

# Wavelength effects in the photolysis of ketones: intramolecular hydrogen abstraction of *o*-methyl-dibenzyl ketones vs. $\alpha$ -cleavage in micellar solution

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## Abstract

The chemical yields of indanols, the products of intramolecular  $\delta$ -hydrogen abstraction produced in the photolysis of *o*-methyl-dibenzyl ketone (*o*-MeDBK) and *o,o'*-dimethyl-dibenzyl ketone (*o,o'*-Me<sub>2</sub>DBK) in SDS micelles are sensitive to the wavelength of excitation: the yields of indanols are about two times smaller for excitation at 254 nm than at ca. 320 nm. At the same time the magnitude of the secondary cage effect, arising from coupling of geminate benzyl radical pairs is increased slightly for excitation at 254 nm relative to 300 nm. In contrast to the results for micellar solution, in hexane no wavelength effect on the yields of indanols is observed. A kinetic analysis of the reaction scheme shows that the decrease in the yield of indanol in micelles for shorter wavelength excitation is caused mainly by a decrease in the recombination probability  $P_r$  of the primary phenacyl/benzyl radical pair resulting from  $\alpha$ -cleavage. This decrease in probability for recombination of the primary geminate pair causes an increase in the formation of the secondary geminate benzyl/benzyl pair and a higher relative yield of geminate cage recombination. Intramolecular hydrogen abstraction as well as further cyclization of the biradical to indanol are not wavelength dependent processes. A Salem correlation diagram for hydrogen abstraction provides theoretical support for the proposed mechanism.

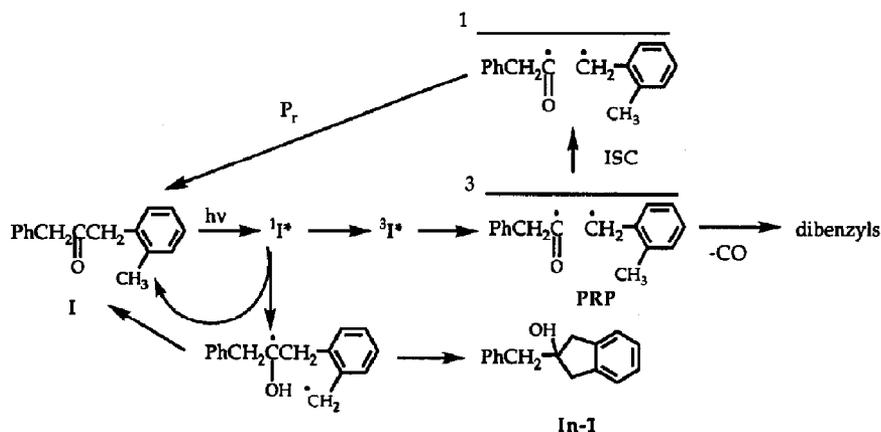
## 1. Introduction

Hydrogen abstraction by photoexcited carbonyl compounds is one of the most thoroughly studied reactions in organic photochemistry [1–3]. The efficiency of this process is determined by a number of factors such as the C–H (or N–H, or S–H, etc.) bond strength of the hydrogen donor, the spin multiplicity of the excited carbonyl compound, the orbital configuration of the excited state (*i.e.*  $n$ ,  $\pi^*$  vs.  $\pi$ ,  $\pi^*$ ) and the structure of the environment. For intramolecular hydrogen abstraction conformational factors are also important.

The photolysis of *o*-methyl-dibenzyl ketone (*o*-MeDBK, **1**) in benzene or ethanol (see Scheme 1) yields 2-benzylindan-2-ol (**In-1**), the product of cyclization following  $\delta$ -hydrogen abstraction, as a minor product, in addition to three bibenzyls expected from coupling of benzyl radicals produced by  $\alpha$ -cleavage [4]. Sensitization with triplet acetone and quenching with 1,3-cyclohexadiene and isoprene have previously been employed to demonstrate that **In-1** is formed exclusively from the singlet excited state of **1**, although the main precursor of the  $\alpha$ -cleavage reaction is the triplet **1**

[5, 6]. The chemical yield of **In-1**, relative to the dibenzyls, was found to increase from 6%–8% in homogeneous solution to 15%–17% in micelles [4]. This increase in formation of **In-1** was assumed to result from two factors: (1) a significant cage effect on the probability of recombination  $P_r$  of the primary phenacyl/benzyl radical pair (PRP) in micelles relative to homogeneous non-viscous solution, which reduces the yield of benzyl radicals and consequently the relative yield of dibenzyls, relative to the cyclization product; (2) a micellar environment effect which causes a preferred orientation of certain conformers which favor  $\delta$ -hydrogen abstraction and therefore increases the relative yield of **In-1** [7, 8].

Thus, photolysis of **1** provides an opportunity to perform a comparative investigation of the competition between  $\alpha$ -cleavage and intramolecular hydrogen abstraction within the same molecule (Scheme 1) under “molecular” (homogeneous solvents) or “supramolecular” conditions (micellar solution). In a previous paper [9], we reported the effect of the excitation energy on the probability of recombination  $P_r$  of a primary geminate radical pair (RP) and on the efficiency of the magnetic

Scheme 1. Photolysis of *o*-MeDBK (I).

isotope effect (MIE) for the photolysis of ketones in micelles. We showed that under higher energy excitation, the magnitude of  $P_r$  due to the recombination reaction of acyl/benzyl RP is decreased, possibly owing to the formation of electronically excited radicals which have enhanced chemical reactivity and/or faster spin relaxation. While this is a violation of Kasha's rule, consideration of Salem diagrams provides a plausible rationalization of why the violation might occur in an  $\alpha$ -cleavage reaction [9]. In this paper, we present the data on the effect of the excitation energy on the yields of the products of the reaction of intramolecular hydrogen abstraction which competes with  $\alpha$ -cleavage under photolysis of 1, *o,o'*-Me<sub>2</sub>DBK (II) and mesitylmethylbenzyl ketone (III) in homogeneous and in micellar solution and we attempt to analyze the sources of the wavelength effect. Although it is expected that  $P_r$  of the RP produced in  $\alpha$ -cleavage in this case will be affected [9], there is no precedent which allows a clear prediction of the wavelength effect on the  $\delta$ -hydrogen abstraction. However, a recent publication [10] suggests that ketyl radicals produced under 266 nm laser photolysis of benzyl in SDS micelles are different in reactivity and exhibit different magnetic field susceptibility than those generated by 308 nm photolysis.

## 2. Experimental details

The ketones, *o*-MeDBK (I), *o,o'*-Me<sub>2</sub>DBK (II) and mesitylmethylbenzyl ketone (MBK, III) were synthesized according to a known procedure [11] and were crystallized from ethanol. Sodium dodecylsulfate (SDS, Bio-Rad) was used as received. The concentration of SDS in water was 0.1 M

and the concentrations of ketones were 3 mM. Photolyses in hexane were carried out with ketone concentrations of 4 mM. The conversions of ketones during the photolyses were 10%–40%.

Photolyses were carried out at room temperature in a quartz cell in Ar purged solutions under flow of Ar in a Rayonet photochemical reactor equipped with sets of lamps emitting 254 or 300 nm radiation, or with the emission of a high pressure Xe-Hg 1 kW lamp (Hanovia) passed through an LP-320 glass filter ( $\lambda > 320$  nm).

Aqueous micellar solutions of ketones (before and after photolysis) were extracted with an equal volume of ethylacetate–methylene chloride mixture (4:1 by volume) containing an internal standard (dibenzyl ketone, DBK). Gas chromatographic (GC) analysis of the organic phase was used to measure the conversion of the starting ketones and the yields of the products. In the case of photolyses in hexane the internal standard was hexadecane.

GC analyses were carried out on a Hewlett Packard 5890 capillary gas chromatograph equipped with 25 M HP-1 or Carbowax 20 M columns. The products of the photolysis were identified by comparison with the retention times of authentic materials. The chemical yields of the products for each photolysis were measured for at least four different conversions.

The indanol products were shown to be completely stable under 254 nm photolysis.

## 3. Results

The chemical yields of indanols in the photolyses of I and II in SDS micelles under different wavelengths of excitation are shown in Table 1. The

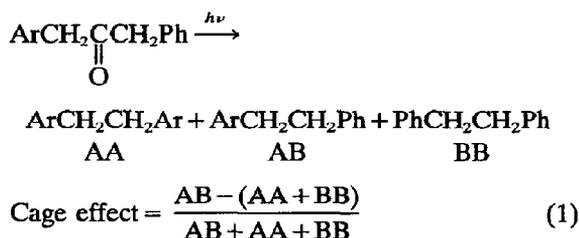
TABLE 1. Chemical yields of indanols during photolyses of *o*-MeDBK (I) and *o,o'*-Me<sub>2</sub>DBK (II) in SDS and hexane with different wavelengths of excitation

Ketone	Solvent	Chemical yield of indanol <sup>a</sup>		
		254 nm	300 nm	> 320 nm
<i>o</i> -MeDBK	SDS	0.070 ± 0.004	0.146 ± 0.005	0.170 ± 0.015
<i>o</i> -MeDBK	Hexane	0.068 ± 0.004	0.073 ± 0.003	NM
<i>o,o'</i> -Me <sub>2</sub> DBK	SDS	0.105 ± 0.015	0.189 ± 0.006	0.204 ± 0.007
<i>o,o'</i> -Me <sub>2</sub> DBK	Hexane	0.083 ± 0.007	0.097 ± 0.007	NM

<sup>a</sup>The chemical yield of indanol is determined as a ratio of the molar amount of indanol formed in the reaction to the molar amount of ketone disappeared. NM not measured.

chemical yield of indanol from I decreases from 17.0% for photolysis at  $\lambda > 320$  nm to 7.0% at 254 nm. The decrease in the chemical yield of indanol in II is two-fold under similar conditions. Since the indanols were shown to be stable to 254 nm excitation, the reason for this decrease in their yield at short wavelength cannot be due to secondary photolysis.

Table 2 summarizes the change in the secondary cage effect, as defined by eqn. (1) under photolysis of I in SDS micelles with different wavelengths of excitation:



From Table 2 the effect of wavelength on the secondary cage effect is seen to be opposite to that on the yields of indanols: the secondary cage effect is slightly increased under higher energy excitation, while the yield of indanol is significantly decreased.

Table 1 also contains chemical yields of indanols produced under photolyses of I and II in hexane at 254 nm and 300 nm. Within the accuracy of the experiment, there is no difference in the yields of indanols for different wavelengths of excitation.

TABLE 2. Secondary cage effect during photolysis of *o*-MeDBK (I) in SDS at different wavelengths

254 nm	300 nm	> 320 nm
0.543 ± 0.022	0.410 ± 0.008	0.389 ± 0.018

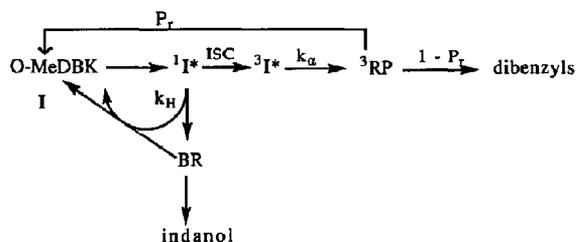
<sup>a</sup>The values are calculated based on eqn. (1) and measurements of the amount of dibenzyls formed during photolyses

It was also found that even in the case of mesitylmethylbenzyl ketone (III), for which intramolecular hydrogen abstraction is the most efficient of all DBK derivatives [6], the chemical yield of indanol in hexane (0.38 ± 0.02) does not depend on the wavelength of excitation. It should be noted that the photolyses of I or II for different excitation wavelengths in SDS as well as in hexane give the same products.

#### 4. Discussion

Scheme 2 is employed as a working paradigm for the analysis of the experimental data reported in Tables 1 and 2. We assume, to a first approximation, that  $\alpha$ -cleavage takes place only from the excited triplet state of the ketones investigated, while intramolecular hydrogen abstraction occurs solely from the excited singlet state [5]. Although this may not be strictly correct since we have shown that in benzene up to 20%–30% of  $\alpha$ -cleavage may take place from the singlet state of I and II [6], in micelles any singlet RPs are expected to undergo very rapid geminate recombination on the scale of other micellar processes.

Since  $\alpha$ -cleavage and intramolecular hydrogen abstraction are the only reactions of excited I, according to Scheme 2, we can define the chemical yield of indanol  $\chi_{\text{in}}$  by eqn. (2):



Scheme 2. Scheme used for analysis of the experimental data for the yield of indanol under photolysis of *o*-MeDBK (I).

$$\chi_{\text{In}} = \frac{\Phi_{\text{In}}}{\Phi_{\text{Dec}}} = \frac{\Phi_{\text{In}}}{\Phi_{\text{In}} + \Phi_{\text{DB}}} \quad (2)$$

where  $\Phi_{\text{In}}$ ,  $\Phi_{\text{Dec}}$  and  $\Phi_{\text{DB}}$  are respectively the quantum yields of indanol formation, ketone decomposition and formation of dibenzyls. In micelles, where  $P_r$  of the primary phenacyl/benzyl RP is expected to be substantial, the large cage effect reduces the value of  $\Phi_{\text{DB}}$ , which may be expressed by eqn. (3):

$$\Phi_{\text{DB}} = \Phi_{\text{[RP]}}(1 - P_r) \quad (3)$$

$\Phi_{\text{[RP]}}$  is quantum yield of geminate RP formation, which is assumed to be the same in micelles and homogeneous solution.

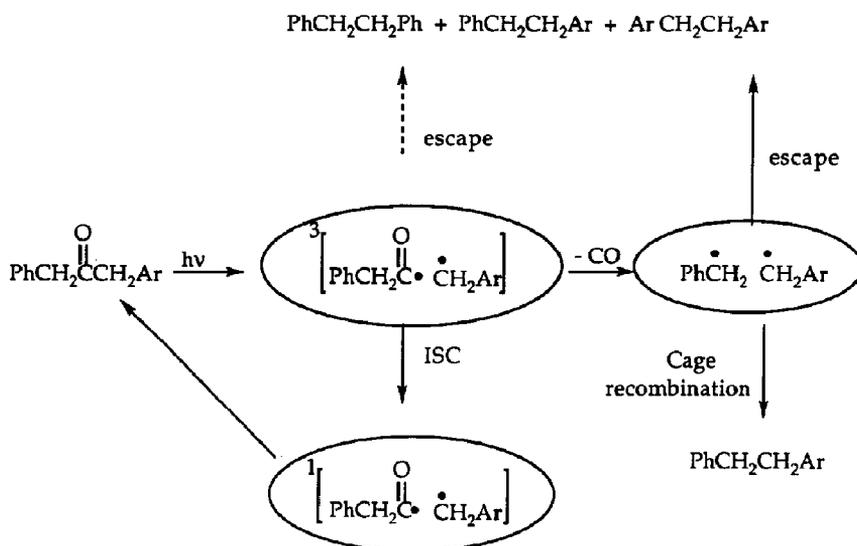
For the photolysis of **I** in benzene with 313 nm light [6], we found that  $\Phi_{\text{In}} = 0.023$  and  $\Phi_{\text{DB}} = 0.35$ , and for **II**,  $\Phi_{\text{In}} = 0.032$  and  $\Phi_{\text{DB}} = 0.26$ , *i.e.* the quantum yield of indanol formation is 8 (for **II**) or even 15 (for **I**) times smaller than quantum yield of RP formation during  $\alpha$ -cleavage. We can safely assume that  $P_r$  is around zero in non-viscous solvents such as benzene or hexane for the triplet RP produced from  $\alpha$ -cleavage of ketones [12]. The chemical yield of indanol in the photolysis of **I** in SDS at 300 nm is twice that in hexane (see Table 1). Taking into account eqns. (2) and (3) and the measured values [5, 6] of  $\Phi_{\text{In}}$  and  $\Phi_{\text{DB}}$ , the recombination probability for phenacyl/*o*-methylbenzyl RP in micelles is estimated to be  $P_r \approx 0.5$ . A similar conclusion is obtained for the value of  $P_r$  for the RP from **II**.

The chemical yield of **In-1** is twice as large in SDS as in hexane at 300 nm excitation (Table 1). However, the chemical yields of **In-1** are similar in micellar and homogenous solutions for 254 nm photolyses. Since with 254 nm photolysis the  $P_r$  of the formed RP in hexane is expected to be the same as the value at 300 nm, *i.e.* zero, we suggest that the reason for the similar chemical yields of indanol in SDS and hexane under short wavelength excitation may be a very small, perhaps nearly zero, value of  $P_r$  for the primary geminate pair even in micelles. For photolysis of **II** with 254 nm the same effect is observed; the yields of indanol (**In-II**) are nearly the same in SDS and hexane.

We now turn to the observation that the secondary cage effect for the formation of dibenzyls (eqn. (1)) under 254 nm photolysis of **I** in SDS is 30% larger than under 300 nm photolysis. Secondary benzyl/benzyl RPs are produced through decarbonylation of geminate primary acyl/benzyl RPs and the higher cage effect in the formation of dibenzyls is consistent with an enhanced de-

carbonylation of the geminate primary RP with 254 nm excitation. Scheme 3 shows how an increase in the rate of decarbonylation of triplet geminate phenacyl/benzyl RP can result in both a decrease in  $P_r$  for the primary pair and in an increase of the secondary cage effect in micelles. If primary RPs are more efficiently converted to geminate secondary RPs this will lead to both a higher secondary cage effect and a higher yield of dibenzyls, because in the primary triplet geminate RP,  $P_2$  is determined mainly by the competition between intersystem crossing (ISC) to a singlet RP and decarbonylation of phenacyl radicals (there is also a competing escape of the primary pairs from the micelles [13] which decreases the secondary cage effect since escaped phenacyl radicals decarbonylate in the aqueous phase and recombine forming a statistical mixture of dibenzyls). In the secondary RP, the cage effect for the formation of dibenzyls is determined by the efficiency of generation of benzyl/benzyl RP from primary geminate pairs by decarbonylation within the micelle, and the competition between cage recombination and escape of the radicals from the micelle. Since at short wavelength excitation of **I**,  $P_r$  for the primary pair is decreased and the secondary cage effect is increased, enhanced decarbonylation of phenacyl radicals appears to be a common process responsible for both effects. The situation can be analyzed in terms of two extreme cases. If the primary triplet RP decarbonylates so fast that almost no radical escape from micelles can compete with decarbonylation, the secondary cage effect will be higher and will be determined by the ratio of geminate recombination of benzyl radicals to radical escape (at the stage of secondary RP). At the other extreme, when the rate of decarbonylation is much slower than the rate of escape of radicals for the primary triplet RP and escape is fast relative to decarbonylation, most of the primary radical pairs will escape into the aqueous phase and eventually decarbonylation will occur, *i.e.* only a small amount of primary geminate RPs will convert to secondary geminate RPs and consequently the total amount of secondary geminate recombination to form geminate dibenzyl will be small. At the same time decarbonylation of the escaped phenacyl radicals in aqueous phase will give a statistical distribution of dibenzyls, which will be the major pathway of dibenzyl formation in this case and the secondary cage effect value will be small.

In a previous paper [9], we showed that the value of  $P_r$  for a benzoyl/sec-phenethyl RP generated by photolysis of methyldeoxybenzoin (MDB) is 0.36 for photolysis at 254 nm *vs.* 0.54 for



Scheme 3. Primary and secondary cage effect for *o*-MeDBK (I) photolysis in micelles.

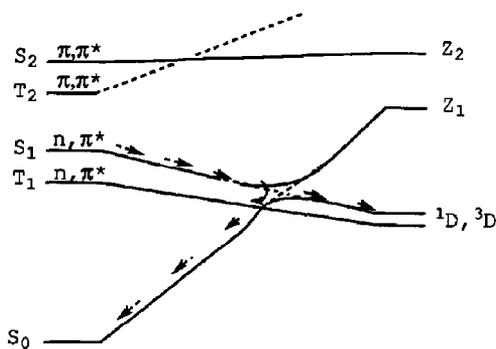
photolysis at 350 nm. This effect was explained as the result of the formation of primary triplet RP for which one of the partners of the pair was an electronically excited linear benzoyl radical. The exact process that competes with ISC to form a singlet RP and then recombination could not be determined, but we speculated that the process might also be decarbonylation [9]. This supposition is supported by the expectation that decarbonylation of acyl radicals will proceed through a linear transition state of acyl radicals. For example, for an acetyl radical CH<sub>3</sub>CO, which has a bent ground state with sp<sup>2</sup> hybridization of the carbonyl carbon, the linear excited state, which has an sp hybridization of the carbonyl carbon, has been calculated to lie about 28 kcal mol<sup>-1</sup> above the ground state [14]. The activation energy of decarbonylation  $E_A$  of the benzoyl radical in the gas phase has been reported to be *ca.* 29 kcal mol<sup>-1</sup> [15]; hence, the decarbonylation rate of electronically excited radicals is expected to be substantially higher than for radicals in the ground state.

For ground state acyl radicals, RCO, in general the magnitude of  $E_A$  is determined by the thermodynamic stability of the radical R that results from decarbonylation. Therefore,  $E_A$  of the phenacyl radical should be smaller than for benzoyl or alkyl acyl radicals. The experimental measurement of the temperature dependence of the decay kinetics for phenacyl radicals provides a value of  $E_A = 6-7$  kcal mol<sup>-1</sup> [16]. The rate of decarbonylation of phenacyl radicals in an excited state should be substantially increased from the normal room temperature value  $6.4 \times 10^6$  s<sup>-1</sup> [17] and may

not be significantly temperature dependent (to the extent that it can be treated as a radiationless transition).

The experimental results of this work support the model of a fast decarbonylation of phenacyl radicals produced with short wavelength photolysis. Based on the chemical yields of In-I, we estimate a  $P_T$  value for the phenacyl/benzyl RP of *ca.* 0.5 for 300 nm excitation and a much smaller value, close to zero, for  $P_T$  for 254 nm excitation. The data for the <sup>13</sup>C magnetic isotope effect (MIE) during DBK photolysis in SDS micelles [9] also show that the efficiency of <sup>13</sup>C isotope enrichment  $\alpha$  is reduced from 1.19 under 308 nm to 1.14 under 260 nm photolysis, a result which is consistent with a smaller  $P_T$  value for the primary RP [18] formed under 254 nm excitation.

A Salem correlation diagram for  $\delta$ -H abstraction by an excited carbonyl group [14, 19] (Scheme 4) provides a theoretical understanding of why the H abstraction reaction is not sensitive to the higher energy of excitation, while the  $\alpha$ -cleavage reaction is [9]. In the Salem diagram for H abstraction, the S<sub>1</sub> n,  $\pi^*$  and T<sub>1</sub> n,  $\pi^*$  states of the excited ketone correlate with respectively singlet and triplet states of the biradical, and the S<sub>0</sub> state of the ketone correlates with a zwitterionic state of the product Z<sub>1</sub>. Owing to an avoided crossing along the reaction trajectory, an efficient internal conversion can occur (see Scheme 4) and the quantum efficiency of the formation of biradical from S<sub>1</sub> is very low because such an internal conversion competes with biradical formation. At the same time, S<sub>2</sub>  $\pi$ ,  $\pi^*$  correlates with a second high energy



Scheme 4. Salem correlation diagram for hydrogen abstraction by a photoexcited carbonyl group.

zwitterionic product state  $Z_2$ . Since there is no first-order surface crossing between the reaction trajectories initiated from  $S_1$  and  $S_2$  excited states of the ketone and since  $Z_2$  has a relatively higher energy, it appears likely that the  $S_2$ - $Z_2$  interconversion will be relatively slow. As a result, the ketone molecules excited to the  $S_2$  state are expected to undergo predominant internal conversion to  $S_1$  and the reaction products of  $S_2$  will be the same as products from  $S_1$ . We note that this situation is not general for intramolecular hydrogen abstraction from ketone triplets, since the surface crossing of a triplet state with  $S_0$  is "not efficiently avoided" (Scheme 4), and an intersystem crossing is required to return the system to the ground state in competition with formation of a triplet biradical. Thus, the singlet nature of the  $\delta$ -hydrogen atom abstraction is an important discriminating feature of the singlet and triplet hydrogen atom abstraction.

Finally, we note that since DBK and its derivatives with substituents at the phenyl rings do not contain a chiral center, the direct method of measuring  $P_r$ , based on photostereoisomerization [20], is not applicable. However, the competing  $\delta$ -H abstraction reaction followed by the cyclization with the formation of indanol in the case of I and II provide a means for an indirect estimation of  $P_r$  for phenacyl/benzyl RP produced in  $\alpha$ -cleavage reaction in micelles.

## 5. Conclusions

The wavelength effect on the chemical yield of indanols, the products of intramolecular  $\delta$ -hydrogen abstraction found in the photolyses of *o*-MeDBK and *o,o'*-Me<sub>2</sub>DBK in SDS micelles is shown to be determined by a decrease in recom-

bination probability  $P_r$  of the primary geminate triplet phenacyl/benzyl RP for photolysis at shorter wavelengths. There is no wavelength effect on  $P_r$  in homogeneous solutions. At the same time the cage effect for geminate combination of benzyl radicals in micelles increases slightly with decreasing wavelength. These results are readily accommodated by the recently proposed paradigm for the photochemistry of *o*-MeDBK and *o,o'*-Me<sub>2</sub>DBK which involves  $\delta$ -hydrogen abstraction from the singlet state and  $\alpha$ -cleavage from the triplet state. The reaction of  $\delta$ -H abstraction is also independent of the wavelength of excitation. This conclusion is supported by a simple analysis of the appropriate Salem correlation diagram.

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