronic states of the aminobenzophenones is given in Figure 2. In cyclohexane, it is proposed that the  $\text{n},\pi^*$  singlet and triplet are the states of lowest energy and that the CT triplet has an intermediate energy, allowing rapid and efficient intersystem crossing between these unlike states.<sup>24,25</sup> In 2-propanol and other polar solvents both the CT singlet and triplet levels are likely to be below the corresponding  $\text{n},\pi^*$  states. In such a case, intersystem crossing between the like CT states would be comparatively slow<sup>24,25</sup> and, as a result, inefficient because of competitive singlet state deactivation.

However, there is an alternative explanation which accommodates the solvent effects on chemical reactivity and

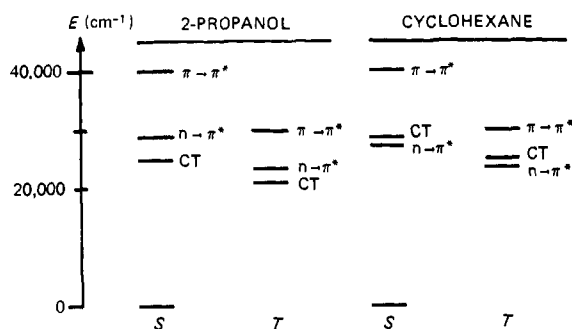


Figure 1. Energy levels for *p*-aminobenzophenones in 2-propanol and cyclohexane as proposed by Porter and Suppan (ref 2).

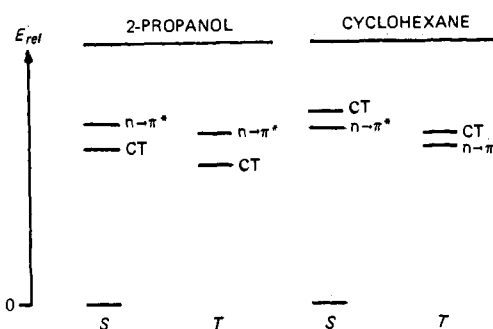


Figure 2. Proposed energy levels for Michler's ketone in 2-propanol and cyclohexane.

intersystem crossing, and recent low-temperature absorption and emission spectroscopic data.<sup>26</sup> The UV absorption of MK in media containing a hydroxylic component, even in very low concentration, shifts dramatically to longer wavelengths as the temperature is lowered, and there is also an excitation wavelength dependence to the phosphorescence spectrum, the phosphorescence decay time and fluorescence-phosphorescence ratio.<sup>26</sup> These data, which we have reproduced in part, are reasonably explained by the presence of several different species, each representing MK in a discrete solvent environment, i.e., nonhydrogen bonded or with one or more hydrogen bonds, each species having a different excitation and emission spectrum and lifetime.<sup>26b</sup> As the temperature is lowered, a shift of the equilibrium in favor of the H bonded species would be favored.<sup>26b</sup> This description is similar to those proposed to explain spectra of 4-aminobenzophenone<sup>20</sup> as well as benzophenone<sup>27</sup> in protic media at 77 K. In aprotic media at 77 K, fluorescence of MK is either very weak or totally absent, while in protic media it increases dramatically (fluorescence/phosphorescence  $\sim 0.1$ – $0.25$ ).<sup>26</sup> Thus, intersystem crossing would appear to be relatively slow in protic vs. aprotic media, assuming a relatively small solvent effect on the fluorescence decay rate. It would appear that H bonded MK at 77 K has an intrinsically longer singlet lifetime and smaller intersystem crossing rate constant (and efficiency) than MK in an aprotic environment.

It is attractive to postulate that the photochemical and photophysical properties of MK at room temperature are also a sensitive function of its microenvironment, and that H bonding to the carbonyl oxygen gives a molecular species quite different from that in aprotic polar and nonpolar solvents. The H-bonded species would be expected to have reduced reactivity toward H abstraction in its lowest triplet state, regardless of its configuration, and might well have a reduced intersystem crossing rate constant as well.

The fact that self-quenching of Michler's ketone is observed in benzene and carbon tetrachloride is not inconsistent with an  $n, \pi^*$  configuration of the triplet in these solvents, since recent studies on benzophenone and thioketones indicate that self-quenching is a general process for all types of ketone triplets and is not restricted to  $\pi, \pi^*$  triplets.<sup>12,28,29</sup> The relatively large values for  $k_{sq}$  (Table VIII) which were obtained ( $10^7$ – $10^8$   $M^{-1} s^{-1}$ ) in these nonpolar solvents, compared with values of  $\sim 10^5$   $M^{-1} s^{-1}$  for  $Ph_2CO$ <sup>15,29</sup> ( $^3n, \pi^*$  ketone) and  $\sim 10^5$   $M^{-1} s^{-1}$  for methyl 2-naphthyl ketone<sup>30</sup> ( $^3\pi, \pi^*$  ketone) suggest that the self-quenching interaction in MK is highly favorable, probably with a great deal of charge-transfer character. These conditions are precisely those that have been suggested as being conducive to excimer formation<sup>31</sup> and give further credence to our suggestion of triplet excimer formation in this system. Whether the long-lived transient observed in flash absorption experiments is indeed the excimer remains a moot point in the face of the negative results from emission

studies. Singer and co-workers<sup>15</sup> have measured  $k_{sq}$  for a series of benzophenones and find that there is a good linear correlation between  $\log k_{sq}$  and  $\sigma^+$  values for substituents on the aromatic ring ( $\rho = -1.7$ ). This indicates substantial electron donation from one molecule to the other in the activated complex for the self-quenching interaction.

The formation of triplet excimers by association of a molecule in its triplet excited state with the corresponding ground-state molecule is a controversial problem. The analogous formation of singlet excimers is well documented.<sup>31</sup> Any stabilization which may exist in triplet excimers must derive principally from charge resonance, while both charge resonance and excitation resonance stabilize singlet excimers toward dissociation.<sup>31–33</sup> Chandross and Dempster<sup>34</sup> demonstrated that 1,3-di- $\alpha$ -naphthylpropane in a sandwich conformation at low temperatures shows excimer fluorescence but only monomer phosphorescence, suggesting that a triplet excimer is not formed in the geometry which is favorable for singlet excimer formation. Calculations of Chandra and Lim<sup>35</sup> support this conclusion. More recently, however, Subudhi and Lim<sup>36</sup> have studied the luminescence of the same compound at room temperature and have detected a broad phosphorescence different from that of the monomer which they attribute to excimer emission, which supports some earlier assignments of triplet excimer emission in naphthalene itself.<sup>37</sup> Other recent examples of triplet excimer formation derive from studies of Slifkin with aromatic hydrocarbons at room temperature<sup>38</sup> and from a study of hexachlorobenzene by Lin and El-Sayed<sup>39</sup> at low temperature.

Thus, there is an increasing body of evidence that triplet excimers may exist under certain conditions, even at room temperature, although their optimum geometry may be quite different from that of the corresponding singlet excimers.<sup>36</sup> There appears to be a general consensus that the dominant stabilizing feature of such species is charge resonance. Michler's ketone would appear to be a good system for the formation of stabilized triplet excimers, although our efforts to characterize triplet excimers in this and related systems have thus far been fruitless.

## Experimental Section

**Instruments.** Analytical gas chromatographic analyses were performed on an F & M Scientific Hewlett-Packard Model 5750 chromatograph, or on a Hewlett-Packard Model 5710 A gas chromatograph equipped with a Model 3373 B digital integrator. Infrared spectra were taken on a Perkin-Elmer Model 337 grating infrared spectrophotometer using a polystyrene standard. Ultraviolet and visible spectra were recorded on either a Cary Model 15 spectrophotometer or a Perkin-Elmer Coleman 124 D double beam spectrophotometer. Emission spectra were taken on either a Fluorispec Model SF-1 fluorescence spectrophotometer, or a Hitachi-Perkin-Elmer Model MPF-2A fluorescence spectrophotometer. Nuclear Magnetic Resonance spectra were taken using a Hitachi-Perkin-Elmer Model R-24 high resolution NMR spectrometer with tetramethylsilane as

standard. Mass spectra were taken on a Varian M-66 double focusing cycloidal path mass spectrometer.

**Materials and Purification Procedures. Benzene.**<sup>40</sup> Mallinckrodt reagent grade benzene (4700 ml) was placed in a Hanovia reactor equipped with a water-cooled Pyrex immersion well and a 550-W high-pressure mercury lamp. Chlorine (Matheson) was introduced by means of a fritted glass bubbler during the 90-min irradiation. After irradiation, the solution was washed with four 500-ml portions of distilled water and two 500-ml portions of sodium carbonate solution. The solution was dried over anhydrous magnesium sulfate and distilled, with a 600-ml forecut being discarded. The distillate (3.2 l.) was stored over molecular sieves Type 4A. This purification procedure<sup>40</sup> offers a simple source of benzene that is free of toluene, cyclohexane, thiophene, and olefinic impurities. The purity of the solvent was checked by GLC using a 10-ft  $\frac{1}{8}$  in. stainless steel column of Carbowax 400, 15% on Chromosorb P, at a column temperature of 40 °C.

**Cyclohexane.** Mallinckrodt Spectrar Grade cyclohexane was washed in turn with concentrated sulfuric acid, sodium carbonate solution, and distilled water. The solution was dried over anhydrous magnesium sulfate and distilled prior to use.

**Ethanol.** Absolute ethanol (30 ml) and 2–5 g of magnesium turnings and several drops of carbon tetrachloride as catalyst were heated at reflux until all the magnesium was converted to the ethoxide. An additional 450 ml of absolute ethanol was added, and the heating at reflux was continued for 1 h. After distillation, the distillate was stored over molecular sieves Type 4A.

**2-Propanol.** Mallinckrodt Spectrar Grade solvent was heated at reflux over magnesium turnings and distilled prior to use.

**1,3-Cyclohexadiene.** Chemical Samples Co. 1,3-cyclohexadiene (99%) was stored in the cold and always freshly distilled immediately prior to use.

**Michler's Ketone.** (Aldrich or K & K) was taken up in benzene and extracted with water until the water layer was no longer colored. The benzene solution was dried and then the solvent was removed using a flash evaporator. The residue was recrystallized several times from benzene or, preferably, ethanol–water to give pale-yellow crystals, mp 173–174 °C (lit.<sup>41</sup> 174 °C). The material gave the following spectral data: IR  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) 3020, 2910, 1600, 1530, 1490, 1450, 1440, 1420, 1385, 1335, 1300, 1190, 1070, 1010, 955, 935, 840; UV  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 334 nm,  $\epsilon$   $2.7 \times 10^4$ ;  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_6$ ) 345 nm;  $\lambda_{\text{max}}$  (IPA) 245, 355 nm;  $m/e$  268 (base), 254, 224, 148, 134.

**Microsecond Flash Photolysis Studies.** The apparatus and procedures have been described previously.<sup>30,42</sup>

**Time-Correlated Single Photon Counting.** The apparatus used had characteristics similar to those described by Halpern and Ware.<sup>43</sup> For these studies, a deuterium-filled gated flashlamp was used for excitation, and the exciting radiation at the appropriate wavelength was isolated with a 0.25-m Jarrell-Ash monochromator. The phosphorescence was viewed at right angles with respect to the excitation through an appropriate glass filter, usually a Corning 0-51 filter.

**Quantum Yield Measurements.** A split-beam technique was used as described previously<sup>44</sup> with a few modifications. A converging lens was placed on the exit of the Bausch and Lomb high-intensity grating monochromator to form a nearly parallel beam which was passed through a Corning 7-54 glass filter to remove all visible light from the beam. After being passed through a converging lens, a beam was subjected to one of two configurations on the optical bench. One of these involved use of a beam splitter and continuous monitoring of the beam intensity by an actinometer as described previously.<sup>44</sup> In the second configuration, the light was focused onto cells housed in a Gilford Model 210 automatic cuvette positioner, containing two parallel sets of cell holders, each capable of holding four cuvettes. The sample was placed in cell compartment 2, and actinometer was placed in compartment 3 as well as in the position behind the sample. Each position compartment was irradiated alternately for equal time intervals, set between 20 to 45 s. Ferrioxalate actinometry<sup>10</sup> was used in all experiments, and the amount of light absorbed by the sample was readily calculated following the usual procedures.

**Triplet Counting Experiments.** In each experiment, solutions of Michler's ketone and benzophenone in the appropriate solvent, each containing an appropriate concentration of 1,3-cyclohexadiene, were placed in a pair of matched cuvettes and purged with nitrogen for ten min through a syringe needle inserted in a serum cap. Solutions were prepared to give an  $\text{OD}_{366}$  of approximately 0.8, which corresponded to about  $3 \times 10^{-5}$  M for MK and 0.01 M for benzophenone. The total

volume of solution in each sample was 25.0 ml. In the benzene experiments, a cyclohexadiene concentration of 0.1 M was sufficient to quench all triplets, but in cyclohexane, 2-propanol, and ethanol much larger amounts had to be used (1.25, 1.5, and 1.5 M, respectively) so that quenching of benzophenone triplets by CHD would occur to the exclusion of photoreduction of the ketone. The optical densities at 366 nm were measured for each solution after nitrogen purging prior to irradiation. The irradiation was done using the Bausch and Lomb monochromator and source and the Gilford cuvette positioner described previously. Irradiation times are indicated in Tables I–IV. The photolysates were thoroughly mixed before a 2-ml aliquot was withdrawn, to which was added 45  $\mu\text{l}$  of a 0.1 M solution of acenaphthene in *tert*-butyl alcohol as the internal standard for the GLC analysis. The analysis for the cyclohexadiene dimers was made on a 20-in. UCW-98 column, 10% on Chromosorb W AW/DMCS, at an oven temperature of 130 °C. The average from a minimum of three injections was used to determine the ratio of dimers to standard.

**Continuous Irradiation of Michler's Ketone in 2-Propanol.** Reactions were carried out in a Rayonet reactor. Photolysates were analyzed by GLC on a 10-ft  $\times$   $\frac{1}{8}$  in. column of 4% QF-1 + 1% Carbowax 20M on Chromosorb W (oven temperature 130 °C, injection port 250 °C) or a 2-ft  $\times$   $\frac{1}{8}$  in. column of 10% UCON 1175 on Chromosorb W (oven temperature 105 °C, injection port 250 °C).

It was also observed that a 2-h irradiation of Michler's pinacol in 2-propanol at 254 nm leads to almost complete disappearance of the UV band centered at 265 nm and a buildup of absorption below 220 nm. Thus, this circumstantial evidence indicates that irradiation of MK in 2-propanol at 254 nm gives Michler's pinacol which undergoes decomposition to unknown products upon further irradiation.

**Continuous Irradiation of Michler's Ketone in Cyclohexane.** A solution of 60 mg of purified MK in 1.2 l. of purified cyclohexane was irradiated at 254 nm while being continuously purged with nitrogen. The solution became intensely yellow, and a copious yellow precipitate filled the reaction flask. The solvent was removed using a flash evaporator, and about 3 g of a nonvolatile material remained, which was subjected to chromatography on Woelm neutral alumina. Early fractions contained large numbers of products with no UV absorption above 300 nm. Of these, only bicyclohexyl was definitely identified on the basis of infrared and mass spectroscopy. Trace amounts of Michler's pinacol and pinacolone were detected in later chromatographic fractions by UV spectroscopy. It was subsequently demonstrated that Michler's pinacol is unstable with respect to irradiation at 254 nm in cyclohexane, as in 2-propanol (see above).

Similar experiments were performed at 350 nm, where the reaction was much cleaner. The major product isolated after column chromatography was shown by UV spectroscopy to be Michler's pinacolone. It was shown (see below) that on column chromatography on alumina, Michler's pinacol is converted principally to the corresponding pinacolone, in agreement with an earlier study of the pinacol derived from *p*-dimethylaminobenzophenone.<sup>17</sup>

**Preparation of Michler's Pinacol.**<sup>45</sup> Aluminum amalgam was prepared as follows.<sup>46</sup> Aluminum turnings (10 g) were etched with 50 ml of dilute sodium hydroxide to the point of strong evolution of hydrogen. The solution was decanted, and the metal was washed with water. It was then treated with 30 ml of 0.5% mercuric chloride solution for 1.5 min, and then the entire process was repeated. The metal was then washed rapidly in turn with water, ethanol, and ether.

To 5 g of purified Michler's ketone in 200 ml of an 80% ethanol solution was added 10 g of freshly prepared aluminum amalgam. After the vigorous reaction subsided, the solution was heated at reflux for 2 h. The insoluble mass was extracted with hot benzene, and the benzene was stripped off with a flash evaporator yielding the pinacol. The pinacol was recrystallized once from acetone and had mp 193–195 °C. Literature values from 193–205 °C have been reported.<sup>47</sup> Spectral data: IR  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) 3550, 3000, 2930, 2870, 2810, 1620, 1520, 1455, 1360, 1160, 955, 915; UV  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_6$ ) 275 nm,  $\lambda_{\text{max}}$  (IPA) 265 nm,  $\epsilon$   $6.5 \times 10^4$ ,  $m/e$  270, 269, 268 (base), 254, 224, 210, 148, 44, 18.

**Preparation of Michler's Hydrol.** A solution of 3.1 g of purified Michler's ketone (0.012 mol) and 0.48 g of sodium borohydride (0.012 mol, a large excess) in 25 ml of 2-propanol was heated at reflux for 24 h. After the solution was allowed to cool, the boric ester complex was decomposed with 30 ml of a 10% sodium hydroxide solution. The solution was extracted with two 40-ml portions of benzene. The benzene was not dried before it was stripped off with a flash evaporator. The hydrol was recrystallized from benzene to give 3.0 g (96%), mp

94–95 °C (lit.<sup>45</sup> 96 °C).

**Preparation of Michler's Pinacolone.** A solution of 0.1 g of Michler's pinacol in 2 ml of glacial acetic acid was warmed to 50 °C for 15 min with occasional swirling. The solution was poured into 5 ml of distilled water, and the reaction flask was washed with two 5-ml portions of distilled water. The solution was neutralized with sodium carbonate and extracted with two 40-ml portions of benzene. The benzene extract was dried over anhydrous sodium sulfate and reduced in volume to about 5 ml. Ligroin was added dropwise until a precipitate began to form. The solution was then refrigerated overnight. After filtration, 0.075 g of pinacolone was recovered, mp 220–221 °C (lit.<sup>45</sup> 232 °C). Spectral data: IR  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) 3010, 2940, 2875, 2825, 1660, 1600, 1520, 1490, 1455, 1365, 1175, 955; UV  $\lambda_{\text{max}}$  (IPA) 260, 340 nm.

**Column Chromatography of Michler's Pinacol.** Michler's pinacol (0.6 g in 5 ml of 1:1 benzene–chloroform) was placed on a 24 in.  $\times$  0.5 in. column of Woelm neutral alumina. The column was eluted with benzene, ether, ethyl acetate, and chloroform. Fractions were isolated which corresponded to Michler's pinacolone (40%), Michler's ketone (17%), and Michler's pinacol (12%), in order of elution from the column, in addition to some unidentified material (13%).

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